The Crystal Structures of Some Biologically Interesting Molecules

Thesis by

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The Crystal Structures of Some Biologically Interesting Molecules

I THE CRYSTAL STRUCTURE OF 1-METHYLCYTOSINE HYDROCHLORIDE

II THE DETERMINATION OF THE CRYSTAL STRUCTURE OF A LUMIFLAVIN COMPLEX

III THE CRYSTAL STRUCTURE OF THIABENDAZOLE

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By Benes Louis Trus

Abstract

I Crystals of 1-methylcytosine hydrochloride, $C_5H_8N_3O^+\cdot Cl^-$, are monoclinic, space group $P2_1/n$, with $\underline{a} = 6.695(3)$, $\underline{b} = 32.30(2)$, $\underline{c} = 6.912(2)$ Å, $\beta = 104.22°$. There are eight formula units per cell, and hence two

per asymmetric unit. Data were collected on an automated diffractometer; the structural parameters were refined to an R index of 0.055 for 2609 reflections. Standard deviations in the bond distances are about 0.004 Å.

Bond distances in the two structurally distinct molecules are in statistical agreement. The environments of both molecules are closely parallel; features of the structure include layers of molecules joined by N-H•••O and N-H•••Cl^- hydrogen bonds, relatively short C-H•••O interactions, and close meshing of methyl groups.

II Crystals of lumiflavin-bisnaphthalene-2,3-diol, $C_{13}H_{12}N_4O_2 \cdot 2C_{10}H_8O_2$, are moloclinic, space group $P2_1/c$ with a = 20.78(2), b = 7.24(1), c = 20.15(2) Å, and β = 116.19 ± 0.04° [λ(Cu-Kα) = 1.5418 Å]. There are four complexes in the unit cell. Data were collected at Tulane University on an automatic diffractometer, the structure was solved at Caltech using direct methods, and the parameters returned to Tulane for final refinement.

This is the first molecular complex of the physiologically active neutral form of isoalloxazine studied. Each flavin is sandwiched between two napthalene molecules with extensive overlap but a moderately large spacing (3.44 Å).

III Crystals of thiabendazole, $C_{10}H_7N_3S$, are orthorhombic, space group Pbca, with a = 17.052(7), b = 10.998(4), and c = 10.030(8) Å. There are eight formula units per cell. Data were collected on an automatic diffractometer; the structural parameters were refined to an R index of 0.066 for 1805 reflections. Standard deviations in bond lengths are about 0.006 Å for bonds involving carbon and nitrogen and about 0.003 Å for bonds involving sulfur.

The two ring systems are approximately planar, but twisted by 9°55' with respect to each other. The C-C bond connecting the two ring systems is 1.442 Å.

IV and V Crystals of the title compounds were obtained as intermediates in the syntheses of the terpenes alnusenone and shinone. The X-ray crystal structures were used to confirm the similar stereo chemistry of these compounds. The decahydro-ethoxy-methoxy-trimethylpycene (called Patrone 3) crystallizes in space group Pbca with eight molecules per unit cell. The cell dimensions are a = 7.094(2), b = 11.823(1), and c = 54.973 (5).The decahydro-methoxy-oxo-trimethylchrysene (CHRY) crystallizes in space group $Pna2_1$ with four molecules in the unit cell. The cell parameters are a = 29.922(4), b = 7.757(1), and c = 7.630(4) Å.

Both molecules are rather flat except for the methyl groups. The packing is determined largely by van der Waal interactions. Both molecules exhibited the configuration expected from the syntheses.

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I

The Crystal Structure of 1-Methylcytosine Hydrochloride

Introduction

This determination of the structure of methylcytosine hydrochloride was undertaken as part of a program of research on the structures of compounds related to nucleic acids. Our particular interests in this compound were focused on the possibility of base stacking and on determining with high accuracy the geometry of a protonated form of cytosine for comparison with unprotonated forms.

Crystal Data

Crystals of 1-methylcytosine hydrochloride, in the form of needles eleongated along a, were prepared by the evaporation of dilute HCl solution. These crystals were unstable in air for more than a few days, so the crystal from which intensity data were obtained was covered with a thin layer of epoxy.

The space group and approximate cell constants were obtained from Weissenberg and precession photographs; more accurate cell constants were obtained by a least-squares fit to 2θ values measured on a diffractometer. The density was measured by floatation in a chloroform-bromoform mixture. Crystal data are given in Table 1.

Experimental

Intensity data were measured on a Datex-automated General Electric diffractometer, using Ni-filtered CuK_α radiation. The crystal had approximate dimensions 0.41 x 0.32 x 0.25 mm., and was mounted along a, the long dimension. Reflections with $2\theta \leq 141.5°$ were scanned in the θ-2θ mode at a rate of 2° per minute, the scan range varying from 2° at 2θ = 10° to 4° at 2θ = 130°. A 30-second background count was recorded on either side of the scan range. Two sets of data were measured and averaged, the crystal being rotated by 180° in phi between sets. Thus, a complete hemisphere of the reciprocal lattice was surveyed. The agreement in net intensity between the two data sets was very good -- within the assigned standard deviations. A standard check reflection was measured every 20 reflections; the intensity of this standard decreased continuously by about 3% during the two weeks of data collection. Absorption corrections were not applied.

Altogether, 2793 independent reflections were measured. Each reflection was assigned a variance $\sigma^2(I)$ based on counting statistics plus an empirical term $(0.02s)^2$, where s is the scan count. Values of F_o^2 and $\sigma(F_o^2)$ were derived from the net intensities by application of the Lorentz and polarization factors and a time-dependent scale factor derived from the fall-off of the check reflection. Any reflection for which the net value of F_o^2 was less than or equal to zero was assigned an intensity and weight of zero. There were 2609 observations in the final data set. The 184 reflections omitted from the calculations included 11 high-angle reflections which were omitted because of grossly uneven backgrounds, apparently due to too narrow a scan range.

Structure solution and refinement

The coordinates of the chlorine atom were derived from a three-dimensional Patterson function, and a subsequent electron density map indicated the positions of the remaining heavy atoms. The resulting structure-factor calculation gave an R ($= \Sigma|F_o - F_c|/\Sigma|F_o|$) of 0.40. Three cycles of full-matrix least-squares adjustment of the coordinates and isotropic temperature factors lowered R to 0.17. The hydrogen atoms were then located on a difference map. Further full-matrix refinement of 146 parameters -- coordinates of all 36 atoms, anisotropic temperature parameters for the 20 heavy atoms, isotropic B's for the 16 hydrogen atoms, a secondary extinction parameter (1) and a scale factor -- led to a final R index of 0.055, a weighted R_w [$= \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma wF^4$, where $w = 1/\sigma^2(F_o^2)$] of 0.009 and a goodness of fit {$= [\Sigma w(|F_o|^2 - |F_c|^2)^2/(M - S)]^{\frac{1}{2}}$ for M = 2609 observations and S = 146 parameters} of 2.4. The largest shift in the final least-squares calculation was 0.4σ.

Scattering factors were those listed in International Tables for X-ray Crystallography (2) except for hydrogen (3). Calculations were performed at the Caltech Computing Center on IBM 7040-7094 and 360-75 systems using the CRYRM (4) and CRYM systems (5). Some of the crystallographic illustrations were produced by ORTEP (6).

The final parameters of the heavy atoms appear in Table 2 and those of the hydrogen atoms in Table 3. Observed and calculated structure factors are listed in Table 4. The final value of the extinction parameter g (1) was $6.8 \pm 0.4 \times 10^{-6}$.

Discussion

Molecular configuration

The bond distances and angles in the two independent methylcytosine cations are shown in Figure 1. The standard deviations in the individual distances are about 0.004 Å, and in the angles 0.15°. Rather surprisingly, the agreement between the dimensions of the two different molecules is considerably better than would be anticipated from the formal esd's. Thus, whereas the standard deviation in the difference between any pair of equivalent bonds would be expected to be about 0.0056 Å (= 0.004 x $\sqrt{2}$), the observed rms difference among the nine pairs of equivalent bonds is only 0.0025 Å. Although this disparity is presumably only a reflection of the poor statistics of small samples, we take it as an indication that our formal esd's are not seriously underestimated.

The average dimensions of the two cations are listed in Table 5. The standard deviations in these values -- about 0.003 Å in the distances and 0.1° in the angles -- are considerably smaller than in other structure analyses of a protonated cytosine moiety, which include methyl cytosine hydrobromide (σ = 0.04 Å) (7) and two forms of cytidylic acid (σ = 0.006 Å) (8) (σ = 0.009 Å) (9). Values from these investigations agree with ours within their esd's.

Also included in Table 5 are the dimensions of the neutral cytosine ring as averaged from the values of Jeffery and Kinoshita (σ = 0.004 Å) (10) for cytosine monohydrate and of Barker and Marsh (σ = 0.003 Å) (11) for anydrous cytosine crystals. Not surprisingly, the most pronounced effects of protonation of the ring are adjustments of the ring angles, focused on an enlargement of the angle at the site of protonation (N(3)) by over 6°. Significant changes in the bond distances include a lengthening of the C(2)-N(3) bond by over 0.02 Å and shortenings of the C(4)-C(5), C(2)-O(2), and C(4)-N(4) bonds; the latter two changes, which involve exocyclic atoms, may reflect in part changes in the hydrogen bonding. The expected lengthening of the N(3)-C(4) bond, by 0.006 Å, is too small to be of statistical significance.

Both six-membered rings are closely planar (see Table 6), but some of the exocyclic atoms are significantly out-of-plane. Bond distances and angles involving hydrogen atoms are given in Table 7.

Packing

The hydrogen bonding arrangement is essentially identical for both methylcytosine cations (see Figure 1). Further details, including average distances, are shown in Figure 2. Of special note are the nicely bifurcated arrangement about one of the $-NH_2$ protons and the relatively short C-H···O contacts -- which, depending on one's personal prejudices, may or may not be hydrogen bonds. (True afficionados of hydrogen bonds involving C-H groups may wish to add to their lists the C(5)-H(5)···Cl groupings.) The hydrogen bond system shown in Figure 2, including the C-H···O arrangement, is very similar to that found in crystals of methylcytosine hydrobromide (7); in the latter compound, bromide ions replace chloride in the positions at the two sides of the $-NH_2$ group, but a methyl group (at a rather short distance N···C of 3.2 Å) replaces the chloride ion in the head-on position.

A second facet of the intermolecular arrangement is a tight interlocking of methyl groups along the a direction. Details of the packing are shown in Figure 3. As a result of the relatively short H···H contacts, the hydrogen atoms are entirely ordered and their temperature factors (Table 3) are smaller than usually found for methyl groups. This packing may also be responsible for the displacement of the methyl group of cation A from the best plane of the pyrimidine ring (Table 6). For both cations the conformation about the N(1)-C(1) bond is gauche, whereas in methylcytosine hydrobromide (7) one methyl hydrogen atom is required by symmetry to be eclipsed with respect to the benzene ring.

Packing drawings of the structure are shown in Figures 4 and 5. Methylcytosine cations of type A lie near $\underline{y}$ = 0 and 1/2, while those of type B lie near $\underline{y}$ = 1/4 and 3/4. Hydrogen bonds involving the chloride ions connect an A cation with a B, forming ribbons two molecules wide, stretching along the $\underline{a}$ direction and oriented parallel to the $\underline{ab}$ plane. Adjacent ribbons in the same plane are held together by interactions between methyl groups (see Fig. 3). The packing forces between planes appear to be predominantly electrostatic, involving the chloride ions. There is little stacking overlap between adjacent cytosine rings; rather, each ring lies above (and below) the gap between two rings in the neighboring planes. By comparison, in the hydrobromide salt (7) each methylcytosine cation lies above the gap in the center of four rings in the neighboring sheet (Fig. 6).

The close similarity in the intermolecular environments of the two molecules in the asymmetric unit is reflected in their similar patterns of thermal motion (Fig. 1).

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Table 1. Crystal data

$C_5H_8N_3O^{+} \cdot Cl^{-}$

Space Group $P2_1/n$

a = 6.695(3) Å

b = 32.30(2)

c = 6.912(2)

β = 104.22(3)°

$\lambda(CuK_\alpha)$ = 1.5418 Å

V = 1449 Å^3

μ = 41.4 cm.$^{-1}$

F. W. = 161.6

Systematic Absences:

h0ℓ, h+ℓ = 2n+1;

0k0, k = 2n+1

Z = 8

F_{000} = 672

D_c = 1.478 g. cm.$^{-3}$

D_m = 1.483 g. cm.$^{-3}$

Table 2. Coordinates and anisotropic temperature parameters for the heavy atoms. Standard deviations are given in parentheses. The temperature factor has the form $\exp -(b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + b_{12}hk + b_{13}h\ell + b_{23}k\ell)$.

		x*	y**	z*	b_{11}*	b_{22}**	b_{33}*	b_{12}**	b_{13}*	b_{23}**
A	Cl(1)	2310(1)	8091(2)	1968(1)	177(2)	61(1)	264(2)	-82(5)	138(3)	61(6)
	Cl(2)	7365(1)	16215(2)	908(1)	211(2)	66(1)	320(2)	-65(5)	195(3)	51(6)
	N(1)	6568(3)	44117(6)	2023(3)	175(6)	66(2)	234(6)	-31(17)	181(10)	-74(18)
	C(2)	5041(4)	46720(8)	2334(4)	171(7)	83(3)	214(7)	69(21)	121(11)	72(23)
	N(3)	5628(3)	50814(6)	2677(4)	159(6)	71(2)	238(6)	148(17)	155(9)	25(18)
	C(4)	7514(4)	52387(7)	2740(4)	169(7)	71(2)	182(7)	33(20)	111(10)	30(20)
	C(5)	9007(4)	49589(8)	2395(5)	147(7)	76(3)	265(8)	-19(20)	163(12)	-59(23)
	C(6)	8480(4)	45582(8)	2052(4)	182(7)	82(3)	245(8)	162(22)	167(12)	15(23)
	C(1)	6079(6)	39688(9)	1754(6)	283(9)	73(3)	334(11)	-99(26)	219(17)	-99(27)
	O(2)	3310(3)	45561(6)	2317(3)	163(5)	106(2)	364(7)	-51(17)	179(10)	-51(20)
	N(4)	7884(4)	56338(7)	3106(4)	238(7)	63(2)	298(8)	71(20)	177(12)	-23(20)
B	N(1)	1327(3)	30401(6)	663(3)	167(6)	67(2)	229(6)	43(17)	124(9)	45(18)
	C(2)	-215(4)	27705(8)	844(4)	163(7)	91(3)	228(8)	16(22)	117(12)	143(23)
	N(3)	329(3)	23567(6)	929(4)	159(6)	77(2)	246(7)	-86(18)	120(10)	71(19)
	C(4)	2181(4)	22033(8)	853(4)	184(7)	72(2)	195(7)	-45(20)	103(11)	42(21)
	C(5)	3708(4)	24920(8)	701(4)	164(7)	78(3)	259(8)	68(20)	159(12)	9(23)
	C(6)	3224(4)	28991(8)	620(4)	162(7)	82(3)	239(8)	-52(21)	106(12)	25(22)
	C(1)	873(5)	34857(9)	557(5)	256(9)	71(3)	312(10)	67(24)	140(15)	-14(26)
	O(2)	-1932(3)	28838(6)	906(3)	163(5)	116(2)	407(8)	133(17)	227(10)	256(21)
	N(4)	2483(4)	18010(7)	916(4)	255(7)	65(2)	298(8)	31(21)	175(12)	79(21)

* x 10^4

** x 10^5

Table 3. Coordinates and isotropic temperature parameters for the hydrogen atoms. Standard deviations are given in parentheses.

		x*	y**	z*	B
A	H(1a)	512(4)	3880(9)	260(5)	6.1(0.8)
	H(1b)	728(5)	3821(9)	222(4)	5.8(0.8)
	H(1c)	549(5)	3877(10)	43(5)	8.3(0.9)
	H(3)	475(4)	5241(7)	292(4)	3.7(0.6)
	H(4a)	692(4)	5811(8)	330(4)	4.5(0.7)
	H(4b)	927(5)	5770(9)	311(4)	6.4(0.8)
	H(5)	1023(4)	5042(7)	240(3)	3.0(0.6)
	H(6)	941(4)	4334(8)	175(4)	4.1(0.6)
B	H(1a)	190(5)	3632(9)	8(5)	6.5(0.8)
	H(1b)	-57(4)	3544(8)	-12(4)	4.8(0.7)
	H(1c)	88(5)	3616(9)	176(5)	6.9(0.8)
	H(3)	-73(4)	2171(8)	100(4)	5.7(0.8)
	H(4a)	139(5)	1604(9)	96(4)	6.5(0.8)
	H(4b)	368(4)	1676(8)	82(4)	4.8(0.7)
	H(5)	494(3)	2407(6)	57(3)	2.7(0.5)
	H(6)	423(4)	3130(8)	51(4)	4.6(0.6)

$* \times 10^3$ $** \times 10^4$

Table 4. Structure Factors

Each group of three columns contains k, $10|F_o|$, and $10F_c$ and is headed by values of h and ℓ common to the group. Asterisks following $10F_c$ indicate reflections given zero weight and omitted from the refinement.

0	K	0
0	0	2516*
2	25	31
4	779	819
6	37	-42
8	703	-736
10	252	-262
12	453	497
14	386	359
16	364	-376
18	285	277
20	58	45
22	154	-150
24	346	345
26	182	175
28	40	-30
30	81	-66
32	8	39
34	118	-109
36	164	156
38	156	154
1	K	0
1	331	337
2	64	-69
3	535	555
4	572	-610
5	256	-259
6	115	-117
7	171	-163
8	1183	1240
9	187	191
10	100	108
11	17	-25
12	40	8
13	181	-184
14	6	2
15	308	-302
16	132	-144
17	118	120
18	277	-274
19	121	-124
20	410	406
21	0	33*
22	255	246
23	0	-10*
24	294	-284
25	35	-18
26	154	158
27	59	-65
28	290	-273
29	78	86
30	260	-254
31	51	-60
32	251	239
33	20	19
34	101	88
35	31	-1
36	14	-4
37	18	24
38	27	17
39	13	19
2	K	0
0	1229	-1180
1	173	-170
2	20	19
3	462	-460
4	585	596
5	478	486
7	163	171
6	51	51
8	1086	1119
9	391	406
10	135	142
11	327	336
12	274	-293
13	12	-19
14	211	-216
15	48	-52
16	73	272*
17	60	-62
18	21	-32
19	61	-63
20	264	251
21	58	-57
22	251	248
23	54	-60
24	365	-342
25	316	310
26	44	56
27	1	-9
28	134	122
29	272	266
30	171	163
31	52	56
32	55	42
33	83	76
34	124	122
35	55	52
36	138	-136
37	36	-27
38	134	-143
3	K	0
1	22	3
2	46	32
3	70	-78
4	41	10
5	378	376
6	103	108
7	282	291
8	546	-554
9	23	21
10	187	-190
11	67	63
12	93	102
13	91	-87
14	131	-130
15	32	-24
16	489	489
17	11	22
18	124	122
19	41	-32
20	354	-341
21	17	32
22	160	-164
23	151	-158
24	124	124
25	144	138
26	26	-41
27	60	-58
28	353	339
29	135	125
30	197	188
31	106	106
32	198	-189
33	0	12*
34	59	-57
35	31	-23
36	48	37
4	K	0
0	478	468
1	47	-45
2	86	-75
3	252	233
4	129	-124
5	55	-47
6	0	4*
7	0	8*
8	185	-161
9	162	-159
10	69	-67
11	226	-235
12	374	376
13	131	143
14	111	115
15	134	137
16	374	-369
17	208	206
18	0	-3*
19	266	258
20	500	-495
21	26	-4
22	82	-78
23	49	43
24	118	113
25	8	11
26	119	108
27	77	83
28	108	-98
29	49	-45
30	20	-25
31	23	-21
32	0	-12*
33	61	54
34	21	-18
5	K	0
1	160	155
2	0	-18*
3	124	129
4	26	-35
5	31	-7
6	130	-128
7	62	-55
8	459	459
9	21	16
10	31	8
11	0	15*
12	24	-8
13	36	24
14	59	50
15	43	40
16	133	-133
17	135	-124
18	110	-100
19	154	-156
20	334	323
21	106	110
22	134	137
23	75	74
24	23	-11
25	146	143
26	54	58
27	96	95
28	151	-143
29	27	-29
30	117	-116
6	K	0
0	155	-146
1	101	-92
2	46	-53
3	108	-103
4	215	207
5	101	-90
6	170	-171
7	49	59
8	32	-48
9	54	-48
10	72	-82
11	252	265
12	418	-422
13	134	-146
14	96	-95
15	37	-31
16	45	57
17	23	-25
18	0	18*
19	24	-15
20	96	99
21	92	93
22	66	71
23	115	107
24	42	-46
25	34	-24
7	K	0
1	15	-5
2	0	-14*
3	36	-21
4	163	159
5	37	28
6	20	-24
7	100	105
8	114	-112
9	128	-134
10	75	-79
11	88	-94
12	73	76
13	31	-37
14	58	-64
15	55	-51
16	85	86
17	59	57
18	33	31
-8	K	1
1	42	-45
2	114	-123
3	76	-72
4	0	1*
5	56	59
6	17	-19
7	37	36
-7	K	1
0	36	-18
1	40	46
2	0	7*
3	88	92
4	0	1*
5	41	48
6	256	247
7	33	-12
8	53	53
9	37	35
10	61	-51
11	28	-31
12	37	-25
13	81	84
14	162	-142
15	116	112
16	50	-46
17	23	-16
18	129	120
19	2	14
20	64	72
-6	K	1
1	32	-30
2	492	488
3	35	-17
4	38	24
5	219	-220
6	470	432
7	175	-163
8	27	-28
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7	71	-66
8	121	127
9	42	-36
10	63	-57
11	117	117
12	0	1*
13	110	116
14	95	97
15	0	-7*
16	0	2*
17	109	-108
18	50	37
19	56	-58
20	102	110
21	90	-107
-4	K	6
0	183	-177
1	39	30
2	23	13
3	137	-134
4	0	8*
5	138	-141
6	42	-48
7	70	75
8	9	9
9	96	92
10	11	17
11	23	18
12	93	-87
13	28	21
14	23	7
15	101	-108
16	88	93
17	111	-112
18	105	-111
19	57	55
20	107	105
21	123	125
22	0	16*
23	78	94
24	36	50
-3	K	6
1	130	-123
2	18	-7
3	96	92
4	0	8*
5	59	58
6	27	32
7	31	-2
8	174	-172
9	42	33
10	32	9
11	173	-177
12	27	4
13	150	-155
14	125	-132
15	25	7
16	32	19
17	78	78
18	20	13
19	77	78
20	5	1
21	21	-14
22	63	62
23	0	0*
24	107	111*
25	161	-189*
26	40	-74*
-2	K	6
0	50	54
1	82	76
2	151	-145
3	187	186
4	199	-192
5	275	272
6	151	142
7	94	-97
8	150	-152
9	97	-91
10	0	-14*
11	35	-30
12	0	4*
13	31	-18
14	16	-8
15	64	73
16	78	-88
17	102	98
18	60	61
19	23	-4
20	0	0*
21	29	-20
22	122	-124
23	36	-29
24	39	-37
25	73	77
26	73	-73
27	0	-13*
-1	K	6
1	84	66
2	125	119
3	59	-64
4	44	-24
5	182	-174
6	62	-52
7	101	-87
8	125	119
9	56	-52
10	107	-100
11	127	125
12	0	-5*
13	131	132
14	97	86
15	0	10*
16	0	10*
17	24	-10
18	80	-78
19	23	13
20	24	3
21	0	-5*
22	21	14
23	88	88
24	135	-133
25	76	74
26	112	118
27	24	26
0	K	6
0	365	-361
1	135	-126
2	191	185
3	221	-214
4	204	-208
5	209	-215
6	210	-205
7	65	-59
8	68	-63
9	51	38
10	27	24
11	18	14
12	32	-11
13	11	15
14	30	13
15	81	-71
16	99	96
17	79	-79
18	93	-97
19	47	52
20	26	-10
21	19	9
22	18	24
23	38	35
24	45	-48
25	25	-4
26	0	-11*
1	K	6
1	74	-73
2	115	-117
3	82	-71
4	71	-73
5	129	126
6	0	-7*
7	62	54
8	86	-91
9	64	70
10	64	69
11	0	-17*
12	53	-49
13	78	-79
14	74	-70
15	48	38
16	36	-43
17	27	-5
18	45	57
19	76	71
20	46	-52
21	0	2*
22	40	40
23	62	-68
24	55	59
25	64	-88
2	K	6
0	0	10*
1	33	26
2	83	-81
3	64	66
4	0	15*
5	46	45
6	142	140
7	25	-8
8	0	9*
9	82	-84
10	27	-23
11	46	-41
12	33	-25
13	13	-22
14	69	-72
15	46	52
16	64	-66
17	47	48
18	76	77
19	23	-19
20	23	20
21	67	-67
22	25	-22
3	K	6
1	0	3*
2	46	51
3	39	-45
4	27	22
5	46	-47
6	22	-15
7	59	-58
8	15	-3
9	17	0
10	52	-54
11	22	10
12	49	-52
13	74	79
14	90	93
15	24	20
16	19	12
17	27	-30
4	K	6
0	31	-27
1	21	25
2	61	60
3	40	-44
4	15	-6
5	0	-3*
6	63	-71
7	0	12*
-6	K	7
1	96	190*
2	0	-108*
3	0	59*
4	0	105*
5	0	-8*
-5	K	7
0	124	127
1	45	40
2	136	138
3	163	-160
4	49	-42
5	50	-43
6	117	123
7	22	26
8	43	-51
9	93	66
10	62	-43
11	46	51
12	24	41
13	24	-35
14	0	8*
-4	K	7
1	157	-154
2	37	39
3	50	42
4	119	-121
5	28	23
6	3	20
7	78	79
8	85	91
9	61	55
10	14	15
11	52	-51
12	0	8*
13	85	-88
14	68	75
15	13	-10
16	0	-26*
17	21	32
18	0	-34*
-3	K	7
0	87	-90
1	23	-11
2	41	37
3	43	42
4	46	51
5	70	61
6	83	80
7	67	-68
8	22	18
9	89	-93
10	78	88
11	15	-18
12	84	-91
13	16	5
14	19	8
15	45	45
16	39	46
17	40	35
18	27	-24
19	0	6*
20	21	30
21	0	-126*
-2	K	7
1	80	79
2	18	-22
3	32	-16
4	98	97
5	32	-27
6	51	-55
7	21	-23
8	75	-83
9	59	-60
10	75	-80
11	53	57
12	14	-11
13	78	81
14	46	-52
15	44	-49
16	99	103
17	71	-78
18	73	82
19	91	-93
20	36	-43
21	83	-100
22	37	95*
-1	K	7
0	41	34
1	21	-24
2	20	27
3	0	-6*
4	48	-52
5	17	-7
6	21	24
7	42	38
8	8	-18
9	95	100
10	26	-20
11	4	0
12	89	88
13	22	2
14	30	10
15	25	-18
16	45	-50
17	50	-53
18	59	-66
19	105	111
20	18	-26
21	61	101
22	0	-99*
0	K	7
1	42	-35
2	29	26
3	0	16*
4	119	-120
5	31	49
6	35	-9
7	35	-31
8	63	67
9	0	2*
10	24	28
11	96	-93
12	20	9
13	120	-121
14	31	31
15	56	53
16	77	-79
17	5	4
18	20	-13
19	59	72
20	39	55
1	K	7
0	101	-103
1	71	75
2	20	9
3	59	-65
4	0	4*
5	50	49
6	43	-48
7	109	-107
8	30	-19
9	89	-94
10	68	-65
11	15	11
12	82	-91
13	15	-8
14	76	-82
15	31	31
16	44	55
17	43	47
2	K	7
1	80	79
2	21	6
3	46	-39
4	70	79
5	24	12
6	0	-1*
7	2	-8
8	76	-85
9	13	-14
10	18	-17
11	0	9*
12	34	-39
-4	K	8
0	42	44
1	53	95
2	39	-11
3	27	40
4	22	22
5	0	17*
6	0	52*
7	0	21*
-3	K	8
1	14	15
2	40	41
3	16	20
4	11	5
5	31	-35
6	5	15
7	59	-84
8	12	9
9	30	78*
10	20	-18
11	0	41*
-2	K	8
0	107	109
1	73	-76
2	59	67
3	87	-95
4	13	19
5	29	37
6	29	-23
7	64	-76
8	17	-20
9	57	62
10	15	26
11	0	37
12	14	28
-1	K	8
1	9	12
2	22	-29
3	1	-2
4	60	-58
5	44	45
6	0	3*
7	81	94
8	38	42
9	28	-45
10	22	31
11	0	-8*
12	0	4*
0	K	8
0	105	-108
1	94	114
2	46	47
3	20	8
4	27	29
5	51	63
6	54	88*
7	31	58
8	33	70

Table 5. A comparison of the dimensions of a neutral cytosine molecule (C) with those of the protonated species (CH^+). Standard deviations are about 0.003 Å in the distances and 0.1° in the angles.

Bond distance (Å)

Bond	C(*a*)	CH^+(*b*)
N(1)-C(2)	1.375 Å	1.381 Å
C(2)-N(3)	1.359	1.383
N(3)-C(4)	1.344	1.350
C(4)-C(5)	1.428	1.409
C(5)-C(6)	1.345	1.350
C(6)-N(1)	1.359	1.359
C(2)-O(2)	1.247	1.216
C(4)-N(4)	1.331	1.314

Bond Angle (°)

Angle	C(*a*)	CH^+(*b*)
C(6)-N(1)-C(2)	122.0	121.1
N(1)-C(2)-N(3)	119.1	114.8
C(2)-N(3)-C(4)	119.4	126.1
N(3)-C(4)-C(5)	122.0	116.8
C(4)-C(5)-C(6)	117.2	118.6
C(5)-C(6)-N(1)	120.4	122.8
N(1)-C(2)-O(2)	119.1	123.4
N(3)-C(2)-O(2)	121.8	122.0
N(3)-C(4)-N(4)	118.0	120.0
C(5)-C(4)-N(4)	120.0	123.3

(*a*) Average from values for cytosine (11) and cytosine monohydrate (10).

(*b*) Average of molecules A and B, this investigation.

Table 6. Least-squares planes of the six-membered rings. The direc-cosines (g_i) are relative to the crystal axes <u>a</u>, <u>b</u>, and <u>c</u>; D is the origin-to-plane distance.

	Ring A	Ring B
g_a	-0.0492	0.0548
g_b	0.1852	0.0575
g_c	-0.9393	0.9528
D	1.112 Å	1.058 Å

Atom	Wt.	Deviation (Å)	
N(1)	7	-0.004	-0.008
C(2)	6	0.001	0.004
N(3)	7	0.003	0.003
C(4)	6	-0.005	-0.007
C(5)	6	0.002	0.002
C(6)	6	0.002	0.006
C(1)	0	-0.078	-0.012
O(2)	0	0.000	0.003
N(4)	0	-0.019	-0.030
H(1a)	0	-0.65	-0.26
H(1b)	0	-0.51	-0.51
H(1c)	0	0.75	0.81
H(3)	0	-0.03	-0.02
H(4a)	0	0.02	-0.08
H(4b)	0	-0.01	-0.07
H(5)	0	0.01	-0.06
H(6)	0	0.03	0.02

Table 7. Bond Distances and Angles involving the Hydrogen Atoms.

The esd's are about 0.03 Å and 2.0°.

Bond	Molecule A	Molecule B
C(1) - H(1a)	1.01 Å	0.96 Å
C(1) - H(1b)	0.92	0.98
C(1) - H(1c)	0.95	0.93
N(3) - H(3)	0.83	0.94
N(4) - H(4a)	0.90	0.98
N(4) - H(4b)	1.03	0.91
C(5) - H(5)	0.86	0.89
C(6) - H(6)	1.01	1.02

Bonds		
N(1) - C(1) - H(1a)	110.9°	110.1°
N(1) - C(1) - H(1b)	108.2°	112.1°
N(1) - C(1) - H(1c)	116.9°	116.2°
C(2) - N(3) - H(3)	116.4°	114.9°
C(4) - N(3) - H(3)	117.5°	119.0°
C(4) - N(4) - H(4a)	122.7°	122.4°
C(4) - N(4) - H(4b)	122.9°	124.3°
C(4) - C(5) - H(5)	120.7°	120.7°
C(6) - C(5) - H(5)	120.6°	120.6°
C(5) - C(6) - H(6)	125.4°	123.8°
N(1) - C(6) - H(6)	111.8°	113.4°

H(1a) - C(1) - H(1b)	106.2°	116.5°
H(1b) - C(1) - H(1c)	107.4°	97.8°
H(1a) - C(1) - H(1c)	107.3°	103.7°
H(4a) - N(4) - H(4b)	114.3°	113.2°

Figure 1. Distances and angles

The standard deviations for heavy atom distances and angles are 0.004 Å and 0.15°. Standard deviations involving hydrogen distances and angles are about ten times larger.

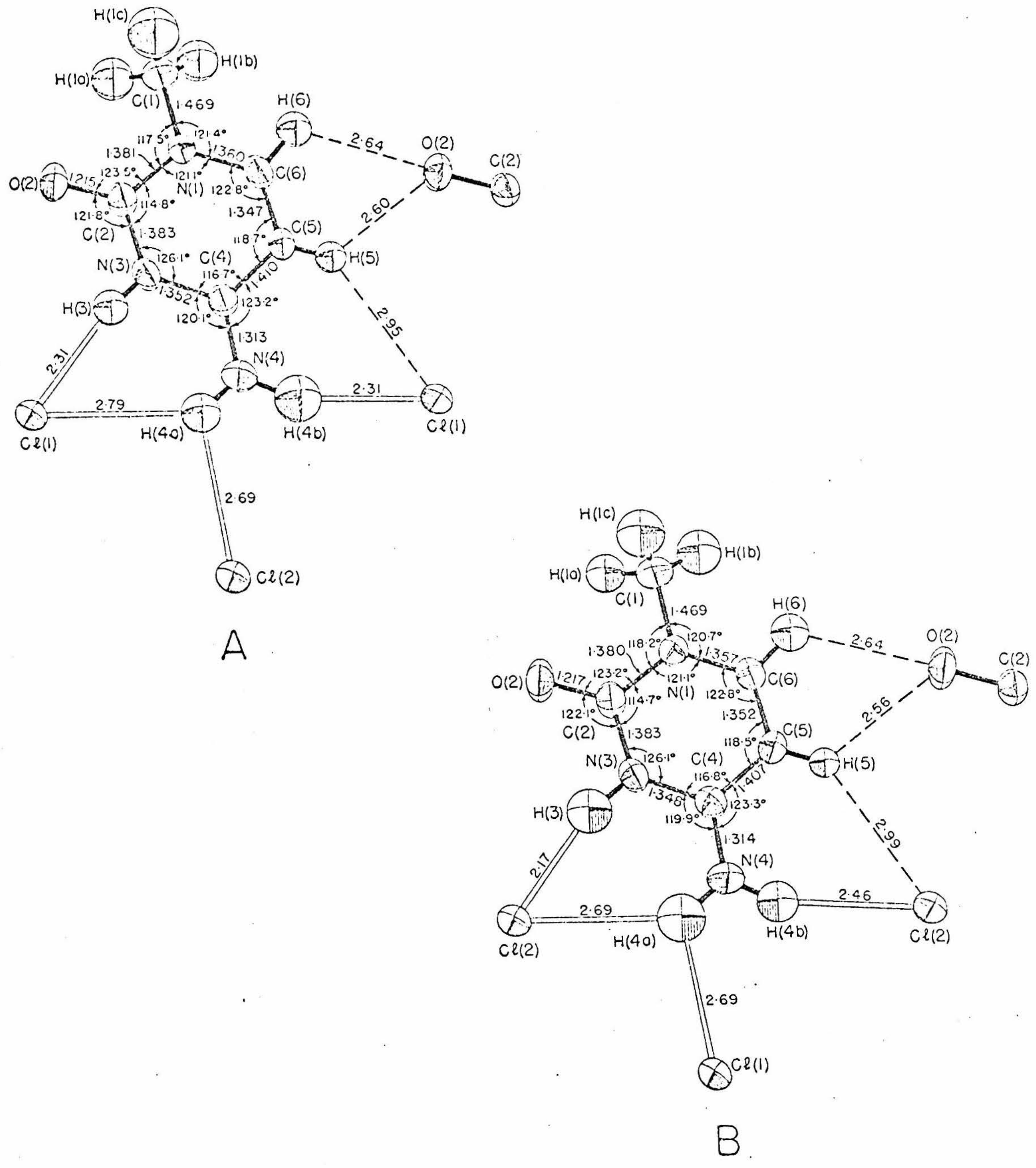


Figure 2. Details of the hydrogen bonding scheme.
The distances are averaged values for molecules A and B.

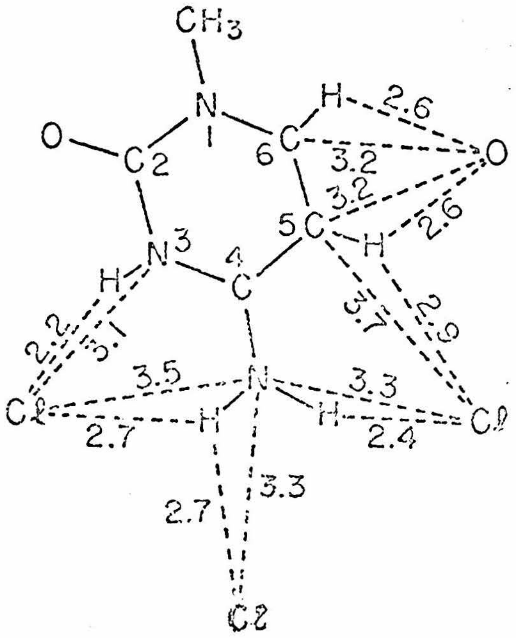
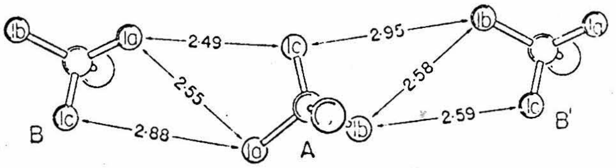


Figure 3. Details of the packing of the methyl groups.
The direction of view is approximately parallel to the b axis and to the C(1)-N(1) bonds. Methyl group E' is related to group B by a unit-cell translation in the a direction.



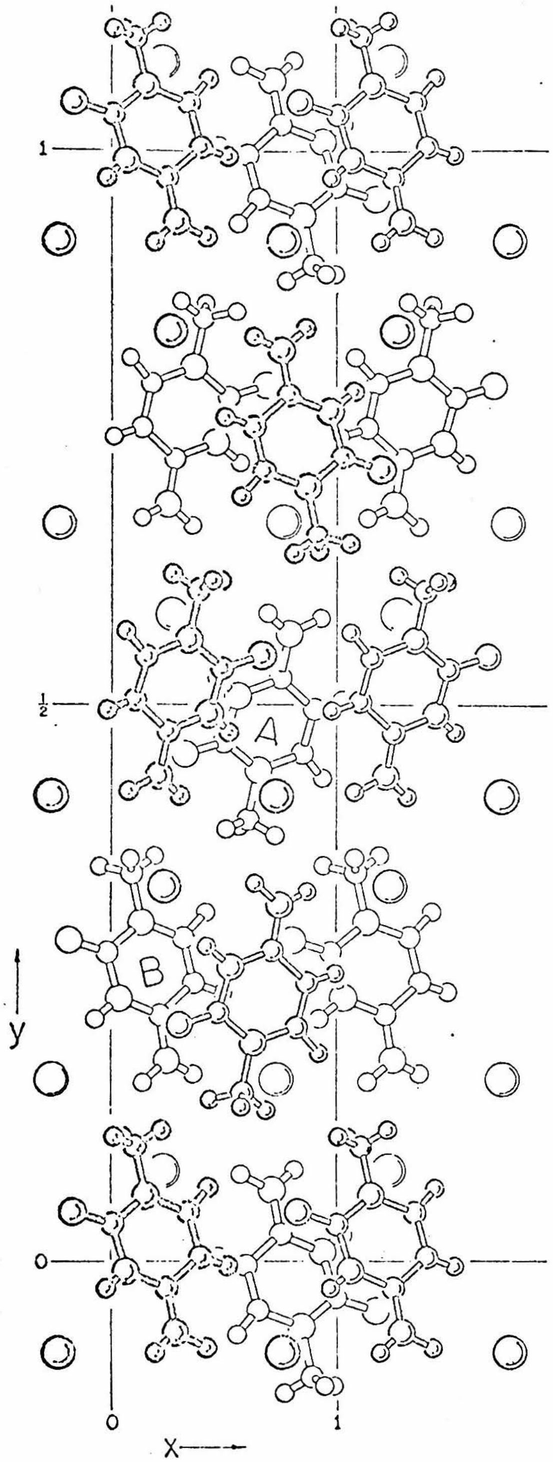


Figure 4
View down the c axis

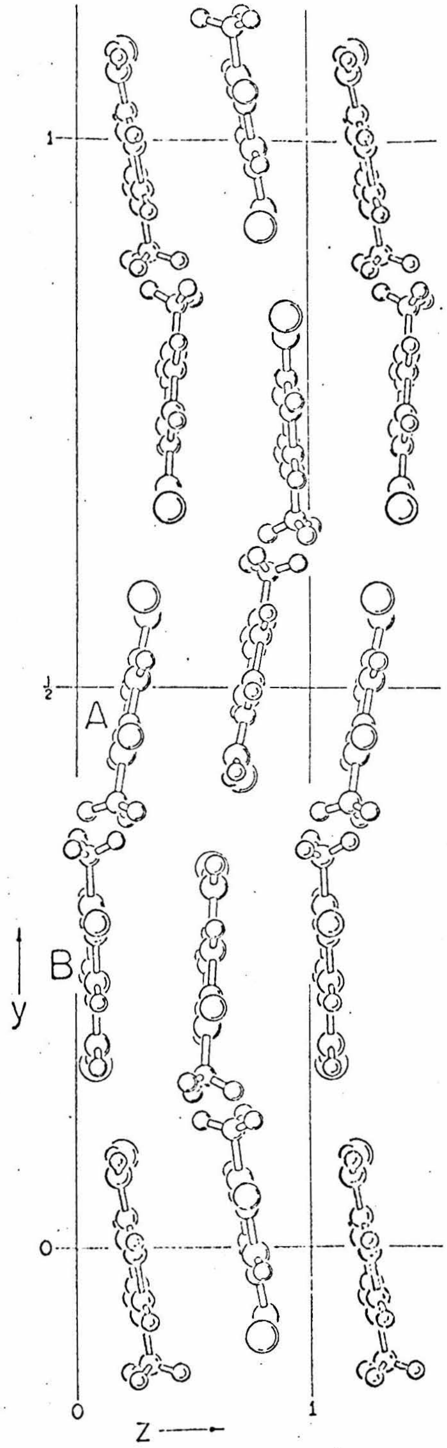


Figure 5
View up the a axis

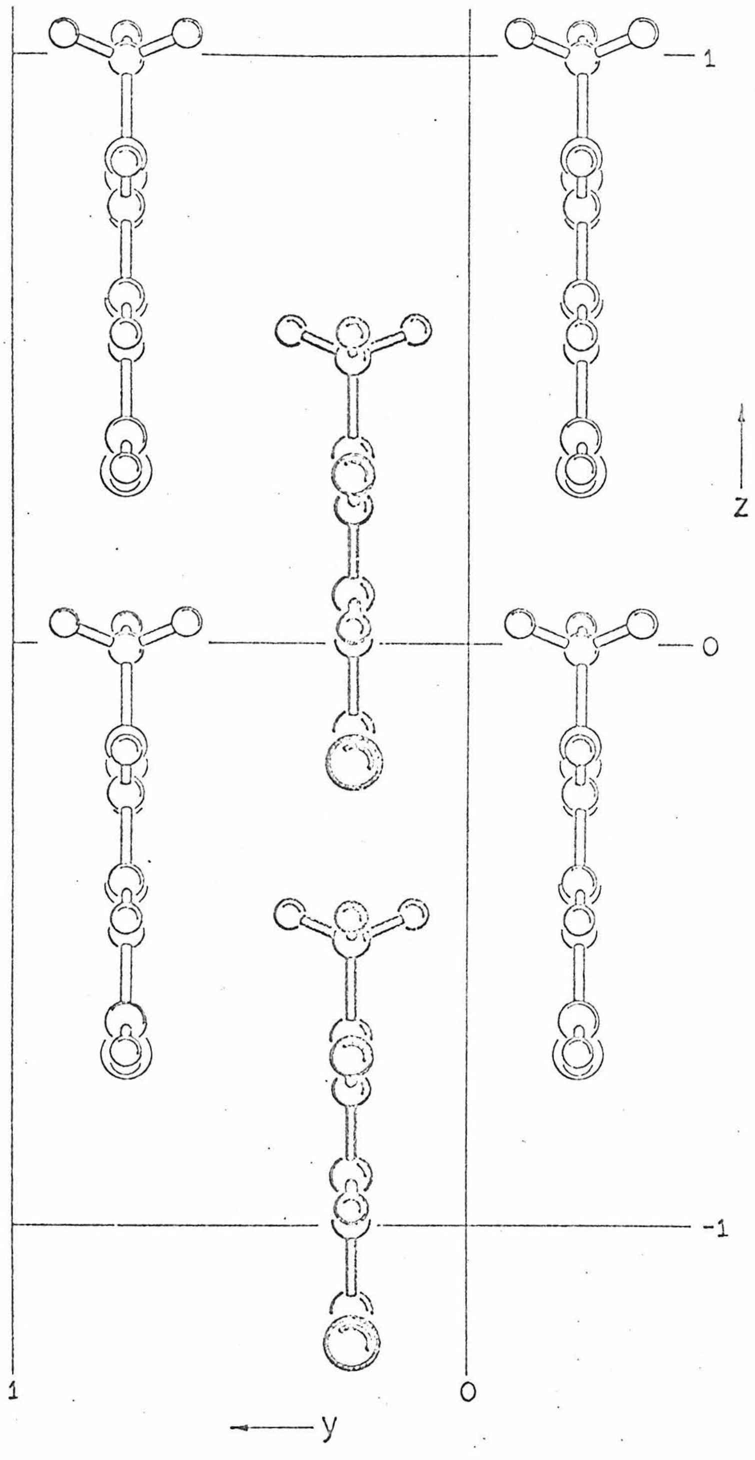


Figure 6
The structure of methylcytosine hydrobromide (7)
as viewed down the a axis

II

The Determination of the Crystal Structure of a Lumiflavin Complex

Introduction

The purpose of this study was to determine the structure of a lumiflavin complex as an aid to the Tulane University's charge transfer project. The structure was solved at Caltech using direct methods and returned to Tulane for least-squares refinement and analysis.

Experimental

Robert Johnston at Tulane University prepared a few yellow crystals from a mixture of lumiflavin, 2-3 naphthalenediol, acetone, and water. The bulk of the product was an orange charge-transfer complex of lumiflavin with two naphthalenediols. In August 1968 Joe Wells began analyzing the structure of the yellow crystal obtained from the same mixture. There was insufficient yellow compound for elemental analysis or spectral studies. The Tulane crystallography group approached the problem from both direct and Patterson methods. By August 1969 the Tulane group had exhausted their facilities for solving the structure of the yellow crystal, and a copy of the data was mailed to Caltech.

Structure Solution

We decided to employ direct methods using Long's program (1) for the itterative application of Sayer's equations (2). The choice of origin is a critical problem. The Tulane group had selected large E's (normalized structure factors) of questionable accuracy. Dr. Richard Stanford proposed a weighting function based on sin Θ with weight = $E N^2 (1 - \sin \Theta)$, where the weight represents the quality of the E. The number of interactions is N, and Θ is the Bragg angle. Table 1 shows the E's considered for the origin choice. Three linearly independent E's were signed to specify the origin, and four other reflections were assigned phases of + and - (2^4 = 16 possible combinations). From these seven reflections 485 reflections with E greater than 1.3 were assigned signs. Table 2 shows the results of the phasing. Set 1 converged quickly (in four cycles), had an even distribution of positive (243) and negative (242) signs, and had the highest consistency, 0.67. A usual consistency index for a correct solution is about 0.8. One reason for the low consistencies in these solutions is that so many reflections were used in the phase determination. Normally one would use a higher E minimum, and thus fewer E's. The low E's were used in order to get good resolution of the ring systems. The Tulane group had used around 10 E's per atom and encountered a continum of of hexagons on the E maps. We lowered the E min to 1.3 to get a 15 to 1 ratio of E's to atoms, hoping to achieve better resolution.

Figures 1 and 2 are the E maps from set 1. From these E maps the molecules were located (Figures 3 and 4). The results indicated that the crystal contains one lumiflavin and two naphthalenediols in the asymmetric unit.

However, the initial R factor was 0.70 using the E-map positions. A difference-Fourier map did not indicate what was wrong with the trial structure, and the model was too poor to be refined by least-squares. However, close scrutiny of the observed and calculated structure factors indicated fair agreement for the low order data. Furthermore, the packing and hydrogen bonding scheme looked quite good for the model. Therefore, a series of difference map calculations, model adjustments, and structure-factor calculations was begun to refine the structure. After 20 sets of calculations with an R near 0.50 it became apparent that all the molecules were moving in the same direction. By moving the molecules more than the difference maps indicated, the R began dropping more rapidly to about 0.42. At this point the model was good enough for least-squares refinement. Two cycles of full-matrix least-squares lowered R to 0.24. The atomic coordinates were returned to Tulane for further refinement.

References to Part II

1. R. E. Long, Ph.D. Thesis, Part III, University of California, Los Angeles (1965).

2. D. Sayre, <u>Acta Cryst</u>, <u>5</u>, 60 (1952).

Table 1. E's > 2.8 ordered by parity of hkℓ. The table lists hkℓ, E, number of interactions, and Dr. Stanford's weight ($w=|E|N^2(1-\sin\theta)$).

eee	eeo	eoe	oee	eoo	oeo	ooe	ooo
-12 2 16 4.97 80 2.16	2 6 3 3.63 66 0.90	-16 1 2 6.02 127 5.69‡	-11 2 16 3.92 80 1.42	-16 3 3 5.47 104 3.25	-13 9 13 4.15 71 1.12	5 1 14 8.10 111 5.32	-17 3 7 6.55 112 4.45
-12 0 16 3.96 98 2.22	-4 6 7 2.96 67 0.73	6 1 14 4.85 70 1.22	1 4 2 3.47 137 4.45‡	4 3 11 4.20 92 2.07	1 4 1 3.95 132 4.96‡	-17 1 12 7.39 123 6.27	-17 3 1 5.43 89 2.19
-2 2 10 3.75 132 4.63	4 4 11 2.82 84 1.08	-16 1 4 4.79 114 3.74	5. 2 12 3.42 79 1.21	-18 3 7 3.58 89 1.47	1 2 1 3.35 177 8.96*	-13 1 18 5.71 91 2.51	3 5 11 3.55 65 0.76
0 6 6 3.74 70 1.02		-12 1 14 4.67 114 4.25	7 0 4 3.38 170 7.26*			-17 3 6 4.64 91 2.07	-13 5 11 3.50 60 0.64
0 2 0 3.62 301 28.3		-18 1 4 4.17 107 2.62	5 2 14 3.30 84 1.20			-13 1 16 4.54 84 1.82	
		4 1 12 4.16 113 3.20				-11 1 16 3.74 103 2.32	
		14 1 6 4.14 93 1.87				-9 1 6 3.74 169 8.17*	
		-18 1 6 4.07 111 2.80				5 1 12 3.68 118 3.00	
		16 1 4 3.74 72 0.98				7 1 4 3.63 157 6.57‡	
		-16 3 2 3.71 96 1.86					

*Origin reflection

‡Variable

Table 2. Lumiflavin Phasing Results

Set	Cycles	No. +	No. -	Consistency Index
1	4	243	242	0.67118
2	5	230	255	0.61020
3	5	223	262	0.51312
4	17	246	239	0.46133
5	4	246	239	0.65071
6	17	245	240	0.60870
7	6	261	224	0.54535
8	17	234	251	0.48266
9	4	242	243	0.63773
10	17	249	236	0.60777
11	8	237	248	0.52200
12	17	235	250	0.48078
13	4	244	241	0.65631
14	17	263	222	0.59210
15	9	233	252	0.51933
16	9	235	250	0.48125

Figure 1. Lumiflavin - Napthalenediol E Map at y = 0.25.

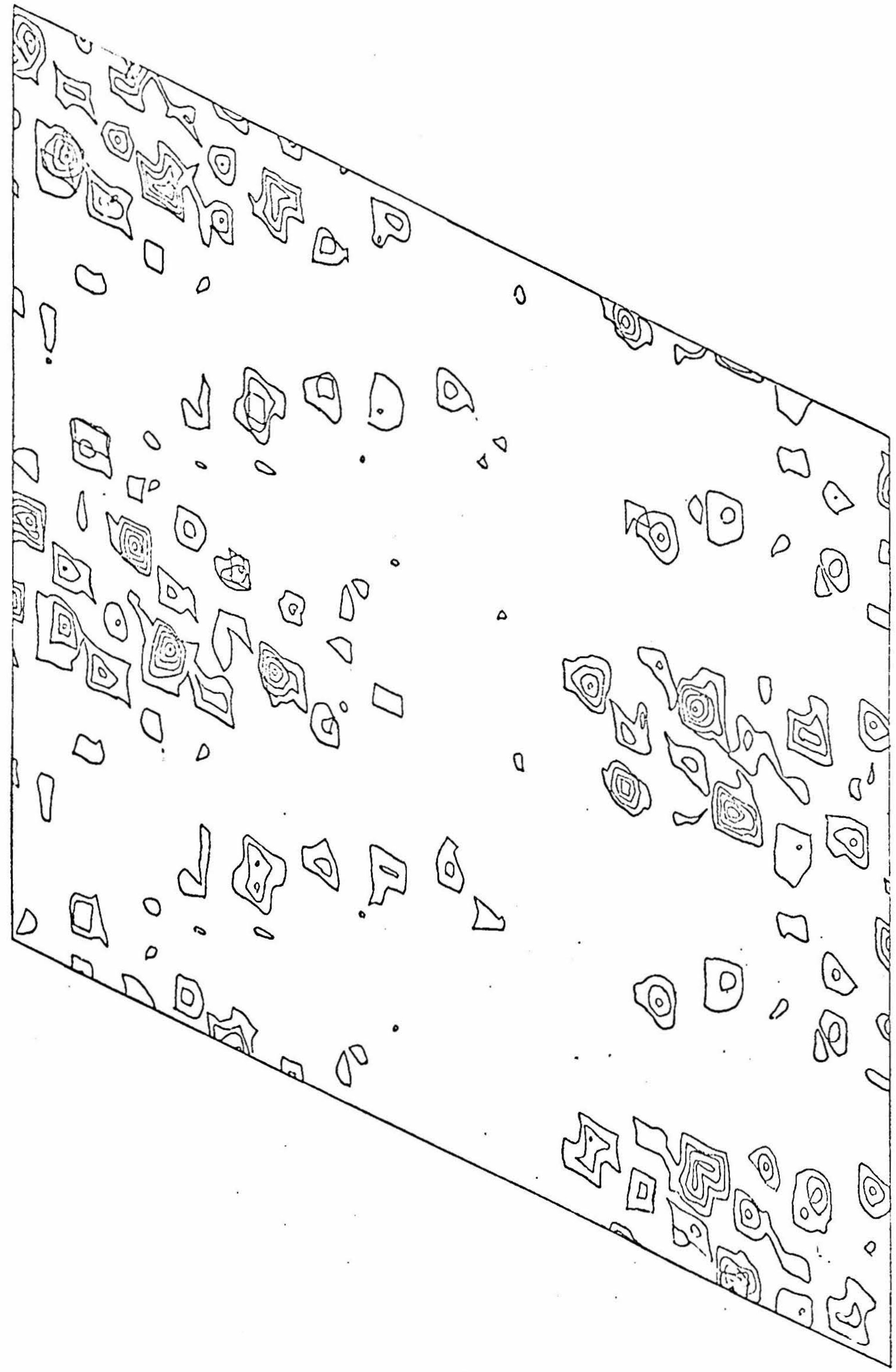


Figure 2. Napthalenediol E Map.

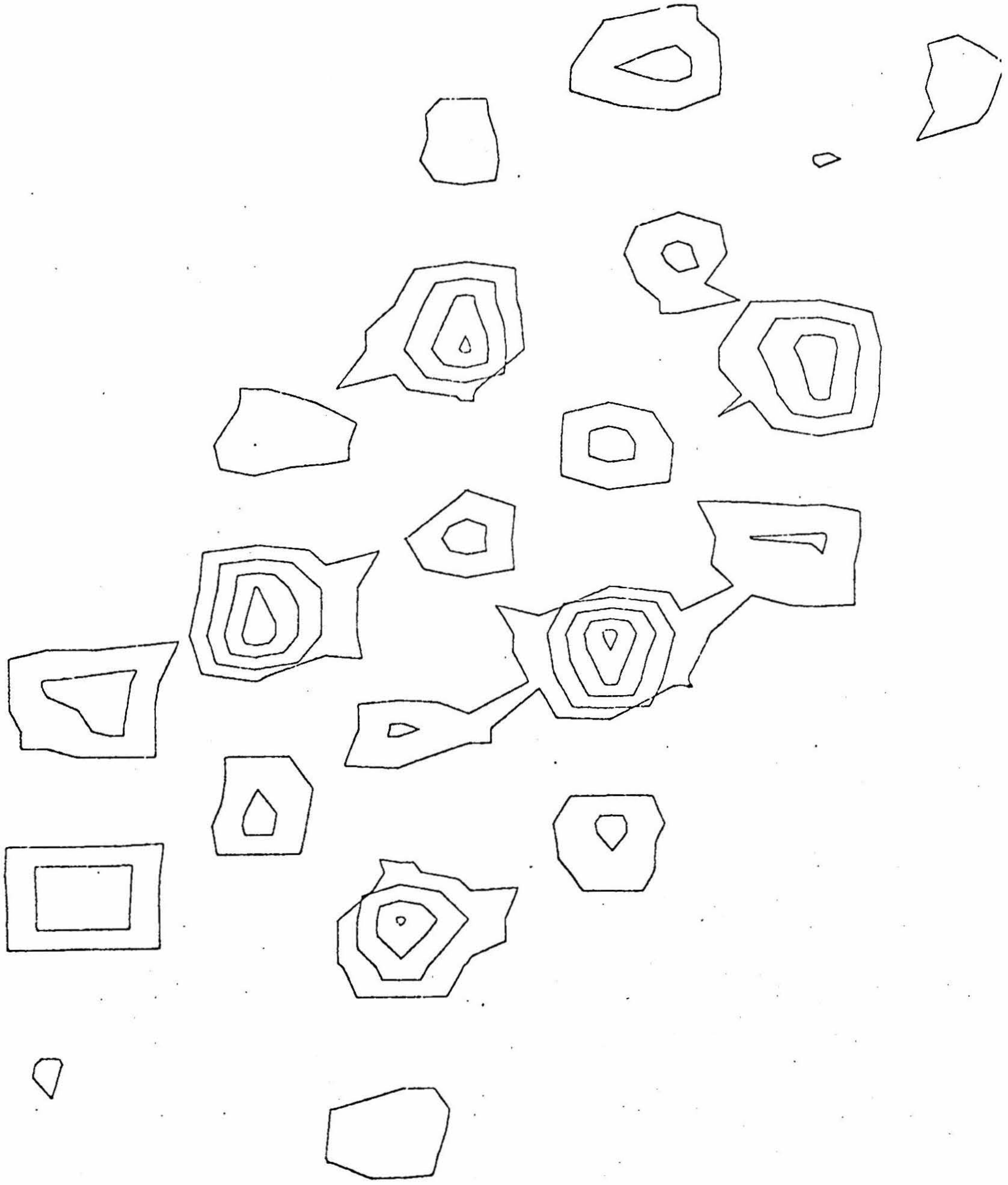


Figure 3. Lumiflavin - Napthalenediol E Map at y = 0.25.

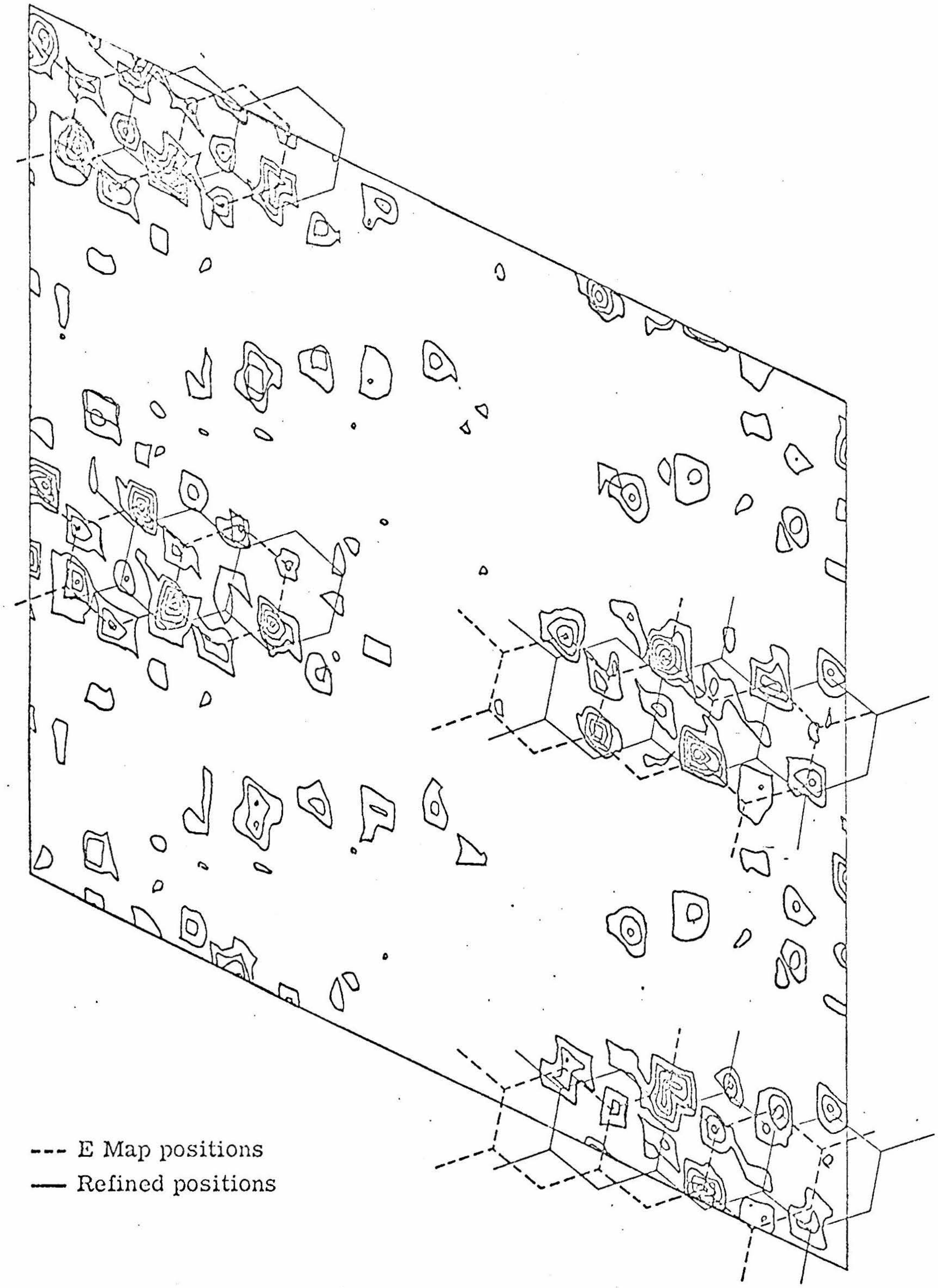
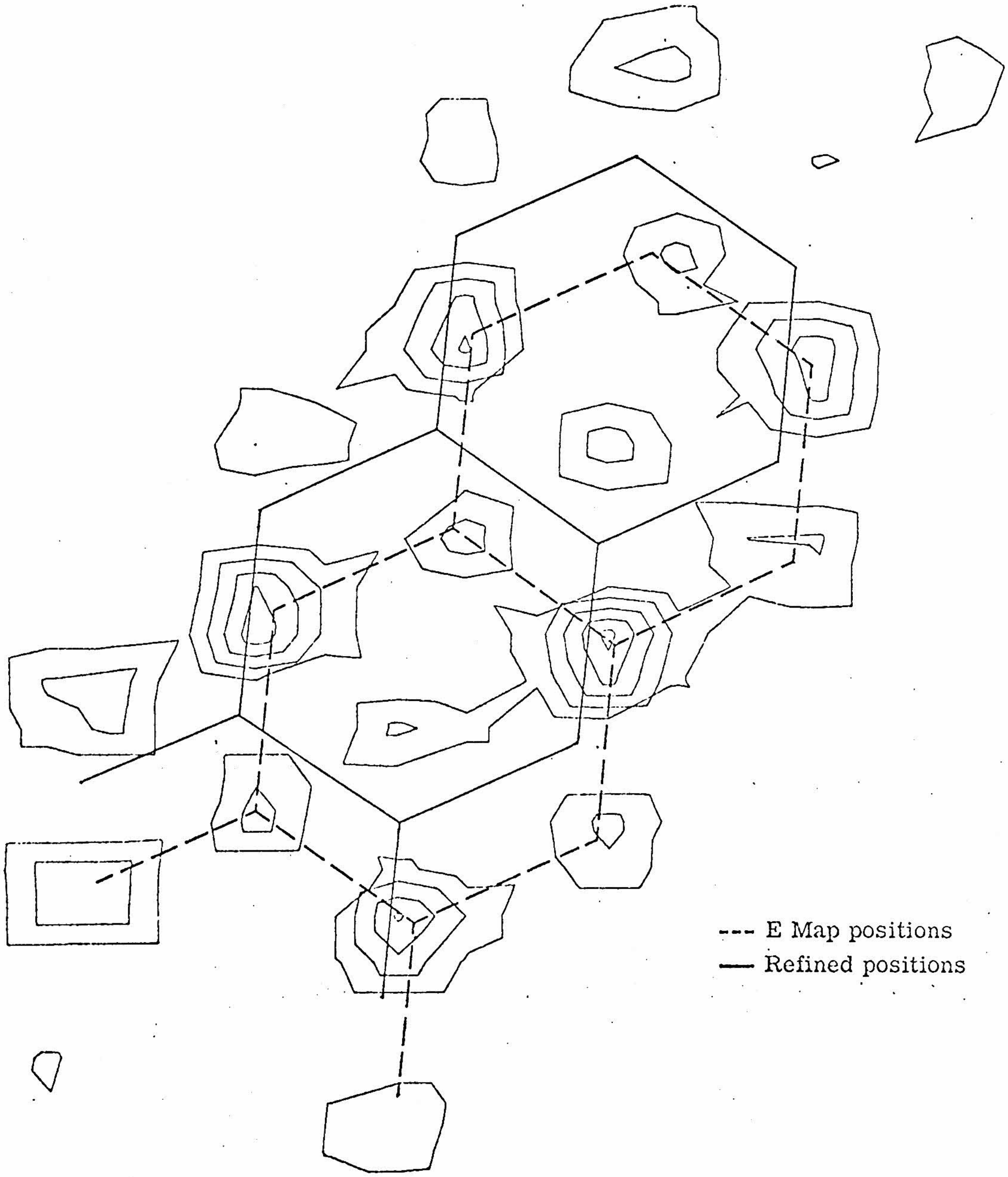


Figure 4. Napthalenediol E Map.



The article "Crystal Structure of the Yellow 1:2 Molecular Complex Lumiflavin-Bisnaphthalene - 2, 3-diol," by Benes L. Trus, Joe L. Wells, Robert M. Johnston, Charles J. Fritchie, Jun., and Richard E. Marsh, Chemical Communications 751 (1971) has been removed to comply with copyright regulations.

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Crystal Structure of the Yellow 1:2 Molecular Complex Lumiflavin–Bisnaphthalene-2,3-diol

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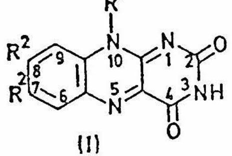
Summary In the first molecular complex of the physiologically active *neutral* form of isoalloxazine studied, lumiflavin–bisnaphthalene-2,3-diol, each flavin is sandwiched between two naphthalenediol molecules with extensive overlap but a moderately large (3·44 Å) spacing, indicating at most weak charge-transfer interaction and in agreement with the yellow colour of the complex, nearly the same as that of the parent lumiflavin.

ISOALLOXAZINE (I) is the aromatic portion of flavin cofactors, the redox-active functional groups in many enzymes including some in the vital mitochondrial electron-transport system. Some of us (Tulane) are studying simple derivatives of (I) which are chosen to be sterically and electronically as similar as possible to the enzyme co-factor riboflavin (vitamin B_2; R^1 = D-ribityl and R^2 = methyl), so as to deduce the relative hydrogen-bonding effectiveness of the functional groups located in ring positions 1—5, and also to study the ability of isoalloxazine to participate in molecular π-complexes as possible models for its electron-transfer reactions. Two π-complexes of N(1)-protonated isoalloxazines[1] have been studied, but since N(1) is protonated only at pH $\leqslant$ O, these cannot be regarded as models of physiological systems.



(I)

Several 2:1 complexes of dihydroxynaphthalenes with various simple 10-substituted (yellow) isoalloxazines have been crystallized and with the exception of the one reported here all of the complexes are orange or red, indicating some degree of perturbation of the isoalloxazine π-system. (In fact, an orange complex of composition apparently identical to that of the yellow one reported here is also being studied.)

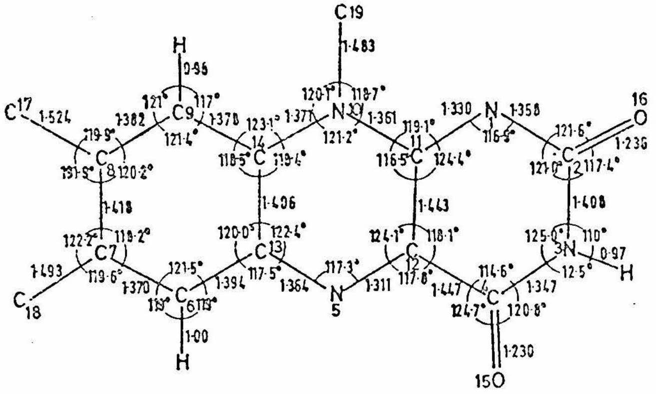


FIGURE 1. *Bond distances and angles in the lumiflavin molecule. Standard deviations are about* 0·008 Å *and* 0·8° *for bonds and angles involving heavy atoms and* 0·04 Å *and* 4° *for those involving hydrogen.*

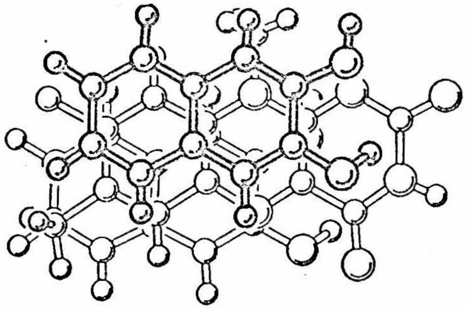


FIGURE 2. *A portion of the structure, showing a lumiflavin molecule sandwiched between two naphthalenediol molecules. The view is in a direction perpendicular to the mean plane of the flavin and nearly parallel to the* b *axis.*

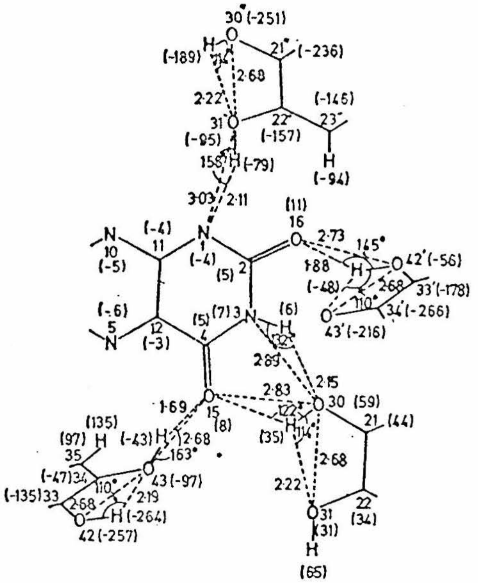


FIGURE 3. *A view perpendicular to the mean flavin plane, showing the pyrimidine end of a lumiflavin molecule surrounded by portions of four naphthalenediol molecules. Figures in parenthesis are displacements (in* Å × 10^2*) from the plane.*

The yellow complex lumiflavin–bisnaphthalene-2,3-diol, $C_{13}H_{12}N_4O_2,2C_{10}H_8O_2$, was crystallized by cooling and evaporation of an acetone–water solution nearly saturated in lumiflavin (I; $R^1 = R^2 =$ Me) and containing a large molar excess of naphthalene-2,3-diol. The crystals are monoclinic, space group $P2_1/c$, with $a = 20{\cdot}78(2)$, $b = 7{\cdot}24(1)$, $c = 20{\cdot}15(2)$ Å [λ (Cu-K_α) = 1·5418 Å], $\beta = 116{\cdot}19 \pm 0{\cdot}04°$, $D_c = 1{\cdot}402(3)$; $Z = 4$; $D_m = 1{\cdot}40 \pm 0{\cdot}01$. Intensity measurements on a Picker 4-circle diffractometer with Ni-filtered Cu-K_α radiation to $2\theta = 100°$ yielded 2826 reflections of which 1753 were greater than 3σ above background. The structure was solved at Cal Tech by use of direct methods of phasing and was refined at Tulane to a current R value of 5·5%. All hydrogen atoms were located unambiguously on difference maps except those of the methyl group at C(8), which appears to be disordered or rotating. The molecular geometry is shown in Figure 1 and in general agrees excellently with bond lengths predicted.[2] The bond lengths also agree reasonably well with comparable ones in 9-bromo-3,7,8,10-tetramethylisoalloxazine.[3] Although the lumiflavin molecule in this structure is sandwiched between translationally related naphthalenediol molecules with extensive overlap of the π-systems (Figure 2), the moderately large spacing of 3·44 Å to *both* upper and lower molecules and the similarity in colour of this complex to lumiflavin itself indicate little perturbation of the isoalloxazine π-system (*i.e.* little charge-transfer bonding).

Of particular interest with reference to protein active-site steric requirements is the test this structure provides for the suggestion of one of us[1a] that the chelate site CO(4)-N(5) will almost always be occupied by a positive group or dipole, and for our other suggestions regarding relative hydrogen-bonding affinities. These suggestions were based entirely on studies of N(1)-protonated flavins, but it is seen (Figure 3) that a hydroxide group, OH(43), from a naphthalenediol molecule indeed lies essentially in the chelate site; it is hydrogen bonded to CO(4) and O(43) is 3·44 Å from N(5). A major predictable difference in hydrogen-bonding affinities of the protonated and unprotonated species is the probable high affinity of unprotonated N(1) for hydrogen-bond donors, and in fact such a bond is present. In agreement with the other suggestions, NH(3) serves as a donor and CO(4) is a double acceptor whereas CO(2) is a single acceptor.

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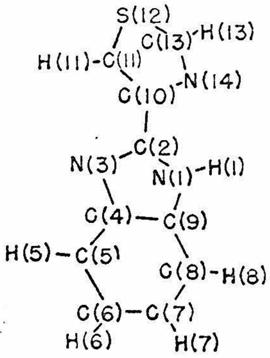
III

The Crystal Structure of Thiabendazole

Introduction

Thiabendazole,

2-(4'-thiazolyl)benzimidazole,



is a broad spectrum anthelmentic useful in the treatment of the parasitic diseases of humans and other animals (1). Though its mode of operation is not known, its effects have been studied. Thiabendazole has been shown to be a good chelating agent (2). Also, thiabendazole has been found to inhibit the rate of NADH oxidation (3).

The crystal and molecular structure of thiabendazole was studied in order to gain additional insight into its inter- and intramolecular forces in the crystal state.

Crystal data

Crystals of thiabendazole were prepared by the evaporation of a methanol solution. The crystals were colorless needles elongated along the c axis.

The space group and approximate cell constants were obtained from Weissenberg photographs; more accurate cell constants were obtained by a least-squares fit to 2θ values measured on a diffractometer. The density was measured by flotation in a chloroform-ethanol mixture. Crystal data are given in Table 1.

Experimental

Intensity data were measured on a Datex-automated General Electric diffractometer, using Ni-filtered CuKα radiation. The crystal had approximate dimensions 0.39 x 0.23 x 0.19 mm. Reflections with $2\theta \leq 150°$ were scanned in the θ-2θ mode at a rate of 2° per minute, the scan range varying from 3° at $2\theta = 12°$ to 4° at $2\theta = 130°$. A thirty second background count was recorded on either side of the scan range. Two standard check reflections were measured after every 40 reflections and served to measure any variation in crystal or instrument stability. There was no significant change in the intensity of these check reflections. Absorption corrections were not applied.

A total of 1947 independent reflections were measured. Each reflection was assigned a standard deviation based on a combination of counting statistics plus an uncertainty of 2% in the time-dependent scale factor. Squares of the structure-factor amplitudes, $|F_o|^2$, and their standard deviations were derived from the net intensities by application of the Lorentz and polarization factors. In the least squares the weight was assigned a value of $1/\text{sigma}^2(I)$. Any reflection for which the net value of $|F_o|^2$ was less than or equal to zero was considered to be below an observational threshold and assigned an intensity and a weight of zero. There were 1805 non-zero observations in the final data set. The data were scaled by Wilson (4) statistics, and $|E|$'s and $|F|$'s calculated.

Structure solution and refinement

The structure was solved by the symbolic method (5, 6, 7) based on the 190 reflections with $E \geq 1.70$. The correct solution had the highest consistency (0.85) and the fewest number of cycles to convergence. Table 2 lists the origin choice and symbols.

An E map based on the signs from the symbolic addition showed the location of all non-hydrogen atoms. Figure 1 shows the original E map compared with the final Fourier in the mean plane of the molecule. The resulting structure-factor calculation based on the E map positions gave an R $(= \Sigma|F_o-F_c| \; \Sigma|F_o|)$ of 0.331 for $\sin^2\theta/\lambda^2$ data ≤ 0.2. Three cycles of full-matrix least-squares adjustment of the coordinates and isotropic temperature factors lowered R to 0.174. A difference map indicated significant anisotropic motion for the sulfur atom and the location of the hydrogen atoms. Anisotropic and positional refinement for all heavy atoms reduced the R to 0.079. Further refinements including hydrogen positions and isotropic thermal parameters, heavy-atom anisotropic and positional parameters, a scale factor, and a secondary extinction factor (8) decreased R to 0.066 with a weighted R $[= \Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w F_o^4]$ of 0.10 and a goodness of fit $\{= [\Sigma w|F_o|^2-|F_c|^2)^2/)M-S)]^{\frac{1}{2}}$ for M = 1805 observations and S = 156 parameters$\}$ of 1.68. The largest shift in the final least-squares calculation was 0.6 σ.

Scattering factors were those listed in International Tables for X-ray Crystallography (9) except for hydrogen (10). Computations were performed at the Caltech Computer Center on the 360-75 using the CRYM system (11). Some of the crystallographic illustrations were produced by ORTEP (12).

The final positional parameters appear in Table 3 and the anisotropic thermal parameters in Table 4. Observed and calculated structure factors are listed in Table 5. The final value of the extinction parameter of Larson (8) was $2.3 \pm 0.2 \times 10^{-6}$.

Discussion

Molecular configuration

The bond distances and angles for thiabendazole are shown in Figure 2. The standard deviation in C-S bond lengths is about 0.003 Å; the standard deviation in the other heavy-atom bond lengths is about 0.006 Å; and the standard deviation of light-atom bond lengths is about 0.05 Å. Standard deviations in heavy-atom angles is about 0.3°, and 1.5° for angles involving light atoms.

The C-S distance of 1.69 Å is shorter than the 1.73 Å in the similar portion of luciferin (13). However, the effective C-S distance would be longer if the significant anisotropic vibration of the sulfur perpendicular to the ring were taken into account by a rigid-body motion analysis. The C-C bond length of 1.442 Å between the two ring systems indicates significant delocalization across the bond. The two rings are tilted only 9°55' with respect to each other. Both ring systems are closely planar (see Table 6). The distances and angles for the benzimidazole system compare favorably with those for the similar portion of indomethecin (14). Of particular curiosity is the difference in bond lengths and angles involving C(6) and C(7). Careful inspection of the data, packing considerations, and resonance models fail to explain the unsymmetrical distances and angles in the lower ring.

There is only one hydrogen bond donor, N(1), but there are two possible receivers, N(3) or N(14). N(3) is the receptor on the hydrogen bond with an N···N distance of 2.86 Å, a H···N distance of 2.10 Å, and an N-H···N angle of 156.5°. There are no other significant close contacts.

Packing

If the C-C bridging bond is considered a groove, the molecules pack together by slipping one groove into another in a crisscross pattern much like the timber in log cabins. This is illustrated by the packing diagrams down the c axis (Figure 3) and down the b axis (Figure 4). The projection down the b axis illustrates the hydrogen bond parallel to c.

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Table 1. Crystal data

$C_{10}H_7N_3S$

Space group P_{bca}

$\underline{a}$ = 17.052(7) Å

$\underline{b}$ = 10.998(4) Å

$\underline{c}$ = 10.030(8) Å

λ = 1.5418 Å

V = 1881(3)

u = 26.3

F_{000} = 1608

F. W. = 201.3

Systematic absences:

$0 k \ell$, $k = 2n + 1$

$h 0 \ell$, $\ell = 2n + 1$

$h k 0$, $h = 2n + 1$

Z = 8

D_c = 1.421 gm cm^{-1}

D_m = 1.414 gm cm^{-1}

TABLE 2. Data from Symbolic Addition

	H	K	L	E	Fixed Phases	Assigned Phases
Origin	2	3	0	3.20	+	
	2	2	1	3.64	-	
	15	1	3	2.77	+	
Symbols	8	11	1	3.82		-
	2	5	8	3.37		-
	8	1	7	3.23		-

TABLE 3. Positional and Isotropic Parameters
Standard deviations are given in parentheses.

	x*	y*	z*	B
N(1)	3536 (1)	7611 (2)	3566 (2)	---
C(2)	3952 (1)	7428 (2)	2452 (2)	---
N(3)	3613 (1)	7851 (2)	1366 (2)	---
C(4)	2905 (1)	8350 (2)	1832 (2)	---
C(5)	2319 (1)	8928 (2)	1130 (3)	---
C(6)	1670 (2)	9342 (3)	1817 (3)	---
C(7)	1641 (2)	9186 (3)	3203 (3)	---
C(8)	2221 (2)	8620 (2)	3892 (3)	---
C(9)	2852 (1)	8202 (2)	3200 (2)	---
C(10)	4698 (1)	6810 (2)	2458 (2)	---
C(11)	5194 (2)	6682 (3)	1414 (3)	---
S(12)	59752 (4)	58225 (8)	18496 (8)	---
C(13)	5596 (1)	5671 (3)	3389 (3)	---
N(14)	4935 (1)	6213 (2)	3602 (2)	---
H(1)	368 (1)	743 (3)	430 (3)	4.9 (0.7)
H(5)	235 (1)	909 (2)	13 (2)	4.4 (0.6)
H(6)	137 (1)	959 (2)	145 (2)	2.2 (0.5)
H(7)	127 (2)	937 (3)	362 (2)	4.6 (0.7)
H(8)	218 (1)	854 (2)	481 (3)	4.1 (0.6)
H(11)	514 (2)	702 (2)	64 (3)	5.7 (0.7)
H(13)	585 (2)	519 (3)	407 (3)	6.2 (0.7)

* Positional parameters and standard deviations multiplied by 10^5 for S(12), 10^4 for nonhydrogen atoms, and 10^3 for hydrogens.

TABLE 4. Anisotropic Thermal Parameters
Standard deviations are given in parentheses.
The thermal expression has the form
$-[B_{11}h^2 + B_{22}k^2 + B_{33}\ell^2 + B_{12}hk + B_{13}k\ell + B_{23}k\ell]$

B_{11}*	B_{22}*	B_{33}*	B_{12}*	B_{13}*	B_{23}*
300 (6)	742 (18)	522 (24)	3 (19)	-59 (22)	77 (36)
251 (6)	678 (18)	682 (25)	-108 (22)	16 (26)	-69 (42)
285 (6)	791 (18)	653 (21)	-53 (17)	-107 (20)	168 (32)
273 (7)	707 (19)	704 (28)	35 (19)	-101 (26)	0 (41)
376 (10)	899 (27)	782 (30)	205 (25)	-171 (27)	113 (43)
399 (10)	983 (28)	1051 (41)	528 (29)	-168 (37)	70 (52)
343 (10)	1132 (29)	1244 (44)	456 (28)	227 (37)	-176 (57)
400 (10)	916 (26)	842 (33)	223 (26)	85 (29)	-58 (45)
286 (7)	682 (20)	776 (30)	32 (19)	-15 (26)	-18 (42)
248 (7)	688 (19)	879 (25)	-86 (19)	-24 (26)	-8 (43)
372 (10)	1374 (35)	1193 (38)	328 (30)	349 (33)	962 (60)
377 (3)	1506 (10)	1606 (11)	592 (8)	537 (9)	710 (17)
376 (9)	1084 (28)	1077 (35)	343 (27)	-197 (31)	-7 (52)
354 (8)	1061 (22)	760 (22)	256 (21)	-58 (22)	10 (39)

* Multiplied by 10^5.

Table 5. Structure factors

Each group of three columns contains h, $10|F_o|$, and $10\ F_c$ and is headed by values of h and ℓ common to the group. Asterisks following $10\ F_c$ indicate reflections given zero weight and omitted from the refinement.

H	0	0
2	105	-140*
4	272	-287
6	107	106
8	700	698
10	374	388
12	76	75
14	118	117
16	506	-486
18	117	115
20	123	103
H	1	0
2	612	-616
4	435	472
6	340	322
8	386	-384
10	418	-401
12	158	156
14	238	231
16	273	-269
18	127	121
20	6	18
H	2	0
0	875	-819
2	163	178
4	70	-65
6	531	-544
8	579	-560
10	119	119
12	486	478
14	225	-226
16	88	76
18	110	103
20	0	-7*
H	3	0
2	2328	2435
4	104	-101
6	597	-585
8	343	-347
10	35	43
12	92	-92
14	338	332
16	197	-191
18	236	-212
20	9	-18
H	4	0
0	856	-814
2	120	119
4	1179	-1131
6	177	176
8	92	-93
10	418	-410
12	102	-99
14	10	-5
16	96	89
18	162	-163
20	33	22
H	5	0
2	164	171
4	153	152
6	499	459
8	137	-142
10	356	-354
12	143	135
14	40	53
16	17	-11
18	56	-61
H	6	0
0	720	-724
2	88	-89
4	1118	1061
6	246	252
8	176	-167
10	71	73
12	410	-402
14	193	194
16	50	46
18	81	-84
H	7	0
2	3	-10
4	174	167
6	317	-299
8	325	332
10	198	-192
12	47	47
14	0	-34*
16	88	77
18	93	89
H	8	0
0	227	-224
2	82	-84
4	12	-10
6	20	23
8	354	337
10	0	17*
12	0	-6*
14	54	57
16	108	117
H	9	0
2	345	-341
4	124	-128
6	306	293
8	43	42
10	161	166
12	106	-102
14	108	-105
16	69	77
H	10	0
0	75	-51
2	0	24*
4	29	25
6	31	-36
8	115	100
10	39	-41
12	9	-3
14	44	-43
H	11	0
2	48	-41
4	86	-84
6	9	-4
8	34	-110*
10	114	125
12	6	-14
H	12	0
0	191	193
2	27	-9
4	76	-76
6	37	-47
8	22	-28
10	70	71
H	13	0
2	59	-64
4	24	23
6	113	-117
H	1	1
1	38	-40
2	435	494
3	163	-168
4	981	1031
5	293	-308
6	171	-183
7	90	-98
8	783	-786
9	120	129
10	38	-38
11	123	121
12	186	202
13	1	-10
14	57	-65
15	173	-171
16	65	73
17	56	-60
18	160	-164
19	27	-35
20	0	-12*
21	36	34
H	2	1
0	143	-137
1	246	223
2	2103	-2126
3	279	290
4	64	77
5	41	43
6	326	349
7	157	-172
8	266	-271
9	101	99
10	469	-484
11	136	143
12	207	-209
13	240	237
14	342	328
15	61	60
16	21	-20
17	9	43
18	66	76
19	35	-43
20	83	-92
21	20	19
H	3	1
1	32	10
2	383	-355
3	291	-261
4	694	676
5	67	70
6	96	83
7	12	10
8	114	79
9	72	74
10	98	-99
11	10	-1
12	25	37
13	63	63
14	96	106
15	67	71
16	89	-89
17	24	-18
18	49	36
19	9	9
20	88	-95
H	4	1
0	521	-525
1	219	212
2	279	233
3	170	-165
4	391	393
5	101	91
6	811	811
7	268	-278
8	41	47
9	180	-184
10	388	-389
11	9	14
12	139	135
13	127	126
14	266	-255
15	50	52
16	70	68
17	89	-87
18	27	-11
19	32	-30
20	139	-143
H	5	1
1	40	43
2	54	47
3	317	304
4	836	-821
5	310	324
6	232	229
7	95	100
8	299	300
9	65	-91
10	148	159
11	22	22
12	402	-398
13	18	26
14	27	35
15	63	71
16	163	143
17	24	22
18	74	73
19	0	16*
H	6	1
0	150	148
1	62	65
2	60	-54
3	43	40
4	245	-246
5	127	-128
6	418	412
7	20	-20
8	196	201
9	20	-7
10	42	33
11	38	-29
12	34	19
13	18	-28
14	61	63
15	23	35
16	68	101
17	0	16*
18	44	48
19	33	-31
H	7	1
1	70	-74
2	253	-253
3	42	41
4	304	-299
5	54	-54
6	141	129
7	136	136
8	214	228
9	153	-156
10	64	-58
11	90	-92
12	53	54
13	41	-54
14	27	-22
15	77	75
16	51	-65
17	35	38
18	48	41
H	8	1
0	90	90
1	141	-140
2	36	-24
3	22	3
4	30	-24
5	39	-45
6	312	-312
7	149	153
8	79	-82
9	34	-25
10	375	360
11	46	-36
12	51	-64
13	0	-6*
14	69	-78
15	9	0
16	49	-46
17	26	29
H	9	1
1	91	-80
2	33	38
3	52	-52
4	48	-49
5	13	-4
6	228	-239
7	107	-105
8	260	257
9	6	-5*
10	34	-32
11	64	-62
12	19	32
13	37	-26
14	32	-42
15	0	-19*
16	55	-52
H	10	1
0	99	91
1	28	-20
2	180	180
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4	85	91
5	28	3
6	81	74
7	65	74
8	268	271
9	111	110
10	26	16
11	18	15
12	36	-25
13	34	46
14	51	34
15	43	-42
H	8	6
0	300	-278
1	65	-75
2	110	117
3	36	-40
4	75	75
5	24	27
6	166	169
7	0	21*
8	77	80
9	24	-7
10	104	-100
11	20	3
12	18	-31
13	22	11
14	14	9
H	9	6
1	12	3
2	103	-111
3	0	23*
4	35	-36
5	38	-36
6	0	-34*
7	87	-96
8	64	-76
9	47	44
10	23	36
11	33	34
12	0	7*
H	10	6
0	0	1*
1	155	163
2	16	9
3	13	0
4	45	-60
5	42	-30
6	33	-37
7	52	-55
8	69	63
9	31	27
10	55	58
H	11	6
1	0	5*
2	94	-90
3	74	-71
4	75	-71
5	50	-54
6	29	33
7	0	2*
H	12	6
0	51	57
1	0	-24*
2	52	-70
H	1	7
1	188	-138
2	229	233
3	42	-42
4	233	237
5	39	26
6	166	168
7	69	-69
8	428	-426
9	62	-61
10	159	172
11	34	-34
12	36	29
13	39	38
14	79	70
15	11	-9
16	23	14
17	53	-57
H	2	7
0	57	-43
1	28	-33
2	65	-53
3	44	-40
4	123	125
5	45	40
6	446	-450
7	107	114
8	115	-115
9	114	129
10	61	-61
11	0	16*
12	91	-88
13	34	43
14	59	55
15	120	105
16	6	-11
17	90	95
H	3	7
1	72	74
2	167	-168
3	39	-37
4	207	205
5	42	-33
6	333	-335
7	85	76
8	151	146
9	56	54
10	212	-218
11	3	17
12	0	-5*
13	0	22*
14	41	-42
15	47	44
16	0	6*
17	21	13
H	4	7
0	401	-379
1	64	-65
2	105	-101
3	156	-160
4	105	-106
5	8	5
6	341	339
7	31	-20
8	10	4
9	77	-80
10	238	-217
11	57	-57
12	86	92
13	0	-13*
14	30	-18
15	26	31
16	105	114
H	5	7
1	138	138
2	46	-41
3	115	104
4	157	-152
5	20	21
6	144	150
7	34	23
8	196	203
9	69	72
10	33	21
11	60	94
12	0	-3*
13	24	-16
14	39	-27
15	20	-20
H	6	7
0	136	145
1	49	57
2	183	-179
3	36	47
4	104	102
5	71	-66
6	43	-33
7	76	-66
8	4	13
9	0	9*
10	26	20
11	31	18
12	42	-32
13	23	-27
14	44	-50
15	19	-5
H	7	7
1	56	52
2	28	-25
3	43	-40
4	282	-282
5	55	-65
6	67	76
7	0	0*
8	114	101
9	0	-13*
10	45	40
11	47	-44
12	105	-92
13	33	-40
14	21	-16
H	8	7
0	164	164
1	13	-5
2	18	-17
3	47	60
4	39	38
5	0	7*
6	73	-79
7	13	-4
8	26	25
9	18	-19
10	89	86
11	18	13
12	24	-39
H	9	7
1	77	-75
2	37	-37
3	27	-28
4	13	-14
5	0	-11*
6	88	-86
7	54	-56
8	27	18
9	81	-72
10	33	-42
H	10	7
0	99	-112
1	27	6
2	132	137
3	0	17*
4	111	-109
5	0	-1*
6	93	-93
7	22	-22
8	22	10
H	11	7
1	0	0*
2	36	40
3	26	27
4	11	6
H	0	8
0	107	94
1	67	53
2	184	190
3	43	26
4	193	193
5	13	20
6	176	170
7	20	9
8	308	317
9	40	53
10	194	-178
11	0	7*
12	43	-63
13	146	130
14	47	44
15	112	114
16	72	81
H	1	8
1	95	90
2	340	-344
3	33	-33
4	214	-228
5	35	22
6	366	360
7	24	30
8	229	-230
9	41	41
10	56	57
11	24	-27
12	116	-121
13	26	21
14	81	-58
15	0	13*
16	37	36
H	2	8
0	435	-405
1	62	-55
2	152	-148
3	46	-55
4	335	337
5	0	9*
6	42	-54
7	53	-63
8	109	-100
9	66	-75
10	28	25
11	16	-14
12	95	-83
13	0	21*
14	90	86
15	20	9
16	67	67
H	3	8
1	33	44
2	43	-46
3	122	125
4	79	-60
5	74	62
6	0	-4*
7	10	19
8	67	46
9	4	13
10	177	193
11	29	-14
12	143	-141
13	58	-49
14	73	-78
15	57	54
H	4	8
0	156	146
1	69	67
2	39	-37
3	48	48
4	406	-408
5	67	-68
6	55	-51
7	44	-38
8	18	10
9	0	-14*
10	0	16*
11	7	2
12	37	-44
13	41	-45
14	38	-37
15	11	0
H	5	8
1	51	35
2	364	-351
3	54	-48
4	131	138
5	29	-23
6	26	-5
7	57	51
8	153	153
9	87	-85
10	31	-33
11	51	-56
12	0	14*
13	26	-31
14	67	-72
H	6	8
0	27	19
1	85	-73
2	201	204
3	23	20
4	59	-54
5	71	76
6	32	36
7	49	52
8	18	-29
9	30	3
10	1	-3
11	43	38
12	125	124
13	27	-9
H	7	8
1	96	-101
2	175	172
3	0	4*
4	52	-46
5	11	27
6	75	-81
7	96	-96
8	139	-104
9	31	-27
10	49	44
11	29	-25
12	38	36
H	8	8
0	277	273
1	28	31
2	102	-112
3	39	29
4	41	-33
5	47	-59
6	32	-34
7	13	14
8	11	11
9	41	42
10	92	89
H	9	8
1	53	52
2	45	56
3	44	-42
4	23	27
5	17	4
6	13	19
7	41	57
8	29	29
H	10	8
0	21	-28
1	0	-3*
2	18	-32
3	55	-62
4	62	68
5	64	73
H	1	9
1	33	-12
2	70	-65
3	37	41
4	77	-80
5	71	56
6	23	-18
7	40	27
8	183	192
9	45	-42
10	80	-91
11	74	-71
12	121	-105
13	20	-15
14	18	-18
H	2	9
0	171	-165
1	0	-8*
2	77	-65
3	59	-42
4	311	-306
5	20	11
6	195	-199
7	21	0
8	23	27
9	87	75
10	18	-1
11	59	-55
12	0	-3*
13	46	-40
14	61	-65
H	3	9
1	27	-12
2	0	23*
3	0	-6*
4	40	-35
5	40	26
6	169	180
7	32	-34
8	82	-96
9	0	16*
10	41	42
11	76	-59
12	66	50
13	0	5*
14	0	-1*
H	4	9
0	138	129
1	0	9*
2	64	60
3	51	-48
4	139	143
5	57	68
6	139	-141
7	68	69
8	0	10*
9	68	66
10	215	198
11	19	0
12	65	-69
13	41	-39
H	5	9
1	33	-18
2	104	97
3	2	18
4	30	43
5	66	-58
6	168	-156
7	13	5
8	16	-7
9	0	-15*
10	26	30
11	72	68
12	32	25
H	6	9
0	65	50
1	0	2*
2	23	29
3	29	-33
4	28	-31
5	21	4
6	78	84
7	24	5
8	99	102
9	22	-8
10	34	-35
11	18	9
H	7	9
1	41	32
2	61	-69
3	12	-13
4	112	121
5	33	-32
6	13	13
7	15	29
8	124	-115
9	0	23*
10	0	-5*
H	8	9
0	166	-174
1	66	-77
2	24	22
3	60	56
4	35	29
5	0	-17*
6	8	-13
7	17	1
8	38	-45
H	9	9
1	0	3*
2	49	43
3	26	-24
4	52	-59
5	0	3*
H	0	10
0	168	-154
1	104	-71
2	273	-284
3	93	-84
4	60	72
5	0	2*
6	186	-184
7	154	151
8	57	-65
9	32	15
10	91	83
11	19	-11
12	13	-3
H	1	10
1	0	-9*
2	241	238
3	22	18
4	11	-8
5	23	4
6	135	-146
7	18	-15
8	23	39
9	21	-12
10	105	94
11	57	67
12	0	-11*
H	2	10
0	254	232
1	24	8
2	47	37
3	27	11
4	167	-164
5	28	-14
6	56	67
7	0	21*
8	124	127
9	51	48
10	27	-34
11	1	17
12	0	9*
H	3	10
1	125	96
2	103	-93
3	38	-25
4	33	-26
5	71	-57
6	74	74
7	0	-18*
8	96	-89
9	113	116
10	31	17
11	53	42
12	37	54
H	4	10
0	227	-222
1	0	-11*
2	144	144
3	8	-9
4	153	153
5	20	-7
6	86	88
7	10	-12
8	78	-75
9	0	-14*
10	19	26
11	49	-62
H	5	10
1	0	7*
2	132	126
3	5	8
4	40	-53
5	26	-14
6	126	-119
7	23	-18
8	4	10
9	20	20
10	3	7
H	6	10
0	48	51
1	67	61
2	53	-72
3	35	18
4	63	-62
5	6	17
6	5	-12
7	66	-68
8	28	-17
9	41	-45
H	7	10
1	44	-49
2	120	-127
3	0	0*
4	19	21
5	57	-56
6	44	42
7	15	-11
H	8	10
0	20	-25
1	34	31
2	8	21
3	7	3
H	1	11
1	82	73
2	5	-19
3	16	0
4	0	8*
5	58	-44
6	68	-71
7	12	15
8	44	42
9	46	44
10	0	-1*
H	2	11
0	127	142
1	0	21*
2	0	-15*
3	52	33
4	124	134
5	22	-1
6	39	-50
7	41	-46
8	0	1*
9	76	-79
H	3	11
1	24	0
2	0	-10*
3	0	1*
4	81	-76
5	27	22
6	32	16
7	44	-35
8	49	-46
9	0	-17*
H	4	11
0	0	-18*
1	72	60
2	39	-30
3	58	51
4	0	-15*
5	0	-14*
6	38	-35
7	51	-50
8	23	-25
H	5	11
1	57	-62
2	4	3
3	74	-66
4	26	14
5	0	0*
6	60	63
H	6	11
0	0	-3*
1	17	-18
2	86	95
3	25	12
4	29	-45
H	0	12
0	90	55
1	20	7
2	12	44
3	70	65
4	14	-19
5	5	17
6	43	-52
H	1	12
1	18	-27
2	12	-16
3	25	30
4	10	-5
5	4	-13
6	44	-59
H	2	12
0	8	-8
1	0	8*
2	14	-6
3	28	32
4	41	-35
5	12	-21
H	3	12
1	80	-72
2	37	37
3	34	-44
4	51	63
H	4	12
0	32	51
1	12	-18

TABLE 6. Least Squares Plane Calculation

Atom	Deviation*	Weight*	Deviation‡	Weight‡
N(1)	0.0030	1.0	0.0805	0.0
C(2)	0.0001	1.0	-0.0639	0.0
N(3)	0.0012	1.0	-0.2842	0.0
C(4)	-0.0041	1.0	-0.2893	0.0
C(5)	0.0063	1.0	-0.4634	0.0
C(6)	-0.0060	1.0	-0.4312	0.0
C(7)	0.0053	1.0	-0.1896	0.0
C(8)	0.0002	1.0	-0.0135	0.0
C(9)	-0.0060	1.0	-0.0658	0.0
C(10)	-0.0180	0.0	0.0033	1.0
C(11)	0.1050	0.0	-0.0033	1.0
S(12)	-0.0616	0.0	-0.0021	1.0
C(13)	-0.2981	0.0	-0.0008	1.0
N(14)	-0.2583	0.0	-0.0013	1.0
H(1)	0.0387	0.0	0.2550	0.0
H(5)	0.0509	0.0	-0.5882	0.0
H(6)	-0.0464	0.0	-0.5646	0.0
H(7)	-0.0521	0.0	-0.2140	0.0
H(8)	0.0187	0.0	0.1536	0.0
H(11)	0.2888	0.0	0.0314	0.0
H(13)	-0.4777	0.0	-0.0236	0.0

* Direction cosines of plane normal (0.4559 0.8801 0.1329) origin to plane distance 10.588 Å.

‡ Direction cosines of plane normal (0.4906 0.8210 0.2921) origin to plane distance 10.796 Å.

Figure 1. The E-map and final Fourier for thiabendazole calculated in the mean plane of the molecule.

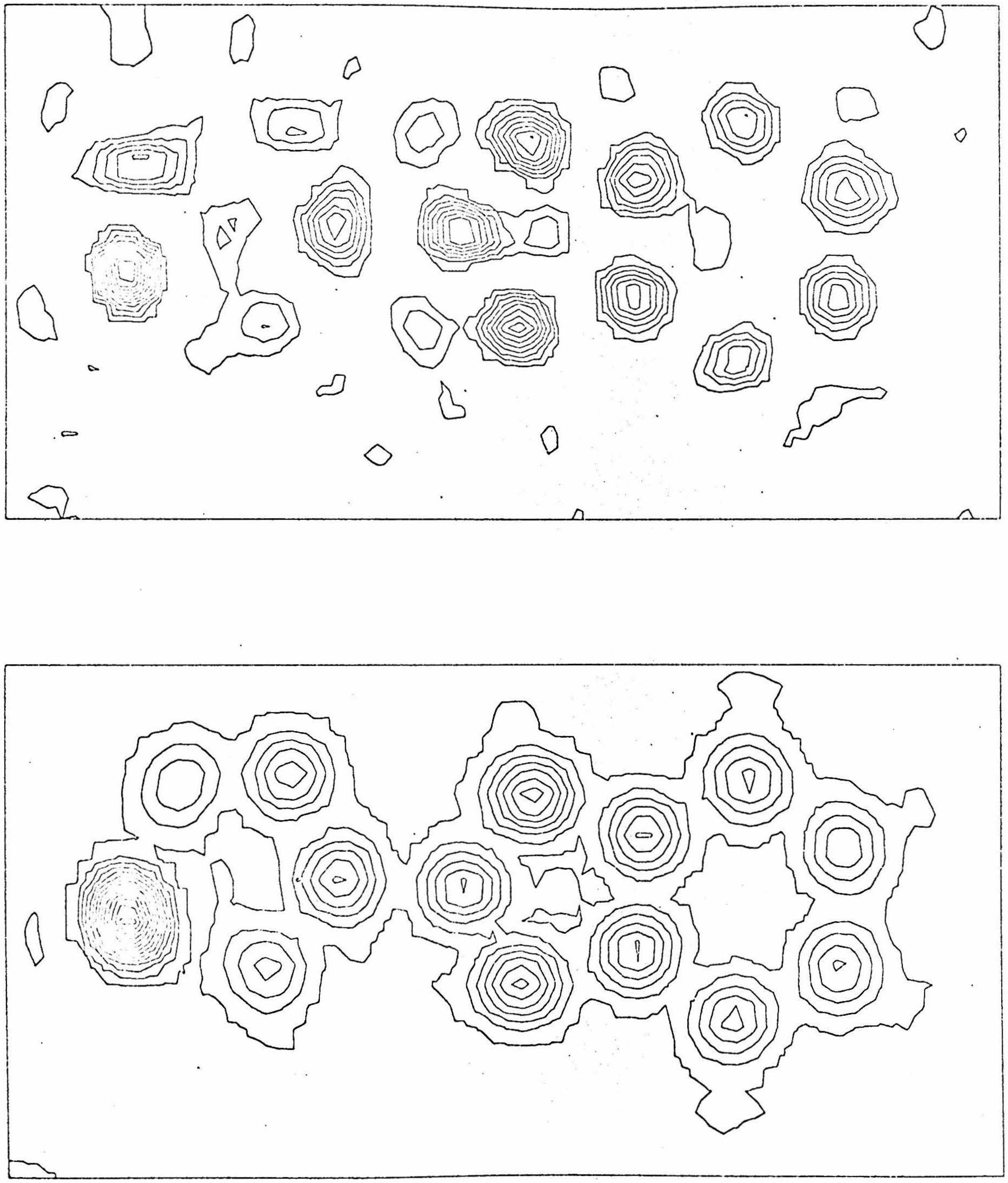


Figure 2. Distances and angles

Standard deviations are about 0.006 Å for bonds involving C and N, 0.003 Å for bonds with S, and 0.05 Å for bonds to hydrogens. Standard deviations for heavy-atom angles are about 0.3° and about 1.5° for angles involving hydrogens.

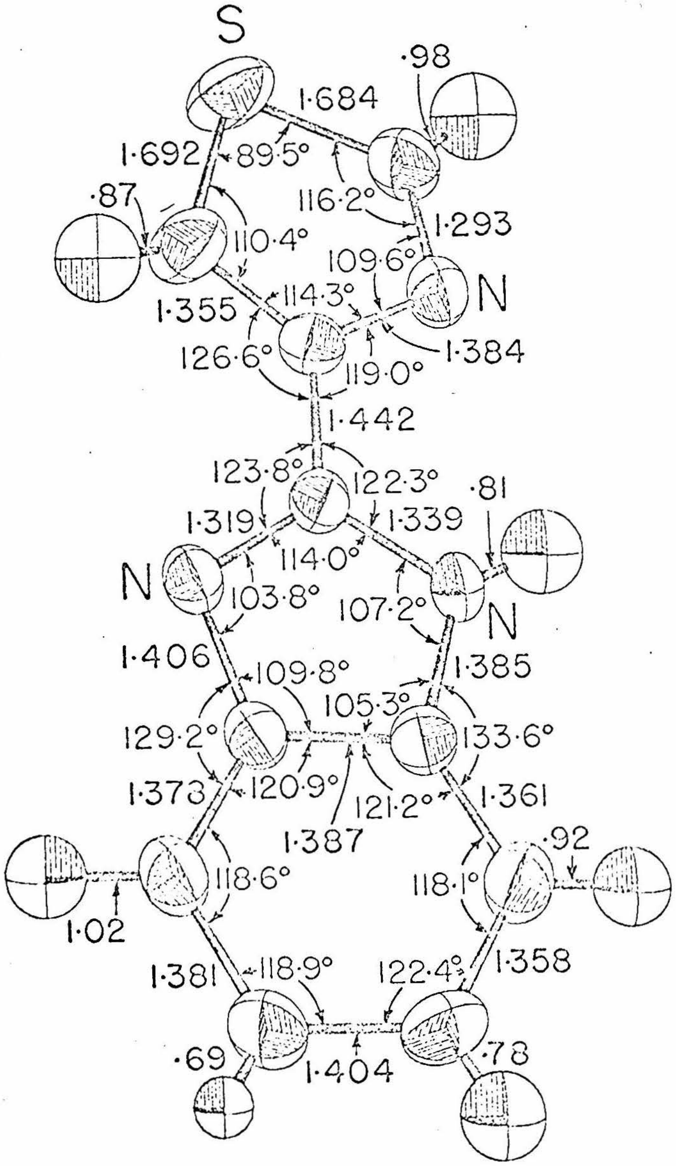


Figure 3. View down the c axis.

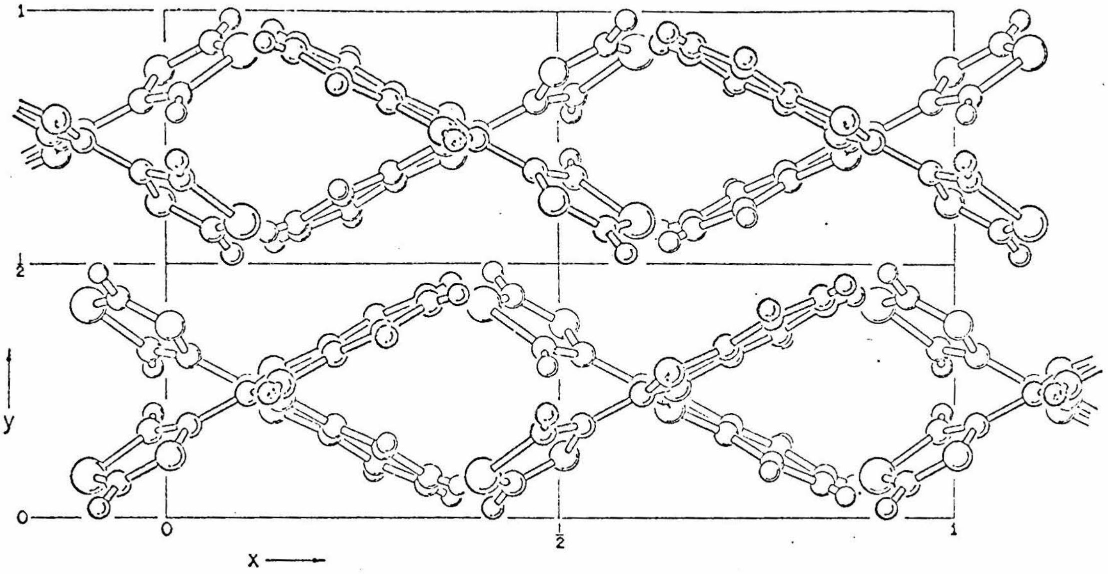
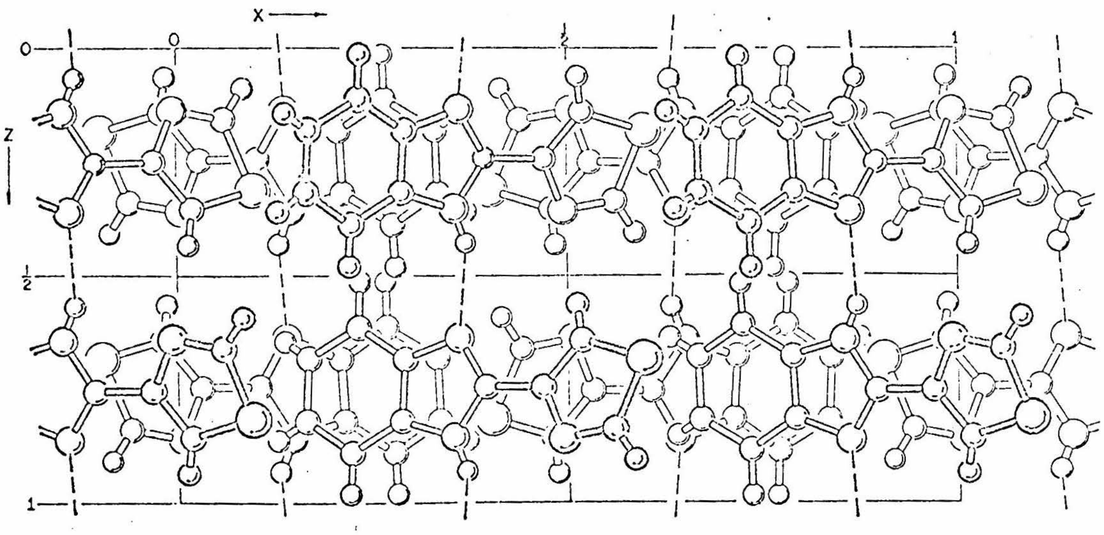


Figure 4: View down the b axis.

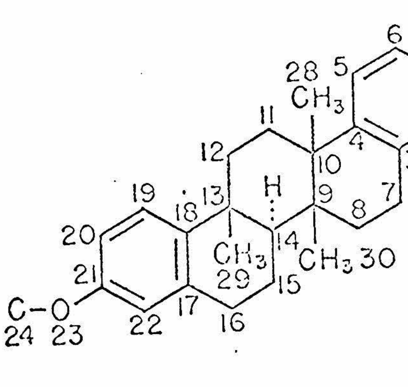


IV

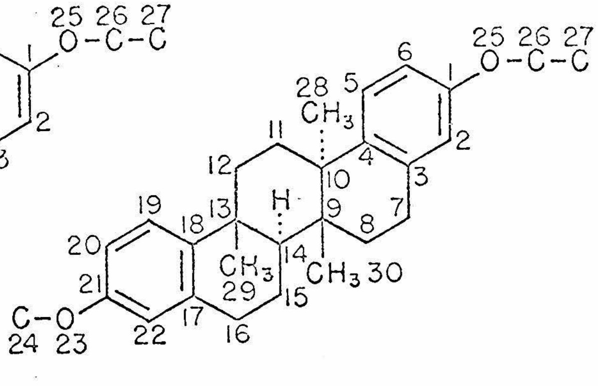
The Crystal Structure of 5,6,6a,6bα,7,8,12b,13,14,14a-decahydro-3-ethoxy-10-methoxy,6aβ,12bβ,14aα-trimethyl-pycene

Introduction

This determination of the structure of 5,6,6a,6bα,7,8,12b,13,14,14a-decahydro-3-ethoxy-10-methoxy,6aβ,12bβ,14aα-trimethyl pycene (Patrone 3) was undertaken as part of a program of research on the structures of terpene intermediates possessing a trans diangularly substituted ring fusion at the C/D rings. Alnusenone is one such terpene. The structure of 5,6,6a,6bα,7,8,12b,13,14,14a-decahydro-3-ethoxy-10-methoxy,6aβ,12bβ,14aβ-trimethyl pycene (Patrone 2) (1) was previously determined by John Bordner and Richard E. Dickerson and is the eighth biproduct in the synthesis of alnusenone (2). Patrone 3 is the ninth intermediate in the synthesis.



Patrone 2



Patrone 3

Experimental: X-ray analysis

Weissenberg photographs of the needle-like crystals indicated the orthorhombic space group Pbca. Accurate unit-cell dimensions were obtained by a least-squares fit to 2θ values measured on a diffractometer. The crystal data are summarized in Table 1.

Intensity data to a resolution of 1 Å (maximum $\sin\theta/\lambda = 0.5$) were collected on a Datex automated General Electric diffractometer using θ-2θ scanning (except near the $\underline{c}^*$ axis, where ω scans were necessary, to separate neighboring reflections). Backgrounds were collected for 30 seconds at each side of the scan, and the scan rate was 2° per minute. Two standard reflections were checked after every 40 reflections. The crystal showed no sign of decomposition in the course of the data collection.

Each reflection was assigned a variance $\sigma^2(I)$ based on counting statistics plus an empirical term $(0.02\ s)^2$, where s is the scan count. Values of F_o^2 and $\sigma(F_o^2)$ were derived from the net intensities by application of the Lorentz and polarization factors. The data were scaled by Wilson (3) statistics, and $|E|$'s and $|F|$'s calculated.

Determination and refinement of the structure

The structure was solved by the symbolic addition method (4, 5, 6). Three reflections (1, 3, 36; 3, 2, 40; and 5, 5, 1) having $E > 4.0$ were assigned positive signs to specify the origin. Two additional reflections (3, 3, 40 and 4, 6, 3) were allowed to have the values + or - giving four sets of solutions. The correct solution was the one with the highest consistency (0.88). An E-map containing the 137 E's > 2.0 clearly indicated a pycene system. A structure-factor calculation followed by a difference map showed the location of the remaining heavy atoms. The hydrogens were located on subsequent difference maps, and were included in the structure factors in idealized positions (0.95 Å from the carbon atoms) but not refined. The hydrogen atoms were assigned isotropic temperature factors with $B = 5.0$ for those of the methyl groups and $B = 4.0$ for the remainder. Full-matrix least-squares refinement of coordinates and anisotropic temperature factors of the heavy atoms, a scale factor, and a secondary extinction factor (7) produced a final R of 0.092.

Results of the X-ray analysis

The final parameters and their standard deviations are listed in Table 2.

In Patrone 2 the configuration of the methyl group C(28) relative to methyl groups C(29) and C(30) is cis, anti, trans while in Patrone 3 it is trans, anti, trans. This simple isomerization results in substantial differences between the conformations of the two compounds.

Stereoscopic views (8) of Patrone 2 and Patrone 3 are shown in Figure 1; selected torsion angles are listed in Table 3. In Patrone 2 the conformations of the B and D rings are one-half boats while they are half chains in Patrone 3. Ring C is a chair in both compounds. The methyl-methyl repulsions in Patrone 2 cause the molecule to be severely bent; thus, the dihedral angle between the planes of the terminal aromatic rings is 72° in Patrone 2 but only 6° in Patrone 3. Methyl groups C(28) and C(30) are closely trans in Patrone 3 (torsion angle = -168.2°), but deviate from cis in Patrone 2 by approximately 45°. Indeed, C(28) in Patrone 2 is very nearly trans to the ring atoms C(12) and C(14). Because the methyl hydrogens on 28 and 30 are so close in the cis Patrone 2, they are seen to be staggered with respect to each other. However, the methyl hydrogens on carbons 29 and 30 are not staggered in Patrone 2. These methyl hydrogens are staggered in Patrone 3.

Both ethyl etherial groupings are approximately coplanar with the adjacent benzene rings, but they are twisted in opposite directions in the two compounds. The terminal carbon atom C(27) of the ethoxy group is coplanar with the benzene ring in Patrone 3, but rotated out of plane in Patrone 2.

Bond distances are listed in Table 4 and angles in Table 5. Equivalent bonds in the two compounds are of equal length within three times their pooled standard deviations (about 0.013 Å). A number of bond angles differ by more than three esd's (0.6°); these differences reflect either the difference in steric interactions, steric interactions involving methyl groups or the different orientations of the methoxy and ethoxy groups.

References to Part IV

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Table 1. Crystal Data

Formula	$C_{28}H_{36}O_2$
F. W.	404.6
Space Group	Pbca
Systematic Absences	$0\ k\ \ell,\ k = 2n + 1$
	$h\ 0\ \ell,\ \ell = 2n + 1$
	$h\ k\ 0,\ h = 2n + 1$
<u>a</u>	7.094(2) Å
<u>b</u>	11.823(1)
<u>c</u>	54.973(5)
Z	8
F_{000}	1760
λ	FeKα = 1.9373 Å
D_c	1.165 g. cm.$^{-3}$
D_m	1.14
μ	10.7 cm.$^{-1}$
V	4611 Å^3
Number of reflections	2387
Non-zero reflections	2260

Table 2a. Final coordinates and anisotropic thermal parameters* for patrone 3

Atom	x†	y†	z‡	β_{11}†	β_{22}§	β_{33}‡	β_{12}§	β_{13}†	β_{23}†
C(1)	-1101(4)	-360(7)	28076(8)	72(4)	22(1)	28(2)	-1(1)	-2(2)	-3(3)
C(2)	-369(4)	-1520(7)	29286(8)	81(4)	20(1)	34(2)	6(1)	1(2)	-8(3)
C(3)	-44(4)	-1114(7)	31669(8)	59(4)	18(1)	31(2)	3(1)	2(1)	2(3)
C(4)	-455(3)	484(7)	32842(8)	59(4)	16(1)	30(2)	3(1)	-0(1)	3(3)
C(5)	-1208(4)	1627(7)	31558(8)	76(4)	18(1)	32(2)	6(1)	-1(2)	-4(3)
C(6)	-1519(4)	1239(8)	29198(8)	81(4)	23(2)	35(2)	7(1)	-9(2)	2(3)
C(7)	762(5)	-2453(8)	32946(9)	110(5)	29(2)	37(2)	19(2)	-3(2)	-10(3)
C(8)	911(4)	-2211(8)	35693(8)	82(4)	24(1)	33(2)	8(1)	-5(2)	-6(3)
C(9)	33(3)	-914(7)	36905(8)	54(3)	14(1)	34(2)	2(1)	-1(1)	-5(2)
C(10)	-31(3)	940(7)	35413(7)	56(4)	17(1)	31(2)	-0(1)	-1(1)	-2(2)
C(11)	-781(4)	2352(7)	36718(8)	72(4)	15(1)	30(2)	3(1)	-1(1)	5(2)
C(12)	-426(4)	2740(7)	39340(8)	74(4)	15(1)	30(2)	3(1)	-0(1)	-2(2)
C(13)	-369(3)	985(7)	40921(8)	57(4)	16(1)	34(2)	1(1)	-1(1)	0(2)
C(14)	375(4)	-498(7)	39570(8)	65(4)	17(1)	28(2)	4(1)	-1(1)	2(2)
C(15)	552(5)	-2198(7)	41190(9)	127(6)	17(1)	41(2)	6(2)	-7(2)	-2(3)
C(16)	1273(5)	-1652(8)	43395(9)	163(7)	23(2)	38(2)	18(2)	-21(2)	-6(3)
C(17)	891(4)	148(7)	44574(8)	87(4)	18(1)	29(2)	3(1)	-4(2)	0(3)
C(18)	181(4)	1417(7)	43390(8)	78(4)	16(1)	30(2)	2(1)	-2(2)	0(3)
C(19)	-85(4)	3093(7)	44615(9)	102(5)	18(1)	36(2)	8(1)	-6(2)	-1(3)
C(20)	298(5)	3469(7)	46910(8)	128(5)	19(1)	30(2)	6(2)	-1(2)	-8(3)
C(21)	987(4)	2196(8)	48070(8)	96(5)	24(2)	28(2)	-1(1)	-4(2)	-3(3)
C(22)	1285(4)	575(8)	46943(9)	89(5)	21(1)	35(2)	2(1)	-6(2)	4(3)
O(23)	1311(3)	2698(6)	50394(6)	152(4)	28(1)	33(1)	5(1)	-13(1)	-10(2)
C(24)	1901(5)	1359(1)	51807(1)	157(7)	37(2)	40(2)	3(2)	-18(2)	-3(4)
O(25)	-1474(3)	-636(6)	25734(5)	98(3)	31(1)	31(1)	8(1)	-8(1)	-14(2)
C(26)	-1055(5)	-2218(9)	24413(9)	105(5)	31(2)	36(2)	4(2)	-2(2)	-9(3)
C(27)	-1617(5)	-2204(1)	21992(1)	159(7)	38(2)	38(2)	8(2)	-6(2)	-23(4)
C(28)	1152(4)	1845(8)	35094(9)	76(4)	30(2)	35(2)	-10(1)	2(2)	4(3)
C(29)	-1582(4)	329(8)	41500(8)	81(4)	30(2)	32(2)	-2(1)	1(2)	1(3)
C(30)	-1120(4)	-1999(7)	36728(8)	87(4)	19(1)	35(2)	-5(1)	-2(2)	1(3)

* Standard deviations by least squares given in parentheses for the least significant digit. The anisotropic thermal parameters are of the form $\exp-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + \beta_{12}hk + \beta_{13}h\ell + \beta_{23}k\ell)$.

† $*10^4$

‡ $*10^5$

§ $*10^3$

Table 2b. Assumed coordinates of hydrogens* for patrone 3

Atom	x†	y†	z†
H(2)	-79	-2616	2850
H(5)	-1519	2706	3233
H(6)	-2010	2076	2834
H(7a)	509	-3699	3266
H(7b)	1492	-2290	3222
H(8a)	854	-3422	3643
H(8b)	1640	-1704	3600
H(11a)	-1532	1880	3673
H(11b)	-760	3509	3584
H(12a)	-958	3591	4004
H(12b)	299	3317	3932
H(14)	1095	55	3929
H(15a)	-152	-2668	4174
H(15b)	937	-3164	4030
H(16a)	1233	-2637	4457
H(16b)	2036	-1502	4289
H(19)	-552	3993	4382
H(20)	89	4618	4769
H(22)	1771	-295	4775
H(24a)	2638	1178	5115
H(24b)	1963	1792	5343
H(24c)	1506	190	5178
H(26a)	-261	-2127	2422
H(26b)	-1234	-3355	2525
H(27a)	-1408	-3297	2111
H(27b)	-1398	-1111	2112
H(27c)	-2418	-2197	2221
H(28a)	1087	2954	3414
H(28b)	1641	976	3430
H(28c)	1454	2150	3665
H(29a)	-1566	-580	4277
H(29b)	-2022	1385	4202
H(29c)	-1914	-199	4009
H(30a)	-1168	-2886	3802
H(30b)	-1155	-2649	3522
H(30c)	-1725	-1133	3684

*Non-methyl hydrogens have an isotropic B of 4.0; methyl hydrogens have a B of 5.0.

† $\times 10^4$

Table 3. Torsion angles[*]

Atoms				Patrone 2[‡]	Patrone 3[§]
28	10	9	30	-44.8°	-168.2°
28	10	9	8	71.4	- 53.6
28	10	9	14	-170.4	67.3
28	10	11	12	178.3	-67.0
28	10	4	3	-102.7	78.7
28	10	4	5	73.3	-98.9
30	9	10	4	-164.4	-51.4
30	9	10	11	73.2	72.3
30	9	14	13	-70.2	-69.4
30	9	14	15	60.9	61.2
30	9	8	7	-174.8	68.1
29	13	14	9	68.0	69.5
29	13	14	15	-65.6	-64.1
29	13	12	11	-72.9	-73.5
29	13	18	17	106.2	98.7
29	13	18	19	-72.9	-77.0
24	23	21	22	163.0	-6.6
24	23	21	20	-19.2	172.3
27	26	25	1	78.5	178.4
26	25	1	2	-176.6	-1.6
26	25	1	6	4.4	177.9

[*] The signs of the torsion angles for Patrone 3 have been reversed to correspond to the same conformer as Patrone 2. The convention used is that of Klyne and Prelog (9).

[‡] $\sigma = 0.6°$

[§] $\sigma = 0.5°$

Table 4. Bond distances

Atom	Atom	Patrone. 2‡	Patrone 3§
C(1)	C(2)	1.37 Å	1.366 Å
C(1)	C(6)	1.38	1.383
C(1)	O(25)	1.37	1.375
C(2)	C(3)	1.38	1.395
C(3)	C(4)	1.38	1.392
C(3)	C(7)	1.51	1.517
C(4)	C(5)	1.38	1.395
C(4)	C(10)	1.54	1.534
C(5)	C(6)	1.37	1.376
C(7)	C(8)	1.51	1.530
C(8)	C(9)	1.54	1.539
C(9)	C(10)	1.55	1.552
C(9)	C(14)	1.56	1.548
C(9)	C(30)	1.55	1.569
C(10)	C(11)	1.54	1.518
C(10)	C(28)	1.54	1.549
C(11)	C(12)	1.51	1.526
C(12)	C(13)	1.53	1.520
C(13)	C(14)	1.56	1.559
C(13)	C(18)	1.53	1.536
C(13)	C(29)	1.54	1.541
C(14)	C(15)	1.53	1.514
C(15)	C(16)	1.50	1.532
C(16)	C(17)	1.52	1.502
C(17)	C(18)	1.39	1.392
C(17)	C(22)	1.39	1.416
C(18)	C(19)	1.40	1.402
C(19)	C(20)	1.38	1.367
C(20)	C(21)	1.38	1.373
C(21)	C(22)	1.36	1.353
C(21)	O(23)	1.37	1.380
O(23)	C(24)	1.39	1.412
O(25)	C(26)	1.42	1.425
C(26)	C(27)	1.46	1.487

Standard deviations in these distances are about ‡ 0.01 Å, § 0.007 Å.

Table 5. Bond angles

Atom	Atom	Atom	Patrone 2[‡]	Patrone 3[§]
C(6)	C(1)	C(2)	118.7°	120.2°
O(25)	C(1)	C(2)	116.2°	125.0°
O(25)	C(1)	C(6)	125.1°	114.8°
C(3)	C(2)	C(1)	121.7°	120.5°
C(4)	C(3)	C(2)	120.4°	120.4°
C(7)	C(3)	C(2)	117.5°	118.6°
C(7)	C(3)	C(4)	122.1°	120.9°
C(5)	C(4)	C(3)	117.1°	117.5°
C(10)	C(4)	C(3)	123.3°	119.0°
C(10)	C(4)	C(5)	119.5°	123.5°
C(6)	C(5)	C(4)	122.6°	122.1°
C(5)	C(6)	C(1)	119.5°	119.3°
C(8)	C(7)	C(3)	112.0°	117.3°
C(9)	C(8)	C(7)	113.5°	114.6°
C(10)	C(9)	C(8)	107.7°	108.1°
C(14)	C(9)	C(8)	109.2°	110.4°
C(30)	C(9)	C(8)	105.8°	105.4°
C(14)	C(9)	C(10)	108.8°	110.6°
C(30)	C(9)	C(10)	112.5°	109.9°
C(30)	C(9)	C(14)	112.7°	112.3°
C(9)	C(10)	C(4)	110.7°	108.9°
C(11)	C(10)	C(4)	111.1°	112.6°
C(28)	C(10)	C(4)	107.4°	106.1°
C(11)	C(10)	C(9)	108.8°	109.8°
C(28)	C(10)	C(9)	111.8°	111.5°
C(28)	C(10)	C(11)	107.0°	107.9°
C(12)	C(11)	C(10)	114.4°	113.9°
C(13)	C(12)	C(11)	112.5°	113.9°
C(14)	C(13)	C(12)	106.6°	107.8°
C(18)	C(13)	C(12)	109.9°	111.1°
C(29)	C(13)	C(12)	109.5°	108.9°
C(18)	C(13)	C(14)	107.3°	108.4°
C(29)	C(13)	C(14)	115.8°	114.8°
C(29)	C(13)	C(18)	107.7°	105.8°
C(13)	C(14)	C(9)	116.9°	115.6°
C(15)	C(14)	C(9)	115.2°	116.1°
C(15)	C(14)	C(13)	109.7°	109.6°
C(16)	C(15)	C(14)	108.5°	110.0°
C(17)	C(16)	C(15)	113.2°	112.9°
C(18)	C(17)	C(16)	121.8°	122.0°
C(22)	C(17)	C(16)	117.8°	118.7°

Table 5. Bond angles (cont.)

Atom	Atom	Atom	Patrone 2[‡]	Patrone 3[§]
C(22)	C(17)	C(18)	120.5°	119.4°
C(17)	C(18)	C(13)	123.3°	122.7°
C(19)	C(18)	C(13)	120.1°	119.9°
C(19)	C(18)	C(17)	116.6°	117.3°
C(20)	C(19)	C(18)	122.6°	122.3°
C(21)	C(20)	C(19)	119.2°	119.8°
C(22)	C(21)	C(20)	119.5°	120.1°
O(23)	C(21)	C(20)	124.7°	115.1°
O(23)	C(21)	C(22)	115.7°	124.8°
C(21)	C(22)	C(17)	121.5°	121.2°
C(24)	O(23)	C(21)	118.7°	118.2°
C(26)	O(25)	C(1)	120.0°	118.5°
C(27)	C(26)	O(25)	112.2°	107.2°

Standard deviations in these angles are about ‡ 0.5°, § 0.4°.

Figure 1a. Patrone 2

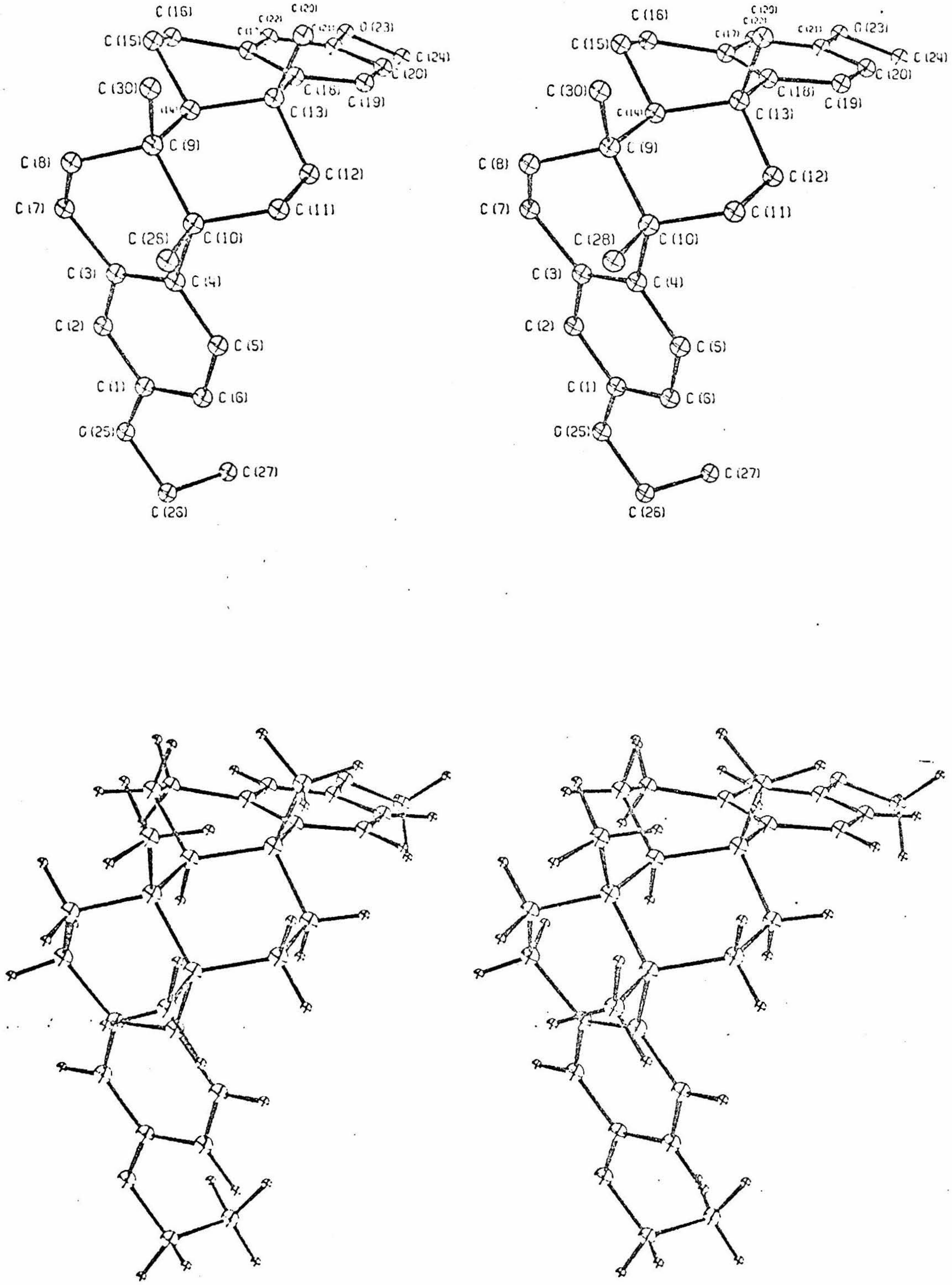


Figure 1b. Patrone 3

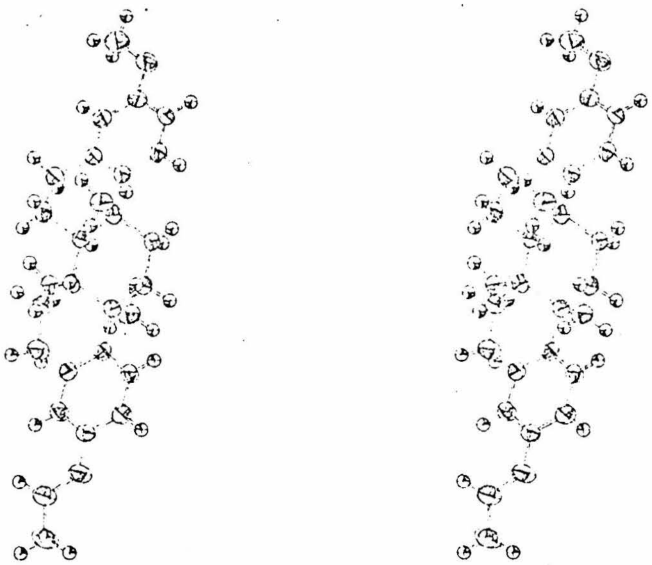


Figure 2. View of Patrone 3 along the b axis

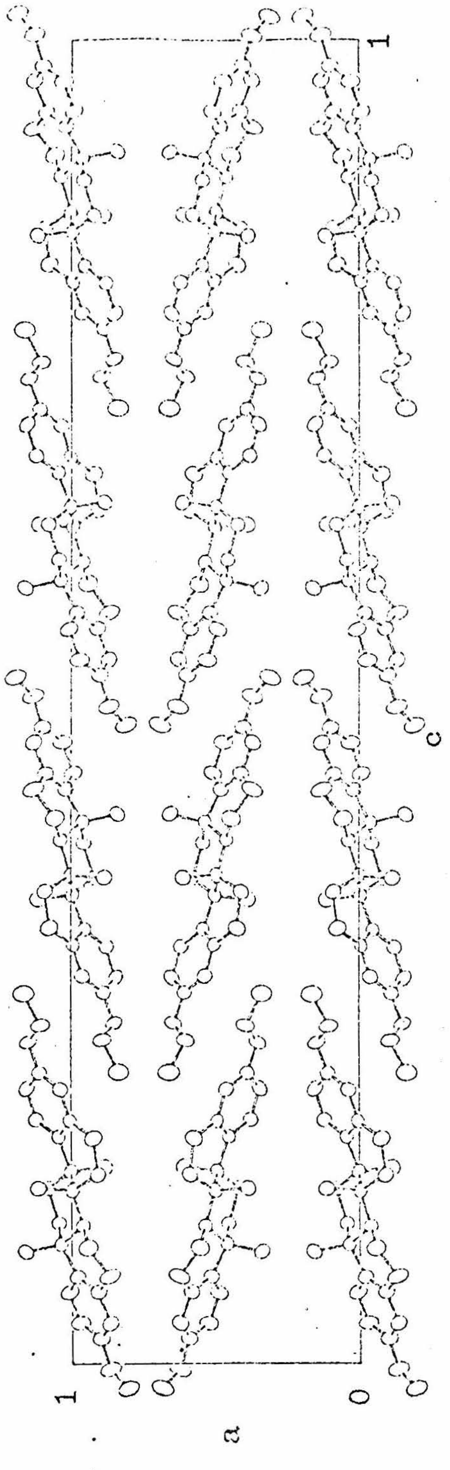
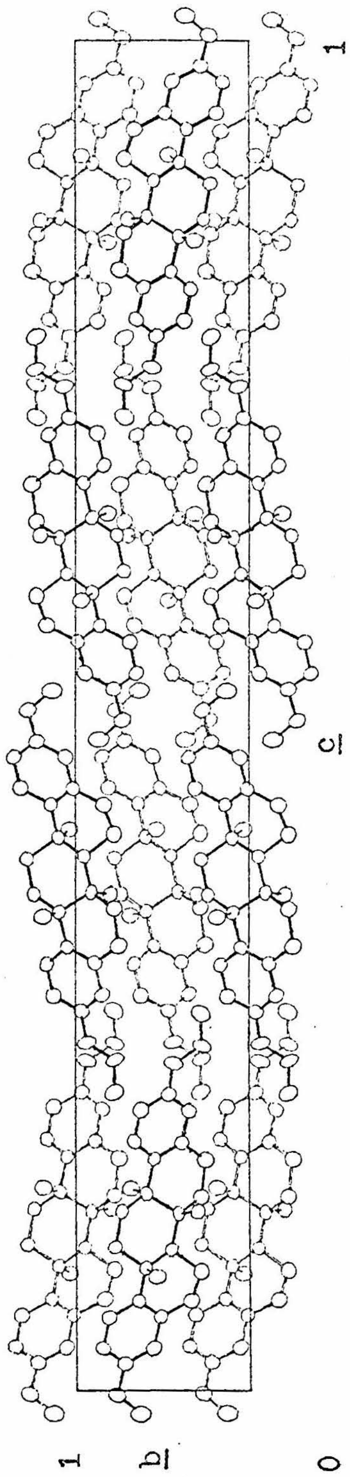


Figure 3. View of Patrone 3 along the a axis



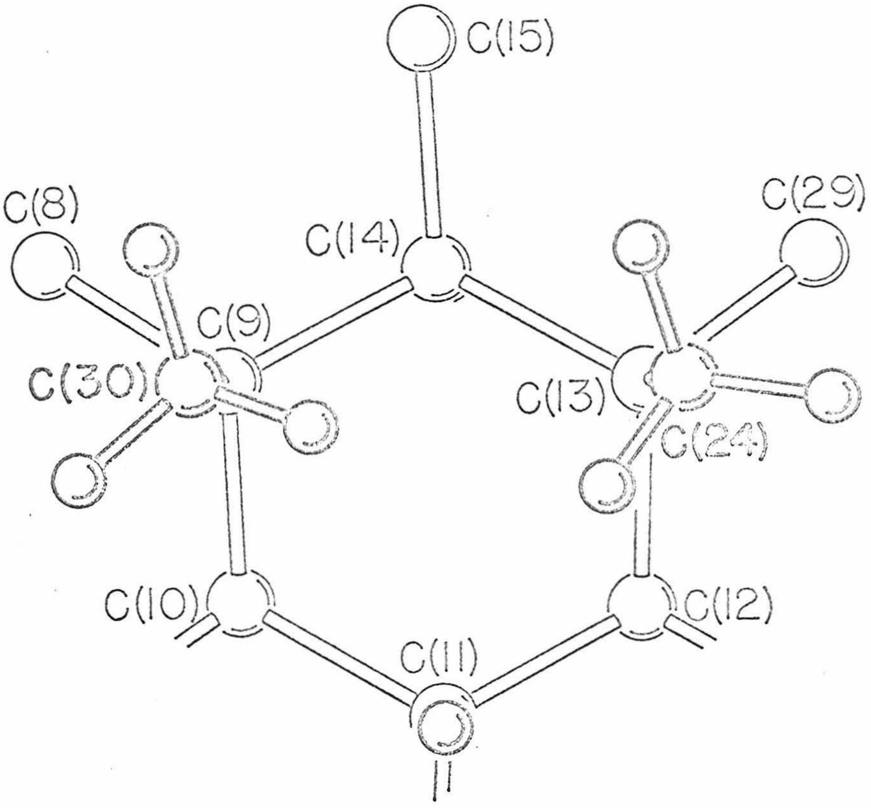


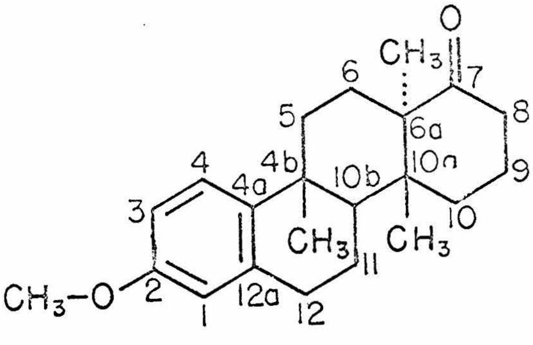
Figure 4. Methyl hydrogens in Patrone 3

V

The Crystal Structure of 4b,5,6,6a,9,10,10a,10bα,11,12-decahydro-2-methoxy-7(8H)-oxo-4bβ,6aα,10aβ-trimethylchrysene

Introduction

This determination of the structure of 4b,5,6,6a,9,10,10a,10bα, 11,12-decahydro-2-methoxy-7(8H)-oxo-4bβ,6aα,10aβ-trimethylchrysene (CHRY) was undertaken as part of a program of research on the structures of terpene intermediates possessing a trans diangularly substituted ring fusion at the C/D rings. Shionone and alnusenone are two such terpenes. CHRY is an intermediate in the synthesis of either shionone or alnusenone.



CHRY

Crystal Data

Crystals of CHRY, in the form of colorless plates elongated along c, were prepared from a diethyl ether solution by evaporation.

The space group and approximate cell constants were obtained from Weissenberg and precession photographs; more accurate cell constants were obtained by a least-squares fit to 2θ values measured on a diffractometer. The density was measured in a zinc chloride solution by flotation. Crystal data are given in Table 1.

Experimental

Intensity data were measured on a Datex-autometed General Electric diffractometer, using Ni-filtered CuKα radiation. The crystal had approximate dimensions 0.12 x 0.22 x 0.33 mm., and was mounted along c, the long dimension. Reflections with $2\theta \leq 150°$ were scanned in the θ - 2θ mode at a rate of 2° per minute, the scan range of 2.5° a 30-second background count was recorded on either side of the scan range. Two standard check reflections were measured after every 40 reflections. The crystal showed no signs of decomposition during the course of the data collection. Absorption corrections were not applied.

Altogether, 1970 independent reflections were measured. Each reflection was assigned a variance $\sigma^2(I)$ based on counting statistics plus an empirical term $(0.02S)^2$, where S is the scan count. Values of F_o^2 and $\sigma(F_o^2)$ were derived from the net intensities by application of the Lorentz and polarization factors. Any reflection for which the net value of F_o^2 was less than or equal to $\sigma(F_o^2)$ was assigned an intensity and weight of zero. There were 1834 observations in the final data set. The data were scaled by Wilson (1) statistics, and $|E|$'s and $|F|$'s calculated.

Structure solution and refinement

The structure was solved by the symbolic addition method (2,3,4) applied to 73 reflections with $E > 2.0$. Table 2 lists the origin choice and symbols. There were no 00ℓ reflections with high E which could be used to fix the origin. The results which led to the correct solution had the higher consistency (0.69). These 73 phases were tangent refined (5) and expanded to 241 reflections with $E > 1.3$.

An E map based on phases from the tangent refinement showed a continum of hexagons (Figure 1a). The best model (Figure 1b) gave the best fit to the h00 data, though other models fit the E map better. The resulting structure factor calculation based on the best model gave an R $(= \Sigma|F_o-F_c|/\Sigma|F_o|)$ of 0.367 for $\sin^2\theta/\lambda$ data ≤ 0.2. A series of difference-map calculations, model adjustments, and structure-factor calculations was begun reducing R to 0.247 for all non-hydrogen atoms. Four cycles of full-matrix least squares adjustment of the coordinates and isotropic temperature factors lowered R to 0.163. Difference maps clearly indicated the location of all the hydrogen atoms. Hydrogen atoms were included in subsequent structure-factor calculations in idealized positions 0.95 Å from the neighboring carbon atom. Anisotropic and positional refinement for all heavy atoms, a scale factor, and a secondary-extinction factor (6) decreased R to 0.048 with a weighted R $[= \Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w F_o{}^4]$ of 0.012 and a goodness of fit $\{= [\Sigma w|F_o|^2-|F_c|^2)^2/(M-S)]^{1/2}$ for $M = 1834$ observations and S = 218 parameters} of 1.95. The largest shift in the least-squares calculation was 0.3σ.

One notes from Figure 1 that the best model was not exactly the correct solution. In fact, they differ by about 0.6 Å along *a*. One explanation is the difficult application of direct methods for this data set. Figure 2 shows that the phases with low and high h from the original 73 phases were determined correctly. However, the middle phases (h ~ 20) were essentially off by 180°. One reason for this is the poor distribution of high E reflections; there are no $E > 2.0$ with $8 < h < 18$ or $28 < h < 33$.

Scattering factors were those listed in *International Tables for X-ray Crystallography* (7) except for hydrogen (8). Computations were performed at the Caltech Computer Center on the 360-75 using the CRYM system (9). Some of the crystallographic illustrations were produced by ORTEP (10).

The final positional parameters appear in Table 3. Observed and calculated structure factors are listed in Table 4. The refined value of secondary extinction (6) is $3.6 \pm 0.2 \times 10^{-6}$.

Discussion

Stereoscopic views (10) of CHRY are shown in Figure 3; selected torsion angles are listed in Table 5. The configuration of the three methyl groups is the same as for Patrone 3. In CHRY the conformations of the B, C, and D rings is half boat, chair, and flattened chain. The significant differences are in torsion angles involving the D ring and the methoxy. The D ring has different hybridization at C(7) and C(8) in the two structures. The methoxy in CHRY is bent out of the plane of the A ring by 15°, but only about 3° in Patrone 3.

The bond distances for CHRY are listed in Table 5; the standard deviation in these distances is about 0.005 Å. These distances are within twice the pooled standard deviation for Patrone 3 for similar atoms. The angles are listed in Table 6; the standard deviation is about 0.3°. The only angles different by more than three times their pooled standard deviation involve atoms C(6a) and C(10a). This is partially explained by differences in the D ring hybridization and partially by methyl interactions between C(4bm) and C(10am). In Patrone 3 the methyl hydrogens are staggered (Figure 4, Part 4). In CHRY the hydrogens are not quite staggered (Figure 4).

The packing of CHRY is illustrated in Figures 5 and 6. The packing along c̲ (Figure 5) can be compared to the packing for Patrone 3 along b̲ (Figure 2, Part 4). The methyl groups in CHRY are located in the empty space between the wide ends of molecules in the next layer. The methyl groups in Patrone 3 are located between the narrow ends of molecules in the next layer. The packing along b in CHRY is similar to the projection of a body-centered cube. On the other hand, the packing along a in Patrone 3 (Figure 3, Part 4) appears to be much more closely packed. There are no significantly short contacts in either structure.

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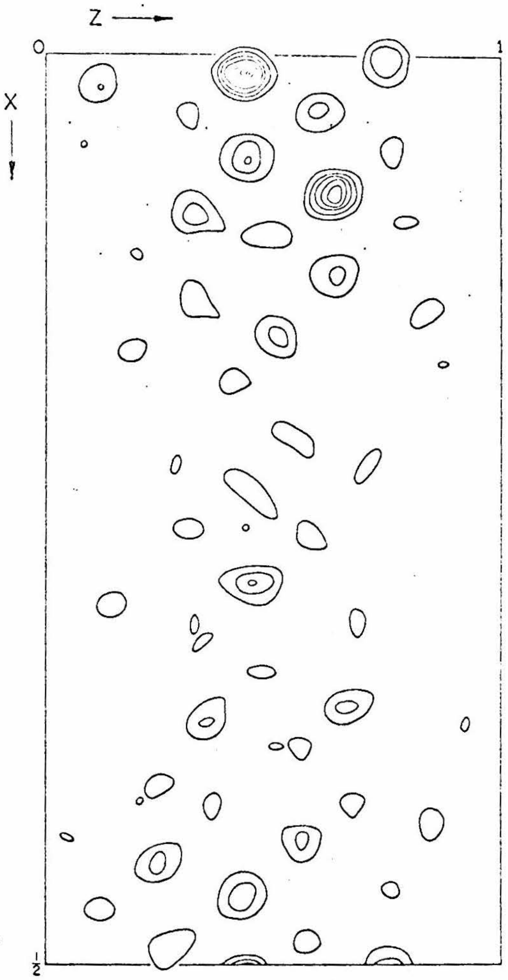


Figure 1a. The composite E map of sections containing the molecule.

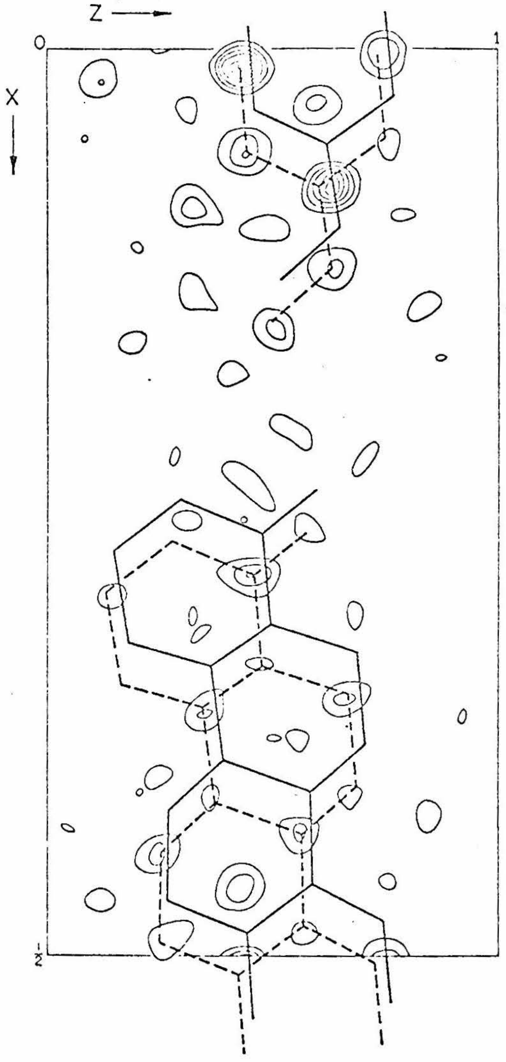
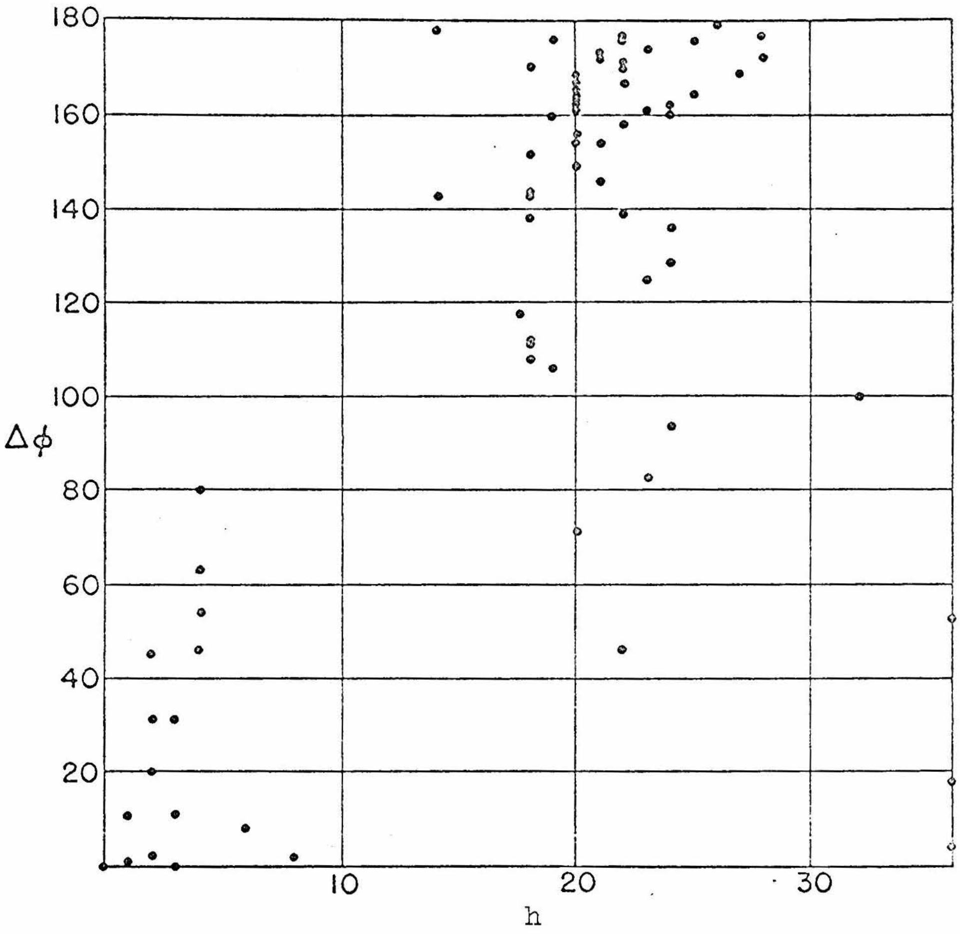


Figure 1b. The dotted lines represent the trial model. The solid lines represent the refined structure.

Figure 2. Deviation of phases from direct methods and the refined structure vs. h



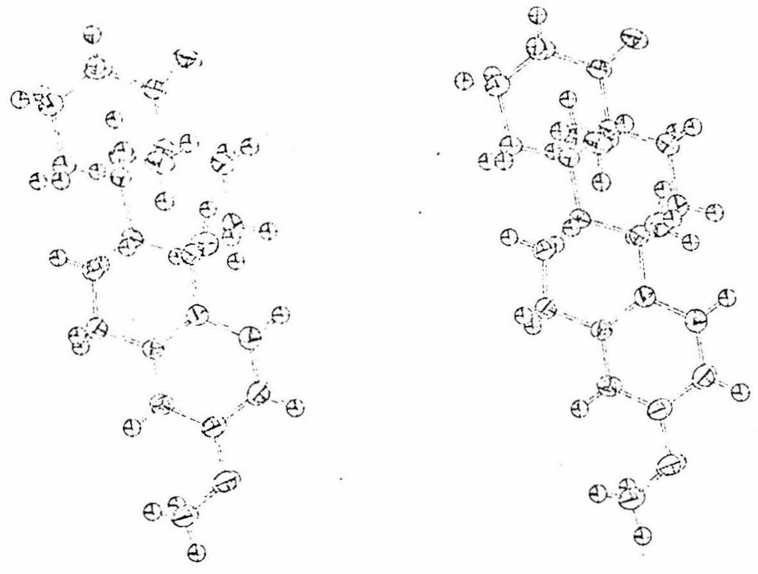


Figure 3. CHRY

Figure 4.

Methyl hydrogens in CHRY.

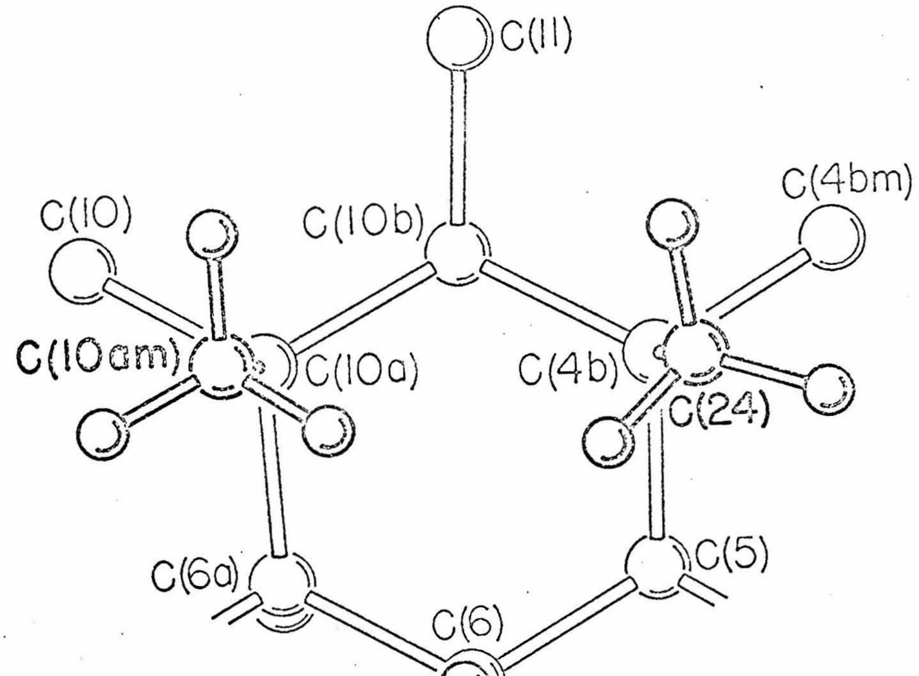


Figure 5. View along the c axis

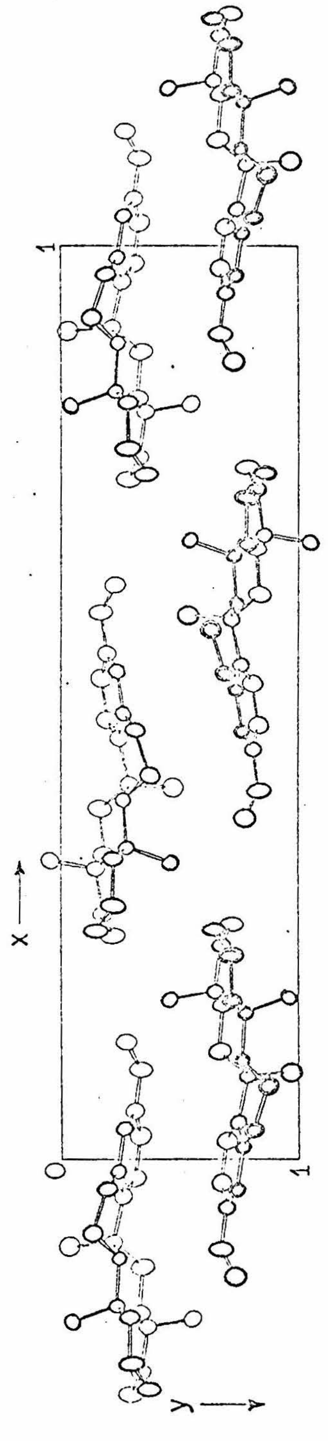


Figure 6. View along the b axis

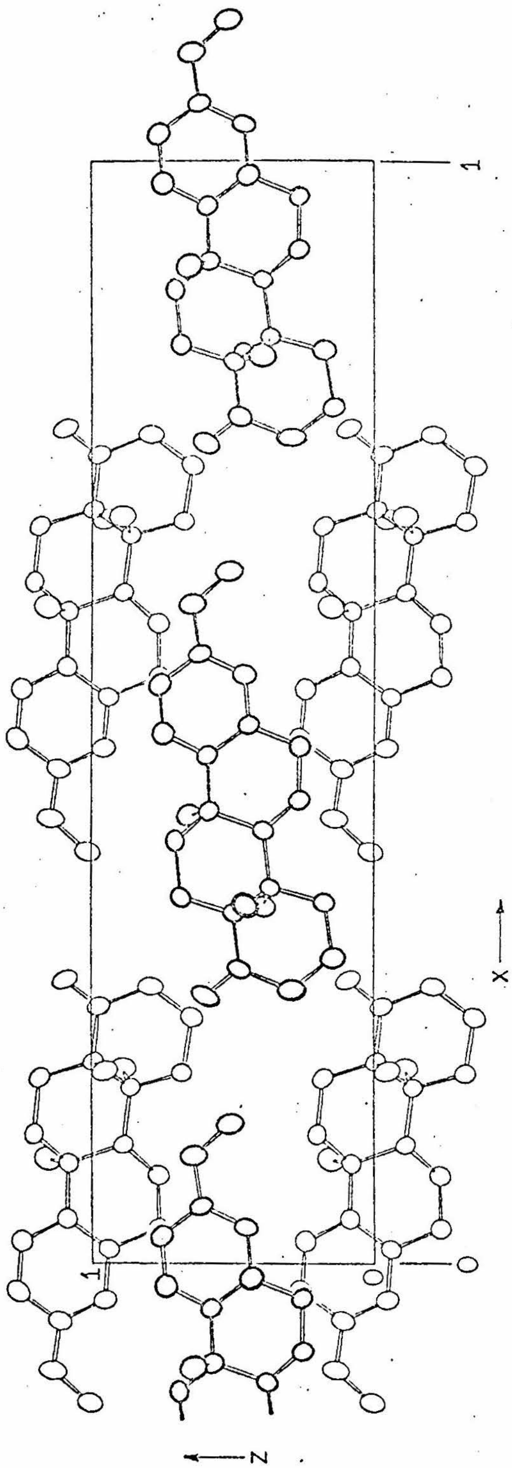


Table 1. Crystal Data

Formula	$C_{22}H_{30}O_2$
F. W.	326.5
Space Group	$Pna2_1$
Systematic Absences	$0\ k\ \ell\quad k + \ell = 2n + 1$
	$h\ 0\ \ell,\ h = 2n + 1$
a	29.922(4) Å
b	7.752(1)
c	7.630(4)
Z	4
F_{000}	712
λ	CuKα = 1.5418 Å
D_c	1.225 g.cm.$^{-3}$
D_m	1.23
μ	6.0 cm.$^{-1}$
V	1770 Å^3
Number of reflections	1970
Non-zero reflections	1834

Table 2. Data from Symbolic Addition

	h	k	ℓ	E	Fixed Phases	Assigned Phase
Origin	22	2	3	3.532	45°	
	4	1	7	3.314	90°	
	3	2	0	2.049	0°	
From σ_2's	0	2	0	1.819	180°	
Symbol	24	1	3	3.061		135°

Table 3a. Final coordinates and anisotropic thermal parameters* for CHRY

Atom	x‡	y†	z†	β_{11}‡	β_{22}†	β_{33}†	β_{12}†	β_{13}†	β_{23}†
C(1)	53323(8)	2356(4)	4577(4)	73(3)	156(5)	176(6)	-6(2)	5(2)	54(10)
C(2)	55205(8)	1922(4)	6165(4)	77(3)	156(5)	184(6)	-3(2)	-13(2)	57(9)
O(2)	59712(6)	1675(3)	6435(3)	75(2)	253(5)	253(6)	5(2)	-13(2)	201(10)
C(2m)	62698(8)	2267(4)	5141(4)	79(3)	196(6)	214(7)	1(2)	-12(3)	28(11)
C(3)	52513(9)	1698(4)	7616(4)	102(3)	206(6)	167(6)	-5(2)	-18(3)	79(11)
C(4)	47964(9)	1946(4)	7461(4)	93(3)	223(6)	140(6)	-8(2)	-2(2)	54(10)
C(4a)	45973(8)	2427(4)	5882(4)	82(3)	144(5)	128(5)	-4(2)	-3(2)	6(8)
C(4b)	40939(8)	2862(4)	5816(4)	77(3)	156(5)	117(5)	-4(2)	-3(2)	-33(8)
C(4b)	40567(10)	4694(5)	6558(4)	117(3)	206(6)	227(7)	-2(3)	-10(3)	-189(13)
C(5)	38301(9)	1643(5)	7035(3)	88(3)	254(7)	110(5)	-9(2)	3(2)	27(10)
C(6)	33223(9)	1815(5)	6827(4)	81(3)	227(7)	137(6)	-2(2)	13(2)	-1(10)
C(6a)	31727(8)	1464(3)	4946(4)	68(3)	146(5)	139(5)	-0(2)	9(2)	-13(9)
C(6a)	32603(8)	-462(4)	4525(4)	87(3)	150(5)	214(7)	-9(2)	17(3)	13(10)
C(7)	26721(8)	1748(4)	4744(4)	70(3)	173(5)	169(6)	-3(2)	11(2)	-9(10)
O(7)	24324(7)	2178(3)	5931(4)	77(2)	285(6)	211(5)	5(2)	25(2)	-71(9)
C(8)	24887(9)	1434(5)	2920(4)	68(3)	275(8)	217(7)	-3(2)	-4(2)	-61(13)
C(9)	27700(9)	2178(5)	1443(4)	82(3)	289(8)	173(6)	-8(3)	-10(2)	-36(12)
C(10)	32792(9)	2201(4)	1765(4)	71(3)	208(6)	143(6)	0(2)	0(2)	-18(10)
C(10a)	34070(8)	2742(3)	3637(3)	66(2)	135(4)	125(4)	1(2)	2(2)	-6(8)
C(10a)	32336(9)	4596(4)	3916(4)	91(3)	147(5)	223(7)	10(2)	2(2)	4(11)
C(10b)	39248(8)	2611(3)	3901(3)	66(2)	120(4)	125(5)	-2(2)	5(2)	-2(8)
C(11)	42031(8)	3711(4)	2665(4)	82(3)	168(5)	150(5)	-6(2)	-5(2)	67(10)
C(12)	46875(9)	3099(4)	2638(4)	81(3)	214(6)	143(5)	-9(2)	0(2)	77(10)
C(12a)	48708(8)	2634(4)	4421(4)	70(2)	141(5)	135(5)	-10(2)	-6(2)	13(8)

*Standard deviations by least squares given in parentheses for the least significant digit. The anisotropic thermal parameters are of the form exp-($\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + \beta_{12}hk + \beta_{13}h\ell + \beta_{23}k\ell$).

† $*10^4$

‡ $*10^5$

Table 3b. Coordinates of the hydrogen atoms for CHRY*

Atom	x†	y†	z†
H(1)	5518	2475	3576
H(2m)	6565	1941	5434
H(2m)	6250	3486	5056
H(2m)	6191	1772	4038
H(3)	5377	1375	8707
H(4)	4613	1791	8463
H(4bm)	4221	4776	7600
H(4bm)	3749	4953	6776
H(4bm)	4168	5495	5715
H(5)	3913	489	6771
H(5)	3908	1902	8211
H(6)	3180	1011	7586
H(6)	3235	2952	7145
H(6am)	3110	-1162	5357
H(6am)	3572	-683	4573
H(6am)	3152	-714	3383
H(8)	2199	1933	2861
H(8)	2466	221	2752
H(9)	2677	3331	1251
H(9)	2716	1512	420
H(10)	3413	2985	966
H(10)	3394	1073	1560
H(10b)	3972	1434	3601
H(10am)	3378	5349	3114
H(10am)	3294	4953	5079
H(10am)	2920	4623	3714
H(11)	4194	4878	3049
H(11)	4082	3637	1516
H(12)	4868	3988	2159
H(12)	4705	2105	1909

* Assumed isotropic B value of 3.7.

† x10^4.

Table 4. Structure factors. Each group of four columns contains h, 10|F_o|, 10F_c, and $\sigma(F_o)$. A -- following the sigma indicates the reflection had zero weight and was omitted from the refinement.

H	0	0	
2	110	110	1
4	26	15	0
6	56	53	0
8	232	237	2
10	94	99	1
12	694	657	--
14	1329	1270	14
16	405	379	6
18	0	4	--
20	265	283	3
22	65	61	1
24	125	128	1
26	158	151	2
28	0	4	--
30	0	13	--
32	28	28	1
34	20	13	1
36	0	0	--
H	1	0	
1	119	114	1
2	922	996	--
3	203	213	2
4	449	473	--
5	394	427	--
6	313	327	3
7	258	263	2
8	102	101	1
9	45	44	0
10	195	190	2
11	156	155	1
12	368	355	3
13	271	266	2
14	618	615	6
15	136	124	1
16	161	157	1
17	206	211	2
18	118	112	1
19	38	40	1
20	208	220	2
21	37	35	1
22	157	155	1
23	28	36	1
24	15	20	2
25	92	98	1
26	50	46	1
27	0	2	--
28	192	205	2
29	11	13	3
30	44	50	1
31	15	11	2
32	73	76	1
33	20	23	2
34	111	106	1
35	21	24	1
36	70	69	1
37	21	23	1
H	2	0	
0	2083	1845	--
1	256	259	2
2	457	468	--
3	1127	1035	--
4	595	551	--
5	83	83	1
6	72	77	1
7	259	269	2
8	612	578	--
9	343	365	3
10	357	347	3
11	176	180	1
12	173	184	1
13	39	36	1
14	448	436	4
15	328	332	3
16	280	275	3
17	120	118	1
18	22	26	1
19	197	197	2
20	33	29	1
21	90	85	1
22	117	113	1
23	60	57	1
24	38	32	1
25	43	38	1
26	24	29	2
27	17	19	2
28	81	84	1
29	97	91	1
30	37	32	1
31	0	0	--
32	43	44	1
33	0	0	--
34	69	68	1
35	14	21	1
36	24	23	1
H	3	0	
1	641	670	6
2	246	266	2
3	291	290	3
4	151	161	1
5	126	106	1
6	84	94	1
7	39	29	1
8	220	233	2
9	79	77	1
10	27	13	1
11	53	57	1
12	154	155	1
13	226	220	2
14	289	288	3
15	241	257	2
16	83	86	1
17	163	169	1
18	101	101	1
19	0	0	--
20	210	206	2
21	0	13	--
22	0	2	--
23	53	55	1
24	50	53	1
25	168	165	2
26	16	10	2
27	58	63	1
28	33	38	1
29	47	50	1
30	18	20	1
31	30	30	1
32	98	92	1
33	11	10	2
34	69	64	1
35	30	28	1
H	4	0	
0	519	506	5
1	366	369	3
2	138	134	1
3	563	552	5
4	19	5	2
5	135	122	1
6	180	173	2
7	22	22	1
8	73	74	1
9	29	29	1
10	96	98	1
11	186	185	2
12	40	35	1
13	173	161	2
14	147	138	1
15	181	181	2
16	146	149	1
17	81	79	1
18	115	117	1
19	225	231	2
20	18	10	2
21	101	104	1
22	15	12	2
23	11	2	3
24	63	68	1
25	39	37	1
26	36	39	1
27	41	46	1
28	10	9	3
29	88	86	1
30	76	68	1
31	67	60	1
32	13	10	1
33	78	75	1
34	24	23	1
H	5	0	
1	118	127	1
2	78	80	1
3	62	71	1
4	156	155	1
5	61	53	1
6	22	23	1
7	22	14	1
8	36	28	1
9	0	5	--
10	13	11	2
11	133	130	1
12	141	138	1
13	49	56	1
14	114	116	1
15	0	2	--
16	0	1	--
17	85	84	1
18	191	193	2
19	30	29	2
20	97	101	1
21	78	75	1
22	122	114	1
23	58	59	1
24	102	100	1
25	31	31	1
26	0	6	--
27	0	11	--
28	0	8	--
29	23	25	1
30	0	4	--
31	14	10	1
32	39	48	--
H	6	0	
0	68	77	1
1	130	130	1
2	61	61	1
3	163	158	2
4	0	3	--
5	108	119	1
6	94	98	1
7	99	103	1
8	24	15	2
9	30	33	1
10	33	27	1
11	45	41	1
12	52	49	1
13	92	92	1
14	39	38	1
15	90	88	1
16	17	11	2
17	48	43	1
18	30	24	1
19	26	28	1
20	36	35	1
21	14	2	2
22	15	14	2
23	46	47	1
24	57	55	1
25	51	47	1
26	47	43	1
27	34	33	1
28	36	39	1
29	6	8	2
H	7	0	
1	0	1	--
2	38	29	1
3	34	36	1
4	83	75	1
5	13	5	3
6	15	0	2
7	22	15	2
8	12	11	3
9	59	56	1
10	36	38	1
11	80	88	1
12	11	12	3
13	0	8	--
14	0	2	--
15	40	44	1
16	12	6	2
17	10	10	3
18	57	56	1
19	22	19	1
20	65	63	1
21	47	52	1
22	52	55	1
23	74	76	1
24	31	36	1
25	13	17	1
26	11	18	1
H	8	0	
0	0	0	--
1	25	19	1
2	33	38	1
3	39	35	1
4	24	19	1
5	22	19	1
6	28	26	1
7	36	36	1
8	22	25	2
9	46	46	1
10	26	27	1
11	26	25	1
12	8	7	3
13	24	25	1
14	0	11	--
15	0	1	--
16	0	10	--
17	12	12	2
18	25	29	1
19	0	3	--
20	15	28	1
21	21	41	--
H	9	0	
1	51	57	1
2	59	54	1
3	30	28	1
4	15	24	2
5	14	20	2
6	0	2	--
7	0	0	--
8	16	21	1
9	17	27	1
10	27	35	1
11	38	53	--
12	12	16	2
13	30	49	--
14	10	22	2
H	0	1	
2	691	818	--
4	464	490	--
6	500	526	--
8	182	182	1
10	599	609	6
12	524	524	5
14	504	490	5
16	118	125	1
18	104	101	1
20	57	58	1
22	22	15	1
24	95	96	1
26	81	86	1
28	114	124	1
30	96	97	1
32	0	5	--
34	46	42	1
36	78	75	1
H	1	1	
0	1281	1622	--
1	107	111	1
2	584	619	--
3	448	466	--
4	169	190	--
5	231	236	2
6	318	324	3
7	306	315	3
8	383	396	3
9	154	164	1
10	172	173	1
11	96	93	1
12	154	148	1
13	68	72	1
14	546	532	5
15	163	164	1
16	43	48	1
17	124	129	1
18	104	102	1
19	181	182	2
20	176	172	2
21	59	53	1
22	53	49	1
23	116	116	1
24	66	63	1
25	84	90	1
26	119	126	1
27	66	69	1
28	132	143	1
29	71	68	1
30	30	24	1
31	47	45	1
32	39	42	1
33	66	60	1
34	48	44	1
35	9	5	2
36	103	99	1
37	0	2	--
H	2	1	
1	800	846	--
2	413	443	--
3	130	128	1
4	265	271	2
5	125	125	1
6	91	84	1
7	109	105	1
8	199	209	2
9	66	70	1
10	138	148	1
11	135	139	1
12	113	107	1
13	167	164	1
14	246	240	2
15	172	175	1
16	176	182	2
17	113	109	1
18	136	139	1
19	65	67	1
20	123	124	1
21	164	158	1
22	183	168	2
23	39	41	1
24	66	66	1
25	24	21	2
26	31	33	1
27	27	28	1
28	143	149	1
29	31	36	1
30	44	38	1
31	43	46	1
32	74	73	1
33	12	7	2
34	23	22	1
35	32	26	1
36	43	45	1
H	3	1	
0	749	739	--
1	184	176	2
2	297	293	3
3	473	474	4
4	168	174	1
5	125	121	1
6	245	243	2
7	43	39	1
8	216	211	2
9	111	102	1
10	207	200	2
11	122	130	1
12	77	77	1
13	104	105	1
14	169	170	1
15	143	138	1
16	149	148	1
17	156	154	1
18	181	191	2
19	89	86	1
20	83	83	1
21	53	53	1
22	55	48	1
23	161	160	2
24	124	124	1
25	105	103	1
26	36	40	1
27	85	86	1
28	35	38	1
29	46	40	1
30	86	79	1
31	35	38	1
32	12	9	2
33	41	37	1
34	33	30	1
35	30	30	1
H	4	1	
1	443	445	4
2	131	125	1
3	286	292	3
4	404	389	4
5	123	117	1
6	128	126	1
7	133	123	1
8	113	109	1
9	148	148	1
10	98	101	1
11	33	36	1
12	144	137	1
13	162	154	1
14	144	149	1
15	142	145	1
16	154	160	1
17	206	204	2
18	180	177	2
19	77	76	1
20	206	203	2
21	80	81	1
22	85	84	1
23	132	127	1
24	70	71	1
25	44	44	1
26	45	47	1
27	55	57	1
28	20	19	2
29	53	52	1
30	52	52	1
31	42	44	1
32	43	41	1
33	0	8	--
H	5	1	
0	161	168	1
1	98	99	1
2	233	222	2
3	255	258	2
4	101	98	1
5	75	80	1
6	210	204	2
7	120	115	1
8	120	120	1
9	216	216	2
10	83	78	1
11	85	88	1
12	98	102	1
13	64	64	1
14	61	61	1
15	40	46	1
16	84	88	1
17	67	71	1
18	165	163	2
19	23	23	2
20	82	78	1
21	68	68	1
22	82	79	1
23	117	119	1
24	56	55	1
25	83	80	1
26	37	38	1
27	16	11	2
28	27	26	1
29	22	17	1
30	23	24	1
31	37	40	1
H	6	1	
1	87	84	1
2	49	53	1
3	149	151	1
4	186	174	2
5	127	129	1
6	126	125	1
7	125	123	1
8	16	15	2
9	76	73	1
10	32	29	1
11	204	207	2
12	36	38	1
13	104	103	1
14	17	14	2
15	109	109	1
16	38	41	1
17	48	47	1
18	120	118	1
19	51	49	1
20	145	142	1
21	46	46	1
22	71	69	1
23	53	52	1
24	34	34	1
25	74	75	1
26	42	43	1
27	18	17	1
28	37	40	1
29	0	12	--
H	7	1	
0	164	166	2
1	88	88	1
2	110	113	1
3	68	66	1
4	68	74	1
5	40	35	1
6	63	62	1
7	37	45	1
8	50	46	1
9	109	111	1
10	59	62	1
11	49	51	1
12	70	70	1
13	65	68	1
14	29	31	1
15	0	9	--
16	48	45	1
17	17	13	2
18	40	43	1
19	52	48	1
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25	22	20	1
26	30	32	1
27	33	30	1
28	22	18	1
29	20	14	1
30	39	38	1
31	33	33	1
H	3	5	
0	242	228	2
1	123	121	1
2	98	97	1
3	105	108	1
4	107	107	1
5	60	61	1
6	157	162	1
7	90	91	1
8	0	12	--
9	29	21	1
10	22	20	2
11	69	69	1
12	89	93	1
13	31	39	1
14	121	120	1
15	50	54	1
16	49	49	1
17	29	33	1
18	21	26	2
19	47	48	1
20	99	94	1
21	68	63	1
22	19	16	2
23	46	44	1
24	26	27	1
25	0	6	--
26	28	29	1
27	45	42	1
28	55	55	1
29	38	41	1
H	4	5	
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2	249	240	2
3	185	180	2
4	38	39	1
5	147	144	1
6	92	84	1
7	76	71	1
8	59	54	1
9	121	114	1
10	23	20	2
11	71	72	1
12	132	135	1
13	84	80	1
14	36	42	1
15	78	75	1
16	82	79	1
17	47	51	1
18	38	38	1
19	81	74	1
20	28	30	1
21	119	113	1
22	102	96	1
23	42	45	1
24	76	75	1
25	60	58	1
26	35	35	1
27	44	45	1
H	5	5	
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1	28	30	2
2	151	144	1
3	87	85	1
4	57	86	1
5	87	81	1
6	46	45	1
7	48	44	1
8	69	65	1
9	71	75	1
10	47	46	1
11	103	101	1
12	100	99	1
13	22	13	2
14	143	137	1
15	48	42	1
16	29	24	1
17	53	54	1
18	65	62	1
19	30	28	1
20	27	28	1
21	14	13	2
22	37	35	1
23	43	44	1
24	45	47	1
25	0	4	--
H	6	5	
1	19	27	2
2	144	142	1
3	55	54	1
4	19	23	2
5	90	88	1
6	65	61	1
7	41	37	1
8	70	69	1
9	60	62	1
10	55	48	1
11	27	30	1
12	61	58	1
13	64	59	1
14	30	24	1
15	22	22	1
16	93	93	1
17	15	13	2
18	30	27	1
19	31	32	1
20	39	39	1
21	29	30	1
22	41	55	--
H	7	5	
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2	44	43	1
3	50	50	1
4	50	47	1
5	63	66	1
6	72	67	1
7	60	61	1
8	41	40	1
9	72	73	1
10	27	26	1
11	58	54	1
12	0	4	--
13	29	24	1
14	40	46	1
15	52	57	1
16	33	35	1
17	25	35	--
H	8	5	
1	19	22	1
2	29	39	1
3	10	18	2
4	35	47	--
5	43	60	--
6	18	23	1
7	7	4	2
8	28	50	--
H	0	6	
0	181	179	2
2	275	294	3
4	352	395	4
6	165	181	2
8	55	61	1
10	62	74	1
12	49	54	1
14	34	38	1
16	58	65	1
18	235	238	2
20	40	43	1
22	113	121	1
24	25	23	1
26	56	58	1
28	35	38	1
H	1	6	
1	36	31	1
2	180	173	2
3	105	100	1
4	297	288	3
5	81	79	1
6	91	85	1
7	36	42	1
8	87	88	1
9	57	58	1
10	98	110	1
11	38	44	1
12	143	152	2
13	23	23	2
14	26	20	2
15	45	41	1
16	155	200	2
17	63	65	1
18	128	135	1
19	40	42	1
20	89	91	1
21	25	26	1
22	0	5	--
23	41	42	1
24	53	47	1
25	58	57	1
26	19	16	1
27	19	25	1
28	61	62	1
H	2	6	
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1	123	118	1
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3	205	198	2
4	301	293	3
5	20	18	3
6	125	116	1
7	128	118	1
8	87	87	1
9	52	45	1
10	39	45	1
11	76	77	1
12	63	69	1
13	57	58	1
14	56	59	1
15	34	33	1
16	66	70	1
17	42	43	1
18	152	151	2
19	70	67	1
20	94	90	1
21	96	91	1
22	69	70	1
23	22	19	1
24	46	43	1
25	26	28	1
26	23	19	1
27	13	14	1
28	19	19	1
H	3	6	
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2	96	85	1
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4	166	162	2
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6	21	19	2
7	122	114	1
8	34	28	1
9	39	36	1
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11	90	89	1
12	130	126	1
13	50	54	1
14	23	19	2
15	89	87	1
16	43	45	1
17	62	57	1
18	96	98	1
19	60	59	1
20	38	35	1
21	105	106	1
22	44	24	1
23	76	73	1
24	92	89	1
25	42	37	1
26	13	14	1
H	4	6	
0	77	70	1
1	67	69	1
2	76	73	1
3	123	118	1
4	167	168	1
5	27	27	2
6	35	39	1
7	96	95	1
8	0	15	--
9	41	40	1
10	14	17	3
11	82	81	1
12	60	62	1
13	37	42	1
14	90	83	1
15	28	24	1
16	23	21	2
17	53	50	1
18	14	17	2
19	23	21	1
20	50	50	1
21	58	59	1
22	36	34	1
23	0	4	--
24	14	20	1
H	5	6	
1	39	35	1
2	55	58	1
3	73	69	1
4	49	55	1
5	23	17	2
6	52	53	1
7	51	52	1
8	77	76	1
9	32	38	1
10	76	77	1
11	41	37	1
12	53	54	1
13	24	24	1
14	49	42	1
15	67	64	1
16	65	63	1
17	27	30	1
18	30	24	1
19	21	18	1
20	28	30	1
21	19	28	1
H	6	6	
0	57	61	1
1	25	24	1
2	33	36	1
3	15	11	2
4	28	27	1
5	34	32	1
6	57	59	1
7	73	77	1
8	8	4	3
9	28	34	1
10	31	30	1
11	15	14	2
12	23	28	1
13	12	12	2
14	42	45	1
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16	10	10	2
17	32	42	1
H	7	6	
1	40	40	1
2	46	47	1
3	18	16	1
4	27	29	1
5	24	23	1
6	16	19	1
7	7	12	2
8	15	17	1
10	25	33	1
11	11	14	1
H	0	7	
2	136	138	2
4	149	184	--
6	25	16	2
8	25	25	2
10	86	98	1
12	63	73	1
14	25	30	2
16	64	68	1
18	65	71	1
20	31	22	1
22	66	64	1
24	99	105	1
H	1	7	
0	136	129	1
1	82	80	1
2	63	67	1
3	28	29	2
4	243	250	3
5	0	8	--
6	78	91	1
7	42	47	1
8	53	64	1
9	36	38	1
10	69	79	1
11	26	32	2
12	0	4	--
13	60	60	1
14	35	43	1
15	18	18	2
16	24	26	2
17	30	32	1
18	73	81	1
19	12	10	2
20	11	16	2
21	51	56	1
22	34	39	1
23	8	11	3
24	51	53	1
25	21	27	1
H	2	7	
1	111	106	1
2	87	81	1
3	70	66	1
4	123	119	1
5	49	46	1
6	23	24	2
7	72	74	1
8	46	43	1
9	0	12	--
10	80	81	1
11	62	66	1
12	66	69	1
13	13	12	3
14	29	29	1
15	41	46	1
16	49	50	1
17	39	41	1
18	53	55	1
19	90	88	1
20	27	28	1
21	50	56	1
22	20	19	1
23	26	31	1
24	96	109	1
H	3	7	
0	131	124	1
1	30	23	2
2	44	41	1
3	48	48	1
4	119	109	1
5	66	65	1
6	30	31	2
7	79	76	1
8	51	50	1
9	89	86	1
10	61	60	1
11	10	12	3
12	49	45	1
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14	50	46	1
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16	23	23	1
17	53	54	1
18	29	34	1
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21	71	73	1
22	68	73	1
H	4	7	
1	80	75	1
2	25	29	2
3	84	77	1
4	32	33	1
5	76	70	1
6	64	63	1
7	39	38	1
8	23	30	1
9	43	36	1
10	33	34	1
11	69	68	1
12	21	16	1
13	27	22	1
14	39	41	1
15	42	41	1
16	41	35	1
17	30	30	1
18	46	45	1
19	49	51	1
20	21	25	1
H	5	7	
0	22	25	2
1	66	60	1
2	50	48	1
3	36	32	1
4	71	67	1
5	21	16	1
6	14	9	2
7	12	10	2
8	28	23	1
9	39	35	1
10	50	44	1
11	23	23	1
12	9	5	2
13	42	40	1
14	25	27	1
15	0	10	--
16	16	12	1
H	6	7	
1	33	27	1
2	18	18	1
3	36	36	1
4	16	14	1
5	33	31	1
6	39	36	1
7	19	15	1
8	50	51	1
9	30	29	1
10	22	17	1
H	0	8	
0	72	72	1
2	38	32	1
4	43	49	1
6	25	22	2
8	17	19	2
10	56	71	1
12	55	62	1
14	0	19	--
16	31	32	1
18	27	32	1
20	27	35	1
H	1	8	
1	43	43	1
2	31	35	1
3	48	45	1
4	35	36	1
5	10	13	3
6	50	52	1
7	19	19	2
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11	16	20	2
12	13	21	2
13	15	12	2
14	28	29	1
15	20	19	1
16	21	22	1
17	17	25	2
18	16	13	1
19	13	19	1
20	19	25	1
H	2	8	
0	71	70	1
1	43	42	1
2	33	30	1
3	72	71	1
4	33	29	1
5	27	25	1
6	41	35	1
7	24	28	1
8	23	19	2
9	30	26	1
10	42	48	1
11	51	49	1
12	53	55	1
13	18	21	2
14	19	24	1
15	10	14	2
16	19	23	1
17	28	38	1
18	30	39	1
19	0	6	--
H	3	8	
1	22	23	1
2	46	48	1
3	53	51	1
4	44	33	1
5	40	38	1
6	24	21	1
7	31	27	1
8	22	24	1
9	31	26	1
10	74	70	1
11	60	60	1
12	0	9	--
13	35	36	1
14	21	27	1
15	27	26	1
16	23	24	1
H	4	8	
0	37	39	1
1	40	38	1
2	54	50	1
3	47	41	1
4	67	60	1
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7	32	28	1
8	49	44	1
9	55	54	1
10	59	57	1
11	51	47	1
12	35	38	1
13	0	9	--
H	5	8	
1	16	10	1
2	35	36	1
3	55	54	1
4	32	30	1
5	13	12	1
6	27	27	1
7	20	22	1
H	0	9	
2	132	132	2
4	13	10	2
6	12	17	2
8	9	13	3
10	0	18	--
12	26	54	--
H	1	9	
0	137	136	1
1	25	25	1
2	51	47	1
3	11	11	2
4	34	44	1
5	14	17	2
6	29	50	--
7	16	26	--
8	0	18	--
9	9	14	2
10	24	37	--
11	9	22	--
12	0	15	--
H	2	9	
1	36	37	1
2	94	90	1
3	51	50	1
4	18	16	1
5	9	9	2
6	8	4	2
7	0	2	--
8	12	16	1
9	0	16	--
10	0	14	--
H	3	9	
0	60	63	1
1	39	38	1
2	17	15	1
3	37	41	1
4	42	39	1
5	7	13	2

Table 5. Torsion angles*

Atoms†				Angle
10am	10a	6a	6am	169.2°
10am	10a	6a	6	-68.5°
10am	10a	6a	7	52.2°
10am	10a	10b	11	69.0°
10am	10a	10b	4b	-60.5°
10am	10a	10	9	-61.5°
6am	6a	10a	10b	-67.6°
6am	6a	10a	10	52.0°
6am	6a	7	O(7)	117.3°
6am	6a	7	8	-62.2°
6am	6a	6	5	66.8°
4bm	4b	10b	10a	-70.2°
4bm	4b	10b	11	62.0°
4bm	4b	5	6	74.4°
4bm	4b	4a	12a	-96.6°
2m	O(2)	2	1	-165.4°
2m	O(2)	2	3	14.9°

*The standard deviation in these torsion angles is about 0.3°. The convention used is Klyne and Prelog.

†All atoms are carbon except where indicated.

Table 6. Bond distances*

Atom	Atom	Distance
C(1)	C(2)	1.378 Å
C(1)	C(12a)	1.403
C(2)	C(3)	1.380
C(2)	O(2)	1.378
O(2)	C(2m)	1.409
C(3)	C(4)	1.380
C(4)	C(4a)	1.395
C(4a)	C(4b)	1.544
C(4a)	C(12a)	1.393
C(4b)	C(5)	1.543
C(4b)	C(10b)	1.559
C(4b)	C(4m)	1.533
C(5)	C(6)	1.534
C(6)	C(6a)	1.528
C(6a)	C(7)	1.522
C(6a)	C(10a)	1.572
C(6a)	C(6m)	1.550
C(7)	C(8)	1.515
C(7)	O(7)	1.200
C(8)	C(9)	1.521
C(9)	C(10)	1.543
C(10)	C(10a)	1.537
C(10a)	C(10b)	1.566
C(10a)	C(10m)	1.544
C(10b)	C(11)	1.521
C(11)	C(12)	1.526
C(12)	C(12a)	1.510

*The standard deviation in these distances is about 0.005 Å. "m" Refers to the methyl carbon.

Table 7. Bond angles*

Atom	Atom	Atom	Angle
C(2)	C(1)	C(12a)	101.0°
C(1)	C(2)	C(3)	119.8°
C(1)	C(2)	O(2)	124.4°
C(3)	C(2)	O(2)	115.7°
C(2)	C(3)	C(4)	119.3°
C(3)	C(4)	C(4a)	122.2°
C(4)	C(4a)	C(4b)	120.2°
C(4)	C(4a)	C(12a)	118.1°
C(4b)	C(4a)	C(12a)	121.5°
C(4a)	C(4b)	C(5)	110.2°
C(4a)	C(4b)	C(10b)	108.6°
C(4a)	C(4b)	C(4m)	105.2°
C(5)	C(4b)	C(10b)	108.8°
C(5)	C(4b)	C(4m)	108.0°
C(10b)	C(4b)	C(4m)	116.0°
C(4b)	C(5)	C(6)	113.0°
C(5)	C(6)	C(6a)	111.8°
C(6)	C(6a)	C(7)	111.0°
C(6)	C(6a)	C(10a)	110.7°
C(6)	C(6a)	C(6m)	108.5°
C(7)	C(6a)	C(10a)	106.5°
C(7)	C(6a)	C(6m)	106.6°
C(10a)	C(6a)	C(6m)	113.7°
C(6a)	C(7)	C(8)	115.2°
C(6a)	C(7)	O(7)	123.5°
C(8)	C(7)	O(7)	121.2°
C(7)	C(8)	C(9)	114.8°
C(8)	C(9)	C(10)	115.7°
C(9)	C(10)	C(10a)	113.4°
C(6a)	C(10a)	C(10)	107.9°
C(6a)	C(10a)	C(10b)	108.6°
C(6a)	C(10a)	C(10m)	110.5°
C(10)	C(10a)	C(10b)	110.4°
C(10)	C(10a)	C(10m)	107.4°
C(10b)	C(10a)	C(10m)	121.1°
C(4b)	C(10b)	C(10b)	115.7°
C(4b)	C(10b)	C(11)	109.5°
C(10a)	C(10b)	C(11)	115.2°
C(10b)	C(11)	C(12)	110.7°
C(11)	C(12)	C(12a)	114.1°
C(1)	C(12a)	C(4a)	119.5°
C(1)	C(12a)	C(12)	118.2°
C(4a)	C(12a)	C(12)	122.4°

*The standard deviation in these angles is about 0.3°. "m" Refers to the methyl carbon.

Appendix

Computer Programming

Numerous computer programs have been written, modified, or adopted to the 370-155 CRYM system. Programs which were written include an initial data processing program to sort and average diffraction data, tetragonal and cubic structure factors - least squares, a program to store E's or external phases on a CRY tape, a unit cell least squares program to calculate accurate cell dimensions from film and diffractometer data, and a program to generate poetry based on the time of day as a random number. In addition, the Oak Ridge structure factors - least squares program XFLS for the 360 has been adapted to be compatable with CRYM formats allowing the chemist anisotropic refinement in any space group.

Programs which have been modified and improved include distances and angles extension to space group 14N and corrections, an edit program to restore lost data if part of the data tape is erased, a Fourier option making Fourier maps easier to visualize, a listing option which searches for inconsistencies in the data tape, and a new publication list program which lists any number of structure factors in any order. Finally, programs have added to CRYM which calculate direction cosines for methyl groups, put hydrogens on chain hydrocarbons, handle diffractometer input and output, calculate spherical absorption corrections, and analyze diffractometer data for time decay.

Other Structures

The Crystal structure of trisacetylacetonatochromium(III) was reinvestigated. The structure as first reported (1) contained one AcAc ring which was vibrating 0.3 to 0.4 Å normal to its mean plane. Because the vibration was approximately parallel to the b axis, this motion was called a lattice wave rather than simple disorder. Cooling the crystal caused the diffuse spots to disappear and reheating caused the diffuseness to return.

The purpose of this reinvestigation was to use accurate three-dimensional diffaction data and full-matix least squares (the original analysis used differential synthesis) to accurately determine atomic positions and and directions of thermal vibration. With an R = 0.10 the reinvestigation converged on the previous results. Therefore, work did not continue on this project.

Dr. T. F. Lai located the Pt, Cl, and P atoms in a crystal of $PtCl_2P(O\phi)_3P(C_4H_9)$ before leaving Caltech.

The refinement was concluded after the remaining atoms were located. The results have not been published.

NSF Summer Science Intern

Beginning the summer of 1970 the National Science Foundation began a program of summer science interns which brought ten graduate students to Washington to work in the Foundation in the branch of their choice to make useful suggestions and write a report for the improvement of the National Science Foundation. I was selected and spent two months in the Undergraduate Education Division. My primary interest was analysis of the undergraduate research programs.

Undergraduate Research Assistance at Caltech

A significant portion of time has been devoted to the supervision of undergraduates in X-ray crystallography research. Some of the undergraduates were only able to get accurate cell constants or a set of data (M. Wimbrow, G. Frankel, D. Ridder) while others were able to complete their project (R. Bell and L. Lindblom) with the undergraduate doing as much of the research by himself as possible. In addition, one graduate student (R. Carhart) was guided through a structure determination and many others have been assisted with their crystallography problems.

References for the Appendix

1. B. Morosin, _Acta Cryst._, _19_, 131.