I.

THE CRYSTAL STRUCTURE OF CYCLOHEX-1-ENYLCYCLOBUTENEDIONE

II.

THE CRYSTAL STRUCTURE OF 3,6-DIMETHYLPIPERAZINE-2,5-DIONE

III.

PROGRAMS FOR THE BURROUGHS MODEL 205 COMPUTER

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ABSTRACT

The crystal structure of cyclohex-1-enylcyclobutenedione has been determined by x-ray diffraction techniques. Complete three-dimensional intensity data were collected about each of two axes using CuKα radiation. A trial structure was evolved which proved to be correct. This structure was refined both in projection and in three dimensions by conventional Fourier and least-squares methods. During the last several cycles of refinement six thermal parameters and three positional parameters for each of the twelve heavy atoms were optimized. An unusually long carbon-carbon bond distance (1.61Å) has been found; this result is not inconsistent with purely chemical properties of the compound.

The crystal structure of 3,6-dimethylpiperazine-2,5-dione has been investigated by means of x-ray diffraction methods. Three-dimensional intensity data have been collected and a trial structure has been evolved. This trial structure seems to be the only structure which affords a suitable hydrogen-bonding scheme and molecular packing. Moreover, it is in agreement with the very distinctive crystalline habit and cleavage of the compound. Apparently because of difficulties in scaling the data, however, the very large number of refinements which were attempted all failed to converge. Consequently, work on this compound has been stopped temporarily until sufficient additional information has been collected to allow all of the intensity data to be put onto a common scale.

A number of programs of general crystallographic interest have been coded for the Burroughs electronic digital computer, model 205. A brief description of these programs is given.

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PART I

THE CRYSTAL STRUCTURE OF CYCLOHEX-1-ENYLCYCLOBUTENEDIONE

Introduction

Cyclohex-1-enylcyclobutenedione, $C_{10}H_{10}O_2$, (Figure 6) was first prepared by C. M. Sharts(1) as part of an intensive study of derivatives of cyclobutadiene now being carried out in these Laboratories by Professor J. D. Roberts and his co-workers. The only similar compound whose detailed molecular structure has been determined is phenylcyclobutenedione, which was studied here by Chi-hsiang Wong.(2) In view of the interesting bonding which almost certainly exists in these compounds, an x-ray study of the cyclohexenyl derivative was undertaken.

Experimental

The sample used in this investigation was kindly supplied by Dr. C. M. Sharts. It was prepared as outlined in his Thesis(1) and had been through several cycles of crystallization from ethanol and hexane alternately. Crystals suitable for diffraction studies were grown just prior to use by sublimation in air at 70°C and a pressure of 1 mm of mercury. The light yellow crystals were in the form of rectangular prisms truncated at each end by a rectangular pyramid; the axis of the prism was chosen as the b axis of the unit cell. Those crystals used in the x-ray diffraction experiments measured roughly 0.2 by 0.2 by 0.4 mm. During irradiation by x-rays the crystals slowly decomposed, becoming over a week or ten days more and more opaque (and seemingly amorphous), first at the surface, then into the interior, but maintaining their shape the whole while. The crystals were not hygroscopic, however, and the decomposition did not seem to proceed rapidly enough to warrant their being mounted in glass capillaries. Accordingly, they were mounted with flake shellac on the ends of glass mounting pins, as is customary.

Rotation and Weissenberg photographs taken about the b axis were indexed on the basis of a monoclinic unit cell whose approximate parameters are:

$$a = 8.31 \text{ Å}$$
$$b = 9.30 \text{ Å}$$
$$c = 11.52 \text{ Å}$$
$$\beta = 96.2^\circ$$

The only systematic extinctions observed were $0k0$ for k odd and $h0\ell$ for h odd; the space group is accordingly indicated to be $P\frac{2_1}{a}$ (C_{2h}^5).

For the determination of accurate unit-cell dimensions rotation photographs about the a and b axes were taken using the Straumanis technique(3) and CrKα radiation, and twenty-two sharp lines in the back-reflection region of the equatorial layer-line were indexed on the basis of the above approximate unit cell parameters. The constants of the observational equations

$$\sin^2\theta_{hk\ell} = Ah^2 + Bk^2 + C\ell^2 + Dh\ell$$

were then fitted by least-squares to the twenty-two measured values of $\sin^2\theta_{hk\ell}$; all of the observational equations were assigned equal weight. The output constants were

$A = 0.0192583 \quad \pm 0.0000016$
$B = 0.0151817 \quad \pm 0.0000037$
$C = 0.0100423 \quad \pm 0.0000022$
$D = -0.00295624 \quad \pm 0.0000023$

The quoted uncertainties are estimated standard deviations calculated from the residuals and the diagonal terms of the inverse matrix of the normal equations. Taking the wavelength of CrKα radiation to be 2.2909Å, the unit cell parameters and their estimated standard deviations are:

$a = 8.3011 \quad \pm 0.0051$Å
$b = 9.296 \quad \pm 0.016$Å
$c = 11.495 \quad \pm 0.018$Å
$\beta = 96.10^\circ \quad \pm 0.11^\circ$

The densities of several crystals of the unsublimed material were determined by flotation in a potassium iodide solution and also in a solution of chloroform and n-heptane. The average density and its estimated standard deviation so obtained are $1.2575 \pm 0.0007 \frac{\text{gm}}{\text{cm}^3}$ at 23°. The crystal density calculated from the above unit cell parameters on the assumption of four molecules of $C_{10}H_{10}O_2$ per unit cell is $1.2211\frac{\text{gm}}{\text{cm}^3}$. Inasmuch as the discrepancy between the observed and the calculated values of the density amounts to some fifty-two times the estimated standard deviation of the measurement, it is almost certainly real. Since it is now known$^{(4)}$ that after standing for several months samples of unsublimed $C_{10}H_{10}O_2$

frequently contain appreciable quantities of an oxygen adduct (perhaps $C_{10}H_{10}O_3$), it is assumed that the fairly old sample used for the density measurements had been so contaminated. A later single measurement on crystals of freshly-sublimed material yielded a density of $1.2203 \frac{gm}{cm^3}$. Since the molecule itself has no symmetry and since there are four molecules in the unit cell, the molecules are in general positions and there is only one molecule in the asymmetric unit. Choosing the origin of the unit cell at a center of symmetry, the symmetry of the space group $P\frac{2_1}{a}$ requires that for each atom, i, located at x_i, y_i, z_i, there be three symmetrically-related atoms at $\bar{x}_i$, $\bar{y}_i$, $\bar{z}_i$; $\frac{1}{2} + x_i$, $\frac{1}{2} - y_i$, z_i; and $\frac{1}{2} - x_i$, $\frac{1}{2} + y_i$, $\bar{z}_i$. Accordingly, fixing the positions of the atoms of a single molecule defines the entire structure.

Weissenberg photographs through the fifth layer about $\underset{\sim}{a}$ and through the fifth layer about $\underset{\sim}{b}$ were taken using CuKα radiation filtered through 0.007" of Ni foil. A pack of three films was used for each exposure, and two exposures were made for each crystal setting, one for about 25 hours and the other for about 2.5 hours. Intensities were estimated on a relative scale by visual comparison with a calibrated intensity strip. They were corrected for Lorentz and polarization factors, but the crystals were small enough that an absorption correction was deemed unnecessary. The structure factors F(hkℓ) were put on an approximately absolute scale by means of Wilson's method$^{(5)}$. The Wilson plot is shown in Figure 2.

The Three-dimensional Patterson Map

Patterson(6) has shown that it is possible to calculate, using only the values of $|F(hk\ell)|^2$, a Fourier synthesis which gives information about interatomic vectors, rather than information about the absolute positions of atoms within the unit cell, as the electron density synthesis does. The advantage of the so-called Patterson map over an electron density map is that the calculation of the former requires no knowledge of the phases (or numerical signs, if the structure is centrosymmetrical) of the structure factors, $F(hk\ell)$.

A three-dimensional Patterson map was computed using the expression

$$P(u,v,w)=\frac{4}{V}\underset{h+k=2n}{\sum_h\sum_k\sum_\ell}|F(hk\ell)|^2\,\frac{\sin^2\theta}{\lambda^2\hat{f}^2}\,e^{-5\frac{\sin^2\theta}{\lambda^2}}\cos 2\pi(hu+\ell w)\cos 2\pi kv$$

$$-\frac{4}{V}\underset{h+k=2n+1}{\sum_h\sum_k\sum_\ell}|F(hk\ell)|^2\,\frac{\sin^2\theta}{\lambda^2\hat{f}^2}\,e^{-5\frac{\sin^2\theta}{\lambda^2}}\sin 2\pi(hu+\ell w)\sin 2\pi kv$$

Here the factor $\frac{\sin^2\theta}{\lambda^2\hat{f}^2}$ is included to sharpen(7) the peaks of the map, and the exponential factor serves as a smoothing function(7); $\hat{f}$ is an average atomic scattering function, and λ is the wavelength (1.5418Å) of the CuKα radiation used in the collection of the intensity data.

The $h0\ell$ Weissenberg photographs suggest that the molecule lies roughly parallel to $(10\bar{1})$, inasmuch as the $(20\bar{2})$,

$(40\bar{4})$, and $(60\bar{6})$ reflections are quite strong and show an approximately normal decline. Accordingly the Patterson map was replotted in two sections parallel to $(10\bar{1})$ as depicted in Figure 3. Those vectors representing distances within a single molecule should lie near Section A, whereas those arising from intermolecular interaction between molecules related by the glide plane should fall in Section B. Thus Section A contains information about the orientation of the molecule and Section B about its placement within the unit cell.

From consideration of the peaks surrounding the origin in Section A the orientation of the molecule soon was derived. Furthermore the supposition that the plane of the molecule is roughly $(10\bar{1})$ was confirmed by the fact that all peaks of the three-dimensional map close enough to the origin to represent intramolecular vectors lay near Section A. Because of the fact that the Patterson map has $\frac{2}{m}$ symmetry, however, the orientation of the molecule was known only with a two-fold ambiguity.

Interpretation of Section B was much less straightforward than that of Section A. Nevertheless two reasonable trial structures soon were derived. Calculation of structure factors, however, showed them both to be grossly incorrect. Upon re-examination of Section B it was decided that, because of doubt as to how much reliance could be placed on the weights of the Patterson peaks, several other trial structures could be evolved which apparently would fit the Patterson equally well. Accordingly this approach was abandoned temporarily.

The Determination of the x and z Parameters

An unmodified Patterson projection down $\underset{\sim}{a}$ was computed using the equation

$$\frac{A}{4} P(v,w) = \sum_{\substack{k \\ k}} \sum_{\substack{\ell \\ \text{even}}} \left|F(0k\ell)\right|^2 \cos 2\pi kv \cos 2\pi \ell w,$$

where A is the apparent area of the (100) plane. The resulting map exhibited only two maxima, both in the form of long ridges of Patterson density approximately parallel to the y direction, one located at $w = 0$ and the other at $w = \frac{1}{2}$. Thus the molecules are oriented with their longitudinal directions roughly parallel to $\underset{\sim}{b}$ and are spaced about one-half unit cell apart along $\underset{\sim}{c}$. The only way to obtain such a molecular spacing is to place the "center of scattering" of the molecule at $z = \frac{1}{4}$. The symmetry then generates other molecules at $z = 3/4$, $z = 5/4$, etc. (See Figure 8.) On the assumption that the "best" plane of the molecule is $(10\bar{1})$, the possible positions of the molecule in projection onto (010) are then restricted to those shown in Figure 4. Corresponding to each of these positions are two orientations determined by whether O_1 is pointing toward $\underset{\sim}{a}$ or away from it. Thus in three dimensions four distinct structures are possible. In projection onto (010), however, centers of symmetry cannot be distinguished from two-fold screw axes, so that only two orientations need be considered.

Attempts were made to refine each of these trial structures by means of electron density and difference maps. The only structure which refined at all well was the one having the oxygen atoms near $\underset{\sim}{a}$. After three cycles of refinement R was 0.19 ($R = \frac{\sum |F_o - F_c|}{\sum |F_o|}$, where the summations are over all of the observed ($h0\ell$) reflections). At this stage it seemed unlikely that further refinement of this projection would prove to be very fruitful. Accordingly it was decided to try to determine the y parameters of each atom and to then refine all of the positional parameters simultaneously by three-dimensional methods. The final electron density map of the (010) projection is shown in Figure 5; x and z parameters derived from this map are listed in Table 1.

The Determination of the y Parameters

On simply a chemical basis, the molecular structures (as distinct from the crystal structures) of phenylcyclobutenedione and cyclohex-1-enylcyclobutenedione should be quite similar. Furthermore, in the crystal structure of each of these compounds the longitudinal direction of the molecule lies roughly parallel to $\underset{\sim}{b}$.(2) Moreover, the lengths of $\underset{\sim}{b}$ are equal for the two compounds to within the error of measure-

TABLE 1

x and z Parameters From the (010) Fourier Projection

x	Atom Code Number	z
0.37	C_1	-0.36
0.35	C_2	-0.40
0.40	C_3	-0.35
0.49	C_4	-0.26
0.53	C_5	-0.20
0.49	C_6	-0.25
0.52	C_7	-0.19
0.59	C_8	-0.10
0.59	C_9	-0.12
0.49	C_{10}	-0.22
0.43	O_1	-0.31
0.66	O_2	-0.07

ment. These facts strongly suggest that, except perhaps for a shift of origin, the projection of the molecule onto $\underset{\sim}{b}$ is roughly the same for both compounds.

On comparison of the two sets of (0k0) reflections, it was observed that the variation of intensity with k was qualitatively the same for both compounds. As a consequence, the hypothesis that the y parameters of both structures are the same was accepted tentatively. Structure factors for all of the observed reflections were calculated using the y parameters for phenylcyclobutenedione and the previously-obtained z parameters for the cyclohexenyl derivative. The discrepancy factor, R, was 0.98, signifying that the agreement between the observed and the calculated structure factors was even worse than that to be expected from a random structure.(8) Accordingly, the above hypothesis was abandoned.

It was next assumed that the <u>relative</u> y parameters of the atoms in the two compounds are the same, but that the origin is shifted; a method similar to that of Booth(9) was then used to compute the shift. If y_i is the y parameter of the $i^{\underline{th}}$ atom relative to some arbitrary origin and y_i' the corresponding parameter relative to the origin of the unit cell, then the primed parameters are related to the unprimed by the relation

$$y_i' = y + y_i, \ i = 1, 2, \ldots, N,$$

where N is the number of atoms in the <u>asymmetric</u> unit.

For the (0k0) reflections,

$$F(0k0) = 4 \sum_{i=1}^{N} f_i \cos 2\pi k y_i'$$

$$= 4 \sum_{i=1}^{N} f_i \cos 2\pi k y_i \cos 2\pi k y$$

$$- 4 \sum_{i=1}^{N} f_i \sin 2\pi k y_i \sin 2\pi k y$$

$$\pm \tfrac{1}{4} F(0k0) = \sqrt{A^2 + B^2} \cos 2\pi k(y+\alpha), \text{ where}$$

$$\alpha = \arctan \frac{B}{A}, \quad A = \sum_{i=1}^{N} f_i \cos 2\pi k y_i, \text{ and}$$

$$B = \sum_{i=1}^{N} f_i \sin 2\pi k y_i,$$

$$\cos 2\pi k(y+\alpha) = \frac{F(0k0)}{4\sqrt{A^2 + B^2}} .$$

Table 2 lists the y parameters of phenylcyclobutenedione,(2) which were used as input to the calculation, and Table 3 gives the pertinent data and results of the calculation for several values of k. As may be seen from Table 3, corresponding to each F(0k0) is a set of several possible values of y. The value finally chosen was -0.11; it was obtained by averaging several nearly-equal values of y, one from each of the various sets. Thus the y so selected is the one which most nearly satisfies the first several observed F(0k0). This y was then

TABLE 2

The y Parameters of Phenylcyclobutenedione(2)

Atom Code Number	y
C_1	0.536
C_2	0.665
C_3	0.793
C_4	0.788
C_5	0.659
C_6	0.531
C_7	0.392
C_8	0.351
C_9	0.191
C_{10}	0.237
O_1	0.181
O_2	0.080

TABLE 3

Calculation of the Molecular Shift Along b

k	F(0k0) obs (electrons)	$(A^2 + B^2)^{\frac{1}{2}}$ (electrons)	α (radians)	Possible y in Fractions of b
2	40.1	20.000	- 0.7932	-0.11, -0.05, -0.01, +0.09, +0.14, +0.16, +0.20, +0.24
4	8.4	2.365	- 0.7144	-0.12, -0.08, +0.13, +0.17, +0.26, etc.
6	24.2	9.230	0.9862	0.00, -0.06, -0.10, +0.02, -0.14, etc.
8	15.3	7.312	-0.6273	+0.04, +0.10, -0.07, -0.10, +0.16, -0.14, etc.

added to the relative parameters of Table 2 to yield the absolute y_i'. These parameters together with the previously-determined x and z parameters then constitute the complete three-dimensional trial structure of cyclohex-1-enylcyclobutenedione.

Refinement of the Trial Structure

If it is assumed that all thermal motion within the crystal is isotropic, the expression for the structure factor $F(h,k,\ell,)$ in space group $P\frac{2_1}{a}$ is

$$F(hk\ell) = 4 \sum_{n=1}^{N} f_n e^{-B_n \frac{\sin^2\theta}{\lambda^2}} \cos 2\pi(hx_n+\ell z_n)\cos 2\pi k y_n, \text{ if } h+k=2m, \text{ or}$$

$$F(hk\ell) = -4 \sum_{n=1}^{N} f_n e^{-B_n \frac{\sin^2\theta}{\lambda^2}} \sin 2\pi(hx_n+\ell z_n)\sin 2\pi k y_n, \text{ if } h+k=2m+1,$$

where f_n is the atomic scattering factor and the sum is taken over all N atoms in the asymmetric unit. Thus, if the isotropic thermal parameters are refined concurrently with the positional parameters, a total of 4N + 1 parameters must be refined--the three positional coordinates x_n, y_n, z_n and the isotropic temperature factor B_n for each of the N atoms, and a scale factor K which is required because the intensities are known on only a relative scale. A very convenient procedure for carrying out such a refinement may be derived$^{(10)}$ from the least-squares criterion that

$$\sum_j w(hk\ell)\left[KF_o(hk\ell)_j - F_c(hk\ell)_j\right]^2$$

be a minimum. Here $F_o(hk\ell)_j$ denotes the observed value of the $j^{\underline{th}}$ structure factor, F_c denotes its calculated value, and the summation is over all observed reflections. K is a scale factor required to convert the observed values of $F(hk\ell)$ from a relative to an absolute scale.

The weights, $w(hk\ell)$, were initially taken as unity. Since hydrogen atoms were excluded from all except the final stages of refinement, N is twelve for this compound. The number of observed reflections is 794. A total of thirty cycles of structure-factor and least-squares calculations were necessary before convergence of the iterative process seemed complete. The calculations were carried out on a Burroughs electronic digital computer model 205; the program used was written by Dr. R. A. Pasternak and later modified extensively by Mr. Albert Hybl.

For the first few cycles of refinement, the B_n were held constant and equal to the B derived from the Wilson plot, and only those reflections for which $\sin\theta_{hk\ell} \leq 0.60$ were included in the refinement. The discrepancy factor, R, started at 0.49 and dropped steadily over eight cycles of refinement to 0.25. At this stage the scope of the refinement was enlarged to include all reflections for which $\sin\theta \leq 0.75$, and refinement of the individual isotropic thermal parameters was initiated. R dropped quickly to 0.22, but would go no lower.

A three-dimensional Fourier synthesis was then computed, using as coefficients the various $F_o - F_c$. Although this "difference map" indicated that some of the heavy atoms (C and O) were vibrating quite anisotropically, no hydrogen atoms were in evidence. Accordingly the positions of the ten hydrogen atoms were computed from the parameters of the carbon atoms, assuming a C-H bond length of 0.9Å, tetrahedral bonding of the methylene groups, and that the methyne C-H bond bisects the angle formed at the methyne carbon atom by the two carbon atoms adjacent to it.

The refinement was continued with the calculated contributions of the hydrogen atoms included in the computation of structure factors; the parameters of the hydrogen atoms were not refined. In addition, in the structure-factor expression the isotropic thermal factor $e^{-B_n \frac{\sin^2\theta}{\lambda^2}}$ was replaced by an anisotropic thermal factor of the form $\exp - (\alpha h^2 + \beta k^2 + \gamma \ell^2 + \delta hk + \epsilon h\ell + \eta k\ell)$, and the least-squares weighting procedure was changed to one similar to that suggested by Hughes,(10) i.e.

$$w = \frac{1}{|F_o|^2} \text{ if } |F_o| \geq 3.2, \text{ and}$$

$$w = \frac{0.3125}{|F_o|} \text{ if } |F_o| < 3.2.$$

R dropped to 0.17 over six cycles of refinement, the last two cycles showing hardly any improvement at all. The positional shifts were larger than might reasonably be expected at this stage and seemed to be oscillating. The thermal shifts, too, seemed unduly large, although this apparent anomaly was much less certain than that of the positional shifts. Therefore, in an attempt to induce more rapid convergence, half shifts rather than whole shifts were used in all further refinements.

Refinement then continued steadily until R reached 0.13. The positional shifts were now in the fifth or sixth significant figure and the refinement was considered completed. The final values of the positional parameters are given in Table 4 and those of the thermal parameters in Table 5. Estimated standard deviations of the positional parameters were calculated from the equation

$$\sigma(x_r) = \sqrt{\frac{\sum w(F_o-F_c)^2}{(u-v)\ D}\ B_r}$$

given, among others, by Cruickshank.(11) Here x_r is the $r^{\underline{th}}$ parameter, u is the number of reflections entering into the summation, v is the number of parameters included in the least-squares process, D is the determinant of the coefficients of the least-squares normal equations, and B_r is the $r^{\underline{th}}$ principal minor of this determinant. The summation includes all observed reflections. The results of this calculation are listed in Table 6.

Discussion of the Structure

Intramolecular distances and angles are given in Figures 6 and 7 and in Table 7. Estimates of their standard

TABLE 4

Final Positional Parameters of Cyclohex-1-enylcyclobutenedione

Atom Code Number	x	y	z
C_1	0.37430	0.41958	-0.34928
C_2	0.30873	0.55178	-0.41472
C_3	0.40730	0.68488	-0.37170
C_4	0.43659	0.68903	-0.24272
C_5	0.53234	0.56181	-0.19372
C_6	0.46661	0.42159	-0.25068
C_7	0.52412	0.28669	-0.19463
C_8	0.62458	0.25142	-0.09580
C_9	0.61136	0.09616	-0.11285
C_{10}	0.49164	0.13525	-0.22774
O_1	0.41061	0.07038	-0.30641
O_2	0.66097	-0.01105	-0.06545

TABLE 5

Final Thermal Parameters of Cyclohex-1-enylcyclobutenedione, for Temperature Factors of the Form $\exp -(\alpha h^2+\beta k^2+\gamma l^2+\delta hk+\epsilon hl+\eta kl)$

Atom Code Number	$10\cdot\alpha$	$10\cdot\beta$	$10\cdot\gamma$	$10\cdot\delta$	$10\cdot\epsilon$	$10\cdot\eta$
C_1	+0.1622	+0.1120	+0.0785	-0.0208	-0.0092	+0.0015
C_2	+0.2611	+0.1720	+0.1176	-0.0199	-0.0036	+0.0041
C_3	+0.2307	+0.1221	+0.0873	-0.0023	+0.0173	+0.0043
C_4	+0.2019	+0.1360	+0.0984	-0.0260	-0.0097	+0.0042
C_5	+0.1830	+0.1181	+0.0842	-0.0117	+0.0023	-0.0002
C_6	+0.1588	+0.1166	+0.0799	-0.0218	+0.0042	-0.0018
C_7	+0.1804	+0.1324	+0.0886	-0.0272	+0.0012	-0.0017
C_8	+0.1895	+0.1475	+0.0979	-0.0176	-0.0021	-0.0023
C_9	+0.1947	+0.1371	+0.0930	-0.0205	-0.0043	+0.0016
C_{10}	+0.1918	+0.1392	+0.0960	-0.0241	-0.0098	+0.0054
O_1	+0.2236	+0.1483	+0.1059	-0.0064	+0.0073	-0.0025
O_2	+0.2145	+0.1395	+0.0983	-0.0202	-0.0149	+0.0074

TABLE 6

Estimated Standard Deviations of the Positional Parameters in Fractions of a Unit Cell Edge

Atom Code Number	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C_1	0.00522	0.00330	0.00332
C_2	0.00700	0.00471	0.00365
C_3	0.00856	0.00434	0.00428
C_4	0.00601	0.00425	0.00414
C_5	0.00642	0.00406	0.00348
C_6	0.00465	0.00330	0.00302
C_7	0.00459	0.00392	0.00274
C_8	0.00472	0.00330	0.00296
C_9	0.00572	0.00361	0.00338
C_{10}	0.00462	0.00414	0.00341
O_1	0.00442	0.00296	0.00256
O_2	0.00444	0.00296	0.00230

TABLE 7

Intramolecular Distances and Angles, Their Estimated Standard Deviations, and Their Estimated Uncertainties at a Confidence Level of 99%.

Bond	Distance (in Å)	(in Å)	Uncertainty (in Å)
C_1- C_2	1.507	0.009	0.023
C_2- C_3	1.541	0.013	0.034
C_3- C_4	1.477	0.018	0.046
C_4- C_5	1.501	0.016	0.041
C_5- C_6	1.533	0.014	0.036
C_6- C_1	1.299	0.012	0.071
C_6- C_7	1.466	0.012	0.031
C_7- C_8	1.376	0.012	0.031
C_8- C_9	1.459	0.012	0.031
C_9-C_{10}	1.608	0.014	0.036
C_{10}-C_7	1.476	0.014	0.036
C_{10}-O_1	1.227	0.012	0.031
C_9- O_2	1.188	0.012	0.031

Angle	Value (in degrees)	(in degrees)	Uncertainty (in degrees)
C_1-C_2-C_3	110.08	0.71	1.8
C_2-C_3-C_4	111.62	0.63	1.6
C_3-C_4-C_5	112.34	0.66	1.7
C_4-C_5-C_6	111.07	0.53	1.4
C_5-C_5-C_1	122.35	0.50	1.3
C_6-C_1-C_2	124.90	0.54	1.4
C_5-C_6-C_7	120.36	0.47	1.2
C_6-C_7-C_8	131.34	0.42	1.1
C_7-C_8-C_9	95.42	0.29	0.75
C_8-C_9-C_{10}	85.29	0.38	1.0
C_9-C_{10}-C_7	85.63	0.37	1.0
C_{10}-C_7-C_8	93.65	0.33	0.85
C_{10}-C_9-O_2	136.06	0.39	1.0
C_7-C_{10}-O_1	136.88	0.41	1.1

deviations and of their uncertainties at a level of 99% confidence also are listed in Table 7. A comparison of the bond distances with those in other compounds containing similar functional groups is given in Table 8. The discussion which follows is based on uncertainties estimated at a level of 99% confidence.

The conformation and dimensions of the six-membered ring are in general agreement with those of similar rings in 3, 4, 5, 6-tetrachlorocyclohexene,(12) 2, 3, 4, 5, 6-pentachlorocyclohexene,(13) ionylidene crotonic acid,(14) and β-carotene.(15) Within the error of measurement, all of the "single bonds" of the six-membered ring are of the same length. Their average length is 1.511Å, with an estimated standard deviation of 0.012Å. The uncertainty of this average distance at a level of 99% confidence is 0.046Å. C_1, C_2, C_5, and C_6 are nearly coplaner. A plane was fitted by least-squares to these four atoms; in terms of fractional coordinates referred to the direct crystal axes its equation is

$$6.6835\,x + 0.1616\,y - 6.8558z = 4.9860.$$

The constant on the right-hand side of this equation is the distance in Angstrom units from the origin of the unit cell to the plane. The distances of all of the atoms of the six-membered ring from this plane are listed in Table 9. C_3 and C_4 are on opposite sides of the above plane.

TABLE 8

A Comparison of the Bond Lengths (in Å) of Cyclohex-1-enylcyclobutenedione with Corresponding Distances in Compounds Having Similar Functional Groups

The methods used (x-ray diffraction or electron diffraction) in determining the structure are also given.

BOND	A XRD	B XRD	C ED	D ED	E XRD	F ED	G XRD	H XRD
C_1-C_2	1.507	1.42			1.501	1.54	1.46	1.500
C_2-C_3	1.540	1.39			1.520	1.54	1.51	1.502
C_3-C_4	1.477	1.39			1.496	1.54 *	1.49	1.493
C_4-C_5	1.501	1.39			1.533	1.54	1.48	1.537
C_5-C_6	1.533	1.37			1.545	1.54	1.48	1.564
C_6-C_1	1.299	1.37			1.340	1.35	1.22	1.327
C_6-C_7	1.466	1.46			1.477			
C_7-C_8	1.376	1.37	1.33	1.34				
C_8-C_9	1.459	1.52	1.54	1.54				
C_9-C_{10}	1.608	1.56	1.54 *	1.54 *				
C_7-C_{10}	1.476	1.53	1.54	1.54				
C_9-O_2	1.188	1.21						
$C_{10}-O_1$	1.227	1.17						

The above letters refer to the following compounds: A, cyclohex-1-enylcyclobutenedione; B, phenylcyclobutenedione;(2) C, cyclobutene;(16) D, 1-methylcyclobutene;(17) E, β-carotene;(15) F, 3,4,5,6-tetrachlorocyclohexene;(12) G, 2,3,4,5,6-pentachlorocyclohexene;(13) H, ionylidene crotonic acid.(14)

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* Assumed equal.

TABLE 9

The Distance in Å of Each Atom of the Six-membered Ring from $6.6835x + 0.1616y - 6.8558z = 4.9860$, The Least-squares Plane of Atoms C_2, C_1, C_6, and C_5

Atom Code Number	Distance from plane (in Å)
C_1	-0.022
C_2	+0.010
C_3	-0.395
C_4	+0.293
C_5	-0.009
C_6	+0.022

TABLE 10

The Distance in Å of Each Atom of the Four-membered Ring and of the Two Oxygen Atoms from $7.0275x + 0.1701y - 6.9854z = 5.0968$, the Least-squares Plane of Atoms C_7, C_8, C_9, and C_{10}

Atom Code Number	Distance from plane (in Å)
C_7	-0.005
C_8	+0.005
C_9	-0.004
C_{10}	+0.004
O_1	+0.002
O_2	+0.000

Whereas the bonding within the six-membered ring is in accord with the results of other investigators, that within the small ring is somewhat unusual. The length of the double bond (1.376Å) of the small ring compares well with that of the double bonds in cyclobutene(16) (1.33Å), in 1-methylcyclobutene(17) (1.34Å) and in phenylcyclobutenedione(2) (1.37Å). In addition, the carbonyl bonds are of about the same length (1.188Å and 1.227Å) as those usually found(18) in aldehydes and ketones (1.23Å) and are in agreement with the distances found in phenylcyclobutenedione (1.17Å and 1.21Å). In contrast, the C_7-C_{10} (1.476Å) and especially the C_8-C_9 (1.459Å) distances differ significantly from corresponding distances in cyclobutene (1.54Å), in 1-methylcyclobutene (1.54Å) and seemingly also in phenylcyclobutenedione (1.52Å, 1.53Å), although this is a difficult matter to decide for the latter compound since no limits of error are given. Furthermore, the C_9-C_{10} distance (1.608Å), strikingly longer than normal, seems to represent a continuation of the trend initiated in the phenyl derivative toward a weakening of this bond. This result is in accord with purely chemical evidence(19). For example, when heated with methanol at 50°, cyclohexenylcyclobutenedione apparently undergoes pyrolytic cleavage at this site with the subsequent addition of two moles of methanol to form a methyl diester. Moreover, on standing in air at room temperature the compound adds oxygen(4), perhaps at this site. In these respects it is considerably more reactive than the phenyl derivative.

The atoms of the four-membered ring and the two oxygen atoms are coplanar within the error of measurement. The least-squares plane of these atoms with all atoms weighted equally is

$$7.0275x + 0.17009y - 6.9854z = 5.0968.$$

The distances of the six atoms from this plane are listed in Table 10. The plane is twisted about the C_6-C_7 bond by about 2°20' with respect to the plane of atoms C_2, C_1, C_6, and C_5; the two planes are significantly non-parallel.

The molecular packing is shown in Figure 8, a projection of the structure down $\underset{\sim}{a}$. The molecules are packed practically parallel to each other throughout the structure and lie roughly parallel to the $(10\bar{1})$ plane. Each molecule is surrounded by twelve neighbors whose closest contacts with the reference molecule correspond to van der Waals distances which, although not abnormal, are slightly longer than those in phenylcyclobutenedione(2). Table 11 is a list of these closest van der Waals contacts. That the forces of intermolecular attraction are less for cyclohexenylcyclobutenedione than for phenylcyclobutenedione could have been anticipated from the facts(1) that the crystal density of the phenyl compound is greater than that of the cyclohexenyl compound, and that the melting point (119°-120°) of the phenyl derivative is considerably higher than that (77°-78°) of the cyclohexenyl derivative. In view of the rather uniform distribution of

TABLE 11

Closest Intermolecular Distances (in Å)

C_1 ... C	3.639
C_1 ... C	3.665
C_2 ... C	3.824
C_3 ... O	3.661
C_4 ... O	3.622
C_4 ... O	3.622
C_5 ... O	3.587
C_5 ... O	3.730
C_6 ... C	3.497
C_6 ... O	3.579
C_7 ... C	3.636
C_8 ... C	3.636
C_8 ... C	3.698
C_8 ... O	3.933
C_9 ... C	3.497
C_9 ... C	3.665
C_{10} ... C	3.698
C_{10} ... C	3.639
O_1 ... C	3.622
O_1 ... C	3.661
O_2 ... C	3.579
O_2 ... C	3.587
O_2 ... C	3.622

van der Waals contacts around each molecule, the absence of preferred cleavage is not surprising.

Positions of the hydrogen atoms, computed in accordance with the assumptions mentioned previously (page 16) but using the completely-refined positional parameters, are listed in Table 12.

Thermal Motion

The temperature-factor parameters listed in Table 5 were transformed by the method of Rollett and Davies$^{(20)}$ into parameters describing the principal axes of the ellipsoid of vibration of each atom. The magnitudes of these principal axes and their direction cosines relative to the reciprocal axes of the unit cell are listed in Table 13.

It seems somewhat uncertain how much reliance can be placed in these results. In the first place, the unusually large thermal motions exhibited by these molecules in the crystalline state at room temperature have limited the amount of diffraction data available; moreover, the quality of the data is not all that it might be. In addition, systematic errors in the intensities due to extinction or to absorption would be expected to affect the temperature parameters quite strongly. For these reasons, the thermal motion is discussed only qualitatively. To the extent that they are valid, however, the thermal motions which emerge from this investigation present a rather interesting situation.

TABLE 12

Calculated Positions of the Hydrogen Atoms

The following assumptions were made: (i) the C-H bond length is 0.9Å; (ii) methylene hydrogens are tetrahedrally bonded; and (iii) the C-H bond direction of a methyne group bisects the angle which the methyne carbon atom makes with the two adjacent carbon atoms.

Atom Code Number	Attached To Atom Number	x	y	z
H_1	C_1	0.356	0.324	-0.374
H_2	C_2	0.288	0.540	-0.507
H_3	C_2	0.219	0.560	-0.418
H_4	C_3	0.362	0.678	-0.418
H_5	C_3	0.500	0.777	-0.394
H_6	C_4	0.478	0.780	-0.223
H_7	C_4	0.347	0.683	-0.196
H_8	C_5	0.625	0.683	-0.196
H_9	C_5	0.563	0.569	-0.221
H_{10}	C_8	0.688	0.309	-0.040

TABLE 13

Magnitudes and Direction Cosines with Respect to the Reciprocal Axes of the Principal Directions of the Thermal Ellipsoids

Atom Code Number	Principal Axis i	B_i ($\mathring{A}^2$)	g_i^1	g_i^2	g_i^3
C_1	1	2.975	+0.100	+0.941	+0.332
	2	4.605	+0.131	+0.309	-0.923
	3	5.950	+0.986	-0.136	+0.013
C_2	1	4.752	+0.057	+0.955	+0.295
	2	6.887	+0.092	+0.379	-0.906
	3	9.530	+0.992	-0.086	+0.193
C_3	1	3.219	+0.000	+0.933	+0.357
	2	5.208	+0.034	+0.359	-0.924
	3	8.392	+1.000	-0.012	+0.138
C_4	1	3.628	+0.096	+0.948	+0.310
	2	5.741	+0.142	+0.258	-0.835
	3	7.415	+0.983	-0.138	+0.226
C_5	1	3.161	+0.049	+0.945	+0.328
	2	4.954	+0.044	+0.322	-0.936
	3	6.664	+0.999	+0.061	+0.132
C_6	1	3.131	+0.118	+0.889	+0.276
	2	4.626	+0.095	+0.317	-0.928
	3	5.850	+0.895	-0.199	+0.493
C_7	1	3.495	+0.132	+0.929	+0.359
	2	5.214	+0.114	+0.333	-0.919
	3	6.632	+0.950	-0.163	+0.165
C_8	1	3.955	+0.093	+0.934	+0.353
	2	5.744	+0.292	+0.264	-0.870
	3	6.920	+0.992	-0.110	+0.136
C_9	1	3.652	+0.083	+0.935	+0.351
	2	5.472	+0.110	+0.335	-0.919
	3	7.121	+0.991	-0.116	+0.180

TABLE 13 (cont.)

Atom Code Number	Principal Axis i	$B_i(\mathring{A}^2)$	g_i^1	g_i^2	g_i^3
C_{10}	1	3.715	+0.096	+0.942	+0.330
	2	5.590	+0.194	+0.300	-0.908
	3	7.059	+0.970	-0.128	+0.310
O_1	1	3.997	+0.027	+0.948	+0.318
	2	6.215	-0.006	+0.317	-0.944
	3	8.133	+0.995	-0.024	+0.092
O_2	1	3.707	+0.092	+0.913	+0.386
	2	5.780	+0.145	+0.326	-0.913
	3	7.855	+0.988	-0.103	+0.220

Atoms C_3 and C_4 might reasonably be expected to undergo greater thermal motion than the other carbon atoms. Actually, C_2 is vibrating with a larger amplitude than any other atom of the molecule, oxygen atoms included. The relative amplitude of atom C_3 seems reasonable; that of C_4, however, is only slightly higher than the average amplitudes of the remaining atoms. No librations or set of coupled librations can explain this anomaly. The vibrational amplitudes of the oxygen atoms are larger than those of the skeletal carbon atoms, as is to be expected.

The principal axes of all of the thermal ellipsoids are roughly parallel, the largest vibrations being nearly along $\underset{\sim}{a}$, the next largest nearly along $\underset{\sim}{c}$, and the smallest vibrations being roughly parallel to $\underset{\sim}{b}$ (see Table 13). Thus, superimposed on the internal vibrations of the molecule is a fairly large vibration of the center of mass of the molecule. Similar results have been obtained(21) for other van der Waals crystals, for example, di-para-xylylene, sym-trichlorobenezene, napthlene, anthracene, et al.

PART II

THE CRYSTAL STRUCTURE OF 3,6-DIMETHYLPIPERAZINE-2,5-DIONE

Introduction

For the past several years, considerable effort has been expended in these Laboratories toward the elucidation of the crystal and molecular structures of compounds of biological interest, especially those related in some way to the proteins. As a consequence, the molecular structures of most of the naturally-occurring amino acids are now known in detail. In addition, the structures of some di- and tri-peptides have been determined as have those of several derivatives and complexes of amino acids.(22)

Relatively little work has yet been done, however, on the effect of cyclization on the stereochemistry of such compounds. In fact, the only compound containing cyclic condensed amino acids having a known structure is piperazine-2,5-dione (diglycine anhydride) whose structure was determined over twenty years ago(23) and has just been refined(24) in these Laboratories. In view of the importance of such cyclic peptides as bacitracin and the vasopressins, it seemed worthwhile to investigate the structure of the next homomer of the series, 3,6-dimethylpiperazine-2,5-dione, (see Figure 9).

Experimental

The material used for this investigation was obtained from the H. M. Chemical Company, Ltd., of Santa Monica, California. Marketed under the label DL-alanine anhydride, C.P. grade, it was used without further purification.

Crystallization of the anhydride was attempted from a variety of both pure and mixed organic solvents including acetone; methyl, ethyl, and isopropyl alcohols; diethyl ether; and dioxane. In addition, many attempts were made to crystallize the substance from aqueous solutions under varying conditions of temperature and pH, and from solutions containing traces of a large-molecule dye such as methylene blue. Invariably the same crystalline habit resulted: long, pliable hairs occasionally thick enough to be called needles, growing usually as a dense clump emanating from a single point, but sometimes as single crystals. The only procedure which ever produced crystals really suitable for diffraction work proved to be slow evaporation from aqueous solution at 70°C. By this means, needles could be grown as large as 0.2-0.3 mm in cross-section, and a few millimeters in length; invariably, however, the crystals were twinned. All attempts to cleave, cut, grind or dissolve these crystals resulted only in the dissociation of the macro-crystal into a number of microscopic hairs. For this reason, no intensity data were ever gathered about any but the needle axis. This rational crystallographic direction was arbitrarily chosen as the c axis of the unit cell.

At room temperature, thermal agitation is so high that even exposures of 400 ma-hr using single crystals of dialanine anhydride and CrKα radiation in a helium atmosphere failed to yield diffraction maxima in the back-reflection region. Accordingly, a set of unit-cell parameters was obtained from Weissenberg and rotation photographs. The resulting parameters are:

$$\begin{aligned} a &= 4.63\ \text{Å} \\ b &= 8.04\ \text{Å} \\ c &= 6.13\ \text{Å} \\ \alpha &= 106^\circ 58' \\ \beta &= 125^\circ 35' \\ \gamma &= 77^\circ 30' \end{aligned}$$

No systematic extinctions occur; therefore, the structure is based on a triclinic lattice. The density of the anhydride, measured by flotation, is $1.31 \frac{gm}{cm^3}$; that calculated on the basis of one molecule of $C_6H_8N_2O_2$ per unit cell is $1.25 \frac{gm}{cm^3}$.

Since there was no good way, at the outset of the investigation, to place all of the data on the same relative scale, no statistical tests for centrosymmetry could be applied. Upon casual inspection of the data, however, a centrosymmetrical structure appeared much the more probable. In addition, it seemed likely that the molecule possessed at least an approximate center of symmetry. Consequently, it seemed reasonable to assume tentatively that the space group is $P\bar{1}$.

Collection of the Intensity Data

Weissenberg equi-inclination photographs were taken through the third layer about $\underset{\sim}{c}$, the needle axis, using a pack of three films and CuKα radiation. The crystals used for making these photographs were twinned in such a way that all of the maxima (rather than only half of the maxima, as is usually the case) having a common $|\ell|$ were recorded on the same film. The results were an apparent doubling of the Weissenberg festoons (see Figure 10), and a considerable complication of the indexing of the photographs. The zero-layer photographs appear normal, one-half of the maxima being superimposed upon the other half.

In order to index the upper-layer photographs the following procedure was used:

(1) Using the unit-cell parameters given above, a list of values of sin $\Theta_{hk\ell}$ was computed for all diffraction maxima, $(hk\ell)$, within the sphere of reflection of CuKα radiation.

(2) Using measurements taken directly from each photograph, the values of sin Θ for a large number of observed maxima were calculated.

(3) By detailed comparison of the observed with the calculated values of sin Θ, key maxima and festoons of maxima could be indexed on each photograph. The rest of the maxima on the film were then indexed by inspection.

Since it seems to appear nowhere else, a derivation of the equations used in (2) above is now given.

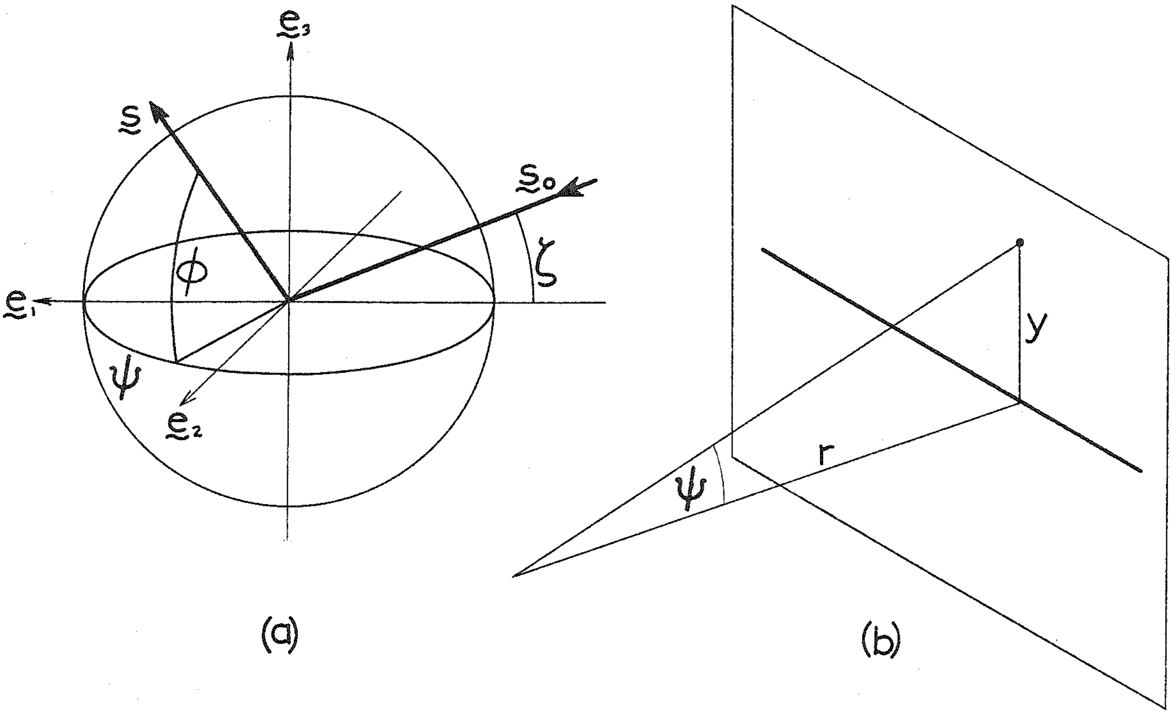

FIGURE 1

In Figure 1a above, $\underset{\sim}{s}_o$ is a beam of x-radiation incident on a crystal located at the origin of the coordinate system defined by the orthonormal vector triple: $\underset{\sim}{e}_1$, $\underset{\sim}{e}_2$, $\underset{\sim}{e}_3$; $\underset{\sim}{s}$ is a diffracted beam. Then

$$\underset{\sim}{s}_o = \underset{\sim}{e}_1 \cos\zeta - \underset{\sim}{e}_3 \sin\zeta ,$$

$$\underset{\sim}{s} = \underset{\sim}{e}_1 \cos\varphi \cos\psi + \underset{\sim}{e}_2 \cos\varphi \sin\psi + \underset{\sim}{e}_3 \sin\varphi , \text{ and}$$

$$\cos 2\theta = \underset{\sim}{s}_o \cdot \underset{\sim}{s} = \cos\varphi \cos\psi \cos\zeta - \sin\varphi \sin\zeta .$$

This equation is given incorrectly by Zachariasen.(25) In taking equi-inclination photographs, the camera is set so that $\varphi = \zeta = \mu$, the "equi-inclination angle". Then for this set-up

$$\cos 2\theta = \cos\psi \cos^2\mu - \sin^2\mu = 1 - 2\sin^2\theta,$$

$$\therefore \sin\theta = \left[1 - \tfrac{1}{2}\cos 2\mu\,(1 + \cos\psi)\right]^{\frac{1}{2}}.$$

As can be seen from Figure 1b, $\cos\psi$ can be calculated directly from r, the camera radius, and y, the distance of the diffraction maximum above the center line. The appropriate equation is

$$\cos\psi = \frac{r}{\sqrt{r^2+y^2}}.$$

The intensities were estimated by visual comparison with a calculated intensity strip. These intensities were corrected for Lorentz and polarization factors, but in view of the size and nature of the crystals, correction for absorption seemed unnecessary. Scaling of the Weissenberg photographs was complicated by the fact that the crystals used were twinned. In a few instances, two maxima having the same index, but arising from different twins were observed on the same photograph. Comparisons of such pairs of maxima indicated that twin A was 1.5-2 times larger than twin B. Because so few suitable pairs of maxima occurred, however, no accurate estimate of the relative sizes of the two twins was made. For this reason correlations among different layers, and even among maxima on the same layer arising from different layers, were, of necessity, left until later in the investigation. The uncorrelated structure factors are given in Table 18.

The Trial Structure

Since there is only one molecule per unit cell, the assumption of $P\overline{1}$ symmetry requires that the center of the molecule be placed at one of the several centers of symmetry; it was placed arbitrarily at the origin. The nature and persistence of the crystalline habit--hairs, bundles of hairs, or needles greatly elongated in the $\underset{\sim}{c}$ direction--suggest strongly that the hydrogen-bonding of the structure is along the c axis. For purposes of finding a trial structure, it was assumed that the hydrogen-bond direction and the c axis are precisely colinear.

The above placement of the center of the molecule requires that F(010) be positive. The seven other (0k0) reflections may be either positive or negative, however, so that if line Fouriers were computed using all possible sign combinations of all the (0k0) data, a total of 128 Fouriers would have to be done. Fortunately, by far the strongest of these reflections are (010), (020), (030), and (040). As a consequence, the gross features of all 128 of the above Fouriers can be displayed easily by the 8 line Fouriers computed from only the first four reflections; these one-dimensional summations are shown in Figure 11.

We seek now those Fouriers which yield reasonable projections of the molecule onto the b axis. With the center of the molecule at the origin of the unit cell, no atom can have a y parameter greater than about 0.36. This fact eliminates from further consideration Fouriers A, C, E, and G, inasmuch as all of these have peaks of electron density near $y = 0.50$.

All reasonable orientations of the molecule require that there be four atoms fairly near the origin (no farther out than 0.18) and a methyl group somewhere between about 0.18 and about 0.36. As a consequence of this fact and of the relative areas under its two peaks, Fourier D may also be ruled out.

Thus, of the eight original Fouriers, there remain only three, B, H, and F, one of which must represent roughly the projection of the molecule onto the b axis. There is little to choose among the three, but since F seems a reasonable compromise between the other two, it was selected tentatively for further study.

Keeping the signs of the first four reflections the same as for F, eight Fouriers were computed covering all sign combinations of the last three reflections; since the value of F(050) is so small, it was not included in any of these calculations. In all of these Fouriers, the peak corresponding ostensibly to the methyl group was misshapen sufficiently to eliminate these Fouriers completely from further consideration. Accordingly, the above procedure was repeated using as a basis Fourier number H. These Fouriers are shown in Figure 12.

A projection of the molecule drawn looking down c (and consequently approximately down the hydrogen-bond direction) was next considered. In this projection, one is looking at the piperazine ring edge-on. Furthermore, the projection of each atom onto a plane perpendicular to c is known. There remains only the problem of rotating this projection about c until its projection onto b is that given by Fourier L. This can be done with a two-fold ambiguity; the ambiguity is easily resolved, however, by consideration of few low-order structure factors, such as $F(\bar{1}\bar{1}0)$. The resulting projection is shown in Figure 13.

Inasmuch as the distances from the origin to the various atoms are known fairly accurately, the z-coordinate of each atom was calculated from the x- and y-coordinates derived above. The projection down c of the trial structure which resulted is shown in Figure 13; its projection onto (100) is given in Figure 14; and the coordinates of each of the five atoms are listed in Table 16.

This three-dimensional trial structure was carried through a large number of cycles of Fourier refinement of the (001) and (100) projections. Refinement of the (100) projection was complicated by the fact that since intensity data had been gathered about only one axis (c), the $0k\ell$ data were not all on the same absolute scale. Consequently, frequent empirical rescaling was necessary.

TABLE 16

The Trial Structure of 3,6-dimethylpiperazine-2,5-dione

n	x	y	z
C_1	-0.031	0.300	0.168
C_2	0.174	0.176	0.104
C_3	0.104	0.097	-0.147
N	0.068	0.053	0.229
O	0.220	0.211	-0.263

This refinement procedure failed to converge. However, a critical re-examination of the trial structure and of the evidence upon which it is based failed to reveal any defect in the structure. The crystals exhibit no detectable optical activity; thus the compound is the *meso*- isomer of dialanine anhydride, rather than a mixture of the *d*- and *l*- isomers, and the molecule certainly contains an at least approximate center of symmetry. Furthermore, the trial structure derived above involves a strong intermolecular hydrogen bonding nearly parallel to $\underset{\sim}{c}$. This fact is necessary to explain the unusually distinctive and persistent habit and cleavage of the crystals. Moreover, this orientation of the molecule is in agreement with a rough Patterson projection onto (100), calculated with the unscaled $0k\ell$ intensities. Finally, no other orientation of the molecule within the unit cell affords nearly as efficient a molecular packing. For these reasons it would seem that the present trial structure is almost certainly correct, at least in its gross features.

Fourier refinement was attempted of a large number of slight variations on the above structure. All of them failed to converge. In several instances, however, the first few cycles of refinement yielded not unreasonable shifts and then, just as convergence seemed imminent, the process would begin slowly to diverge. In view of this behavior and of the confidence placed in the trial structure, it was concluded tentatively that the refinement process probably would converge if three-dimensional refinement techniques could be used. Since such techniques require that all of the data be used simultaneously, this project was discontinued until sufficient additional information has been collected to allow all of the intensity data to be put onto a common scale.

PART III

PROGRAMS FOR THE BURROUGHS MODEL 205 COMPUTER

Introduction

In the course of the work reported above, a number of programs have been coded for the Burroughs electronic digital computer, Model 205. Those of general crystallographic interest are described briefly below.

P1, P$\bar{1}$ Structure Factors and Least-squares Program

The input to this program consists of a set of atomic positional and thermal parameters and a list of observed structure factor moduli. The output from the calculation are a list of calculated structure factors, each with its calculated phase, and a set of first-order least-squares corrections to the positional and thermal parameters. Either isotropic or anisotropic temperature factors may be used as input to the structure-factor calculation, but the least-squares corrections calculated are always anisotropic. If desired, a portion of the least-squares calculation may be suppressed so that only the positional parameters or only the thermal parameters are refined. Moreover, a first-order correction to the scale factor can be calculated.

The quantity minimized by the least-squares portion of the program is

$$\sum w(hk\ell)\Big[\,|F_o(hk\ell)|^2 - K|F_c(hk\ell)|^2\Big]^2,$$

where the subscript o means observed; c, calculated; and K is the scale factor. There is no provision for calculating the weights, $w(hk\ell)$, within the program. Weights calculated externally may be incorporated as part of the input, however. In the least-squares matrix of coefficients of the normal equations, only the diagonal terms are retained.

The program is limited to five different types of atoms and to forty atoms per asymmetric unit.

H^2 and $\sin^2\theta$ Program

A lattice vector is defined as

$$\underset{\sim}{H} \equiv h\underset{\sim}{a}^* + k\underset{\sim}{b}^* + \ell\underset{\sim}{c}^*,$$

where $\underset{\sim}{a}^*$, $\underset{\sim}{b}^*$, and $\underset{\sim}{c}^*$ are the basis vectors of the reciprocal unit cell. This program calculates $\sin^2\theta$ and H^2 for any reciprocal-lattice vector within the sphere of reflection. Input to the program consists of the six reciprocal lengths and angles, and a list of the h, k, ℓ, for which the calculation is to be performed.

The large program tape contains, in addition to the program, data words corresponding to all combinations of the indices from zero through nine. Provision has been made so that other data may be used either in addition to, or instead of, the data now on the program tape.

Printout is performed for only those reciprocal-lattice points within the sphere of reflection.

Unit-cell Parameters Program

From the definition of $\underset{\sim}{H}$ in (b) above, it follows that

$$H^2 = Ah^2 + Bk^2 + C\ell^2 + Dhk + Eh\ell + Fk\ell, \qquad (1)$$

where $A = a^{*2}$, $B = b^{*2}$, $C = c^{*2}$, $D = 2a^*b^*\cos\gamma^*$, $E = 2a^*c^*\cos\beta^*$, $F = 2b^*c^*\cos\alpha^*$.

The purpose of this program is the reduction by least-squares of a set of observations of $H^2(hk\ell)$ to the set of coefficients in equation 1. Suppression of two or of all three of the coefficients of the cross-product terms is provided for.

The program converts the set of observations to normal equations directly, then solves these equations by the Crout method. The round-off error does not exceed 3 in the sixth significant figure.

Wilson-Statistics Program

The purpose of this program is the calculation, by Wilson's statistical method, of an overall temperature factor and a scale factor for putting a set of structure-factor moduli on an approximately absolute scale. The equation used is

$$2\,\ell n K + 2B\,\overline{\frac{\sin^2\theta}{\lambda^2}} = \ell n\,\frac{\overline{f^2}}{\overline{|F_o|^2}}, \qquad (2)$$

where

$$KF_o(hk\ell) = e^{-B\frac{\sin^2\theta}{\lambda^2}} \sum_n f_n e^{2\pi i h \cdot r_n}. \qquad (3)$$

The initial output consists of a list of ten values of $\overline{\frac{\sin^2\theta}{\lambda^2}}$ from 0.05 to 0.95; N, the number of reflections in each range; and the value of $\ell n\frac{\overline{f^2}}{|F_o|^2}$ for each range. Then using these intermediate results, the program fits, by least squares, the constants in equation 2, and prints out the resulting 2 ℓnK and 2B. In the latter portion of the program the points may be weighted equally, or each point may be assigned a weight proportional to its corresponding $\frac{1}{N^2}$.

PART IV

APPENDIX

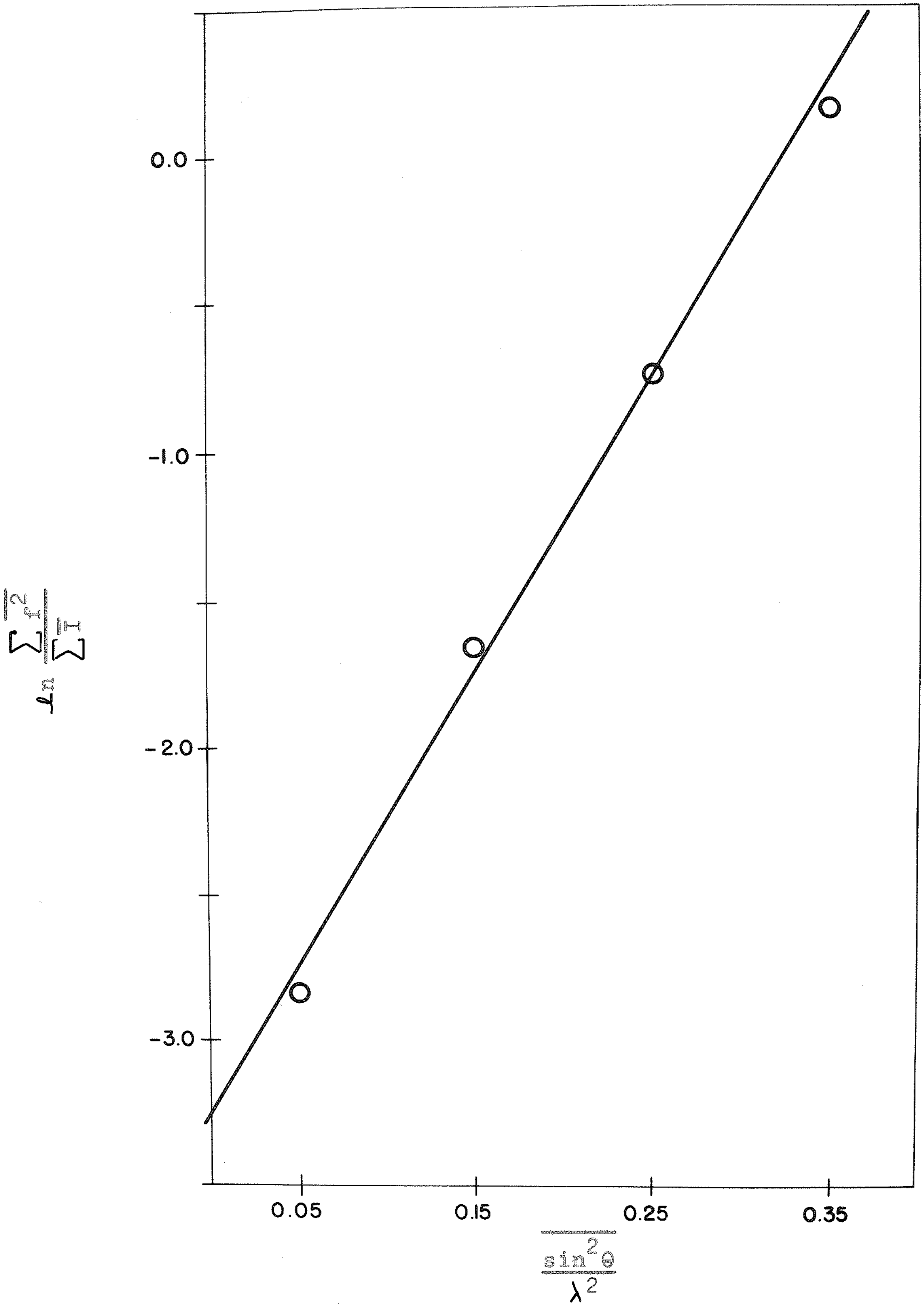

FIGURE 2

Wilson plot for cyclohex-1-enylcyclobutenedione. All observed reflections are included.

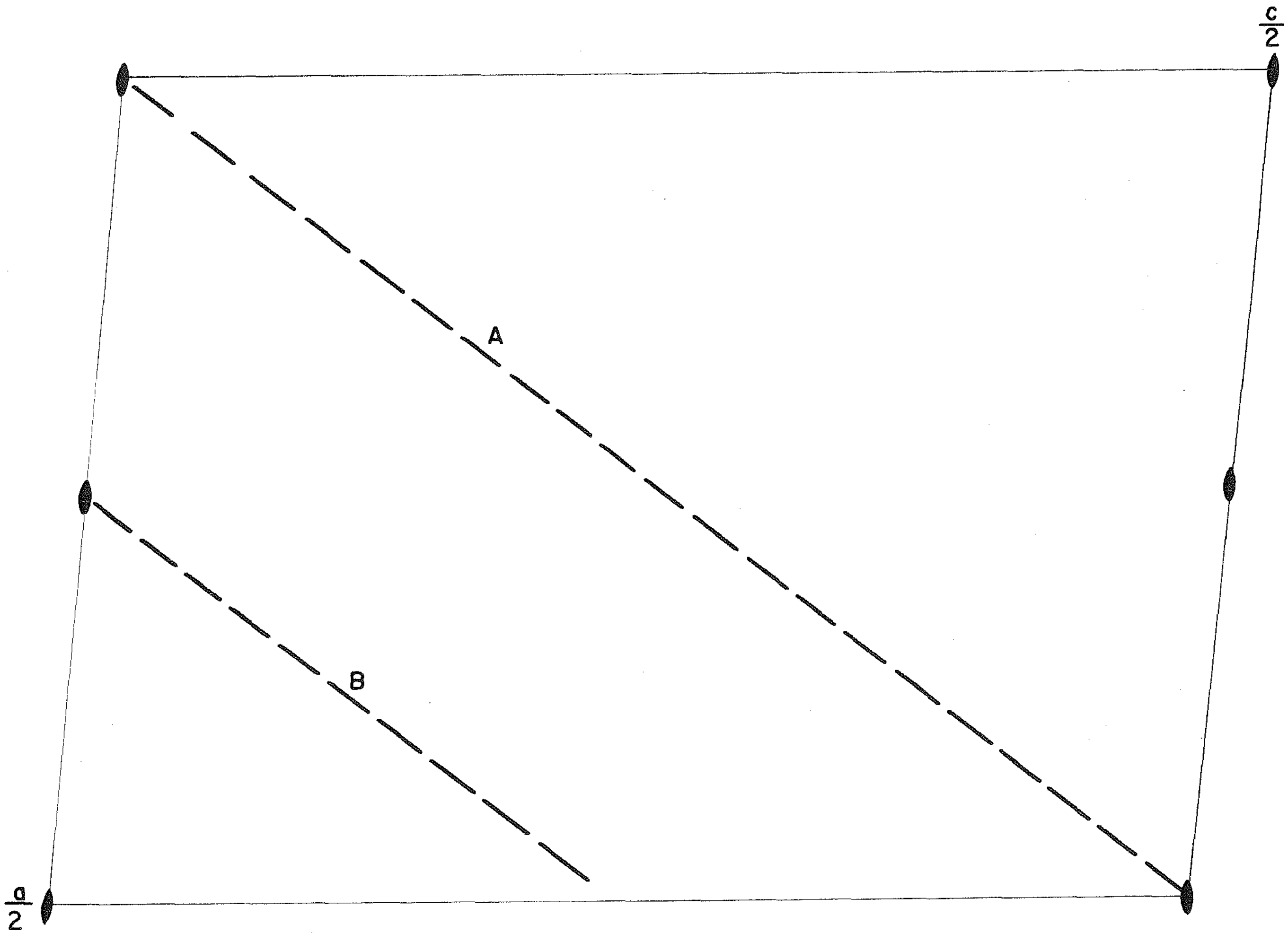

FIGURE 3

The three-dimensional Patterson map was replotted into the planes whose traces are shown here.

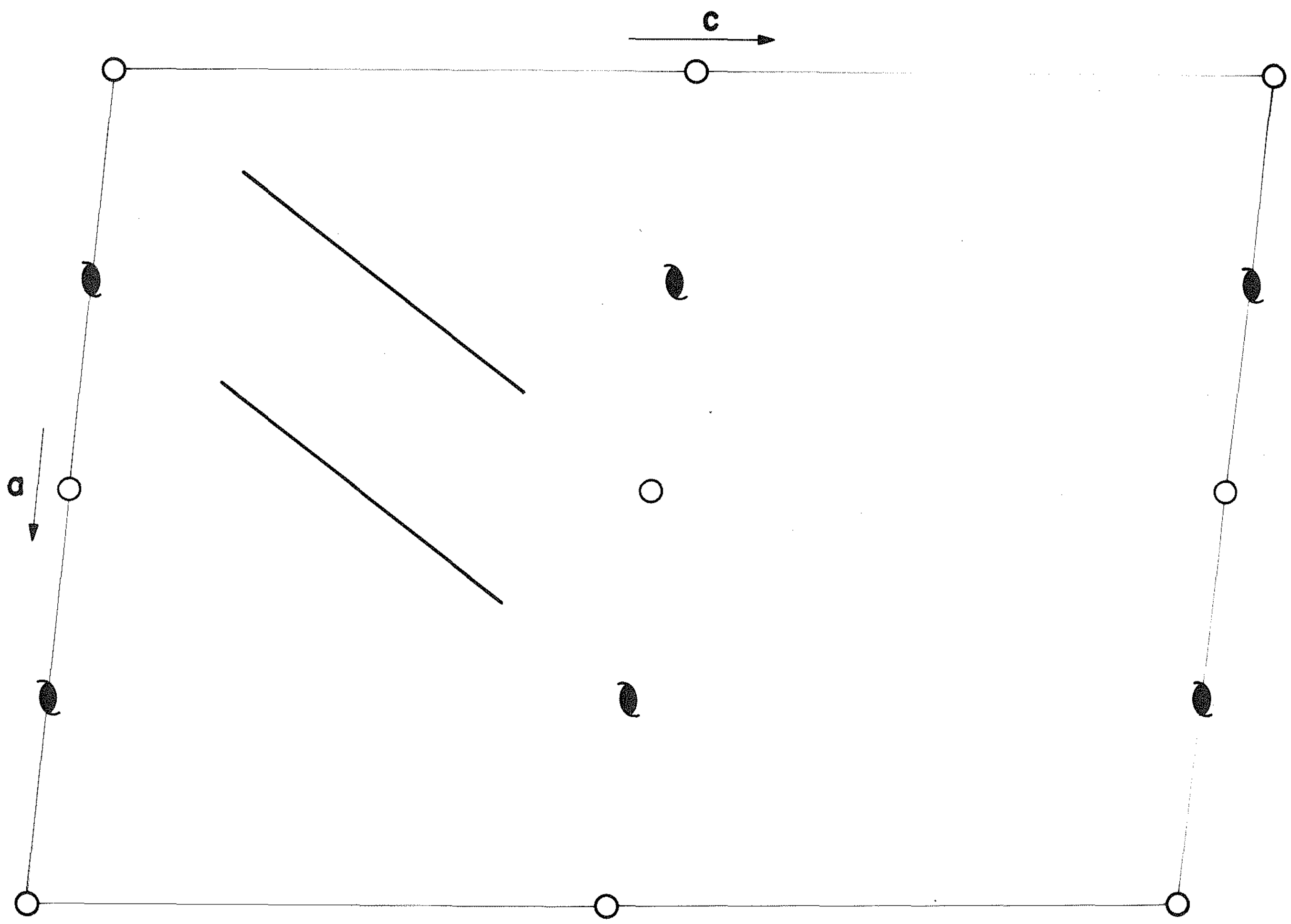

FIGURE 4

Possible positions of the molecule in projection onto (010), looking approximately down the longitudinal direction of the molecule.

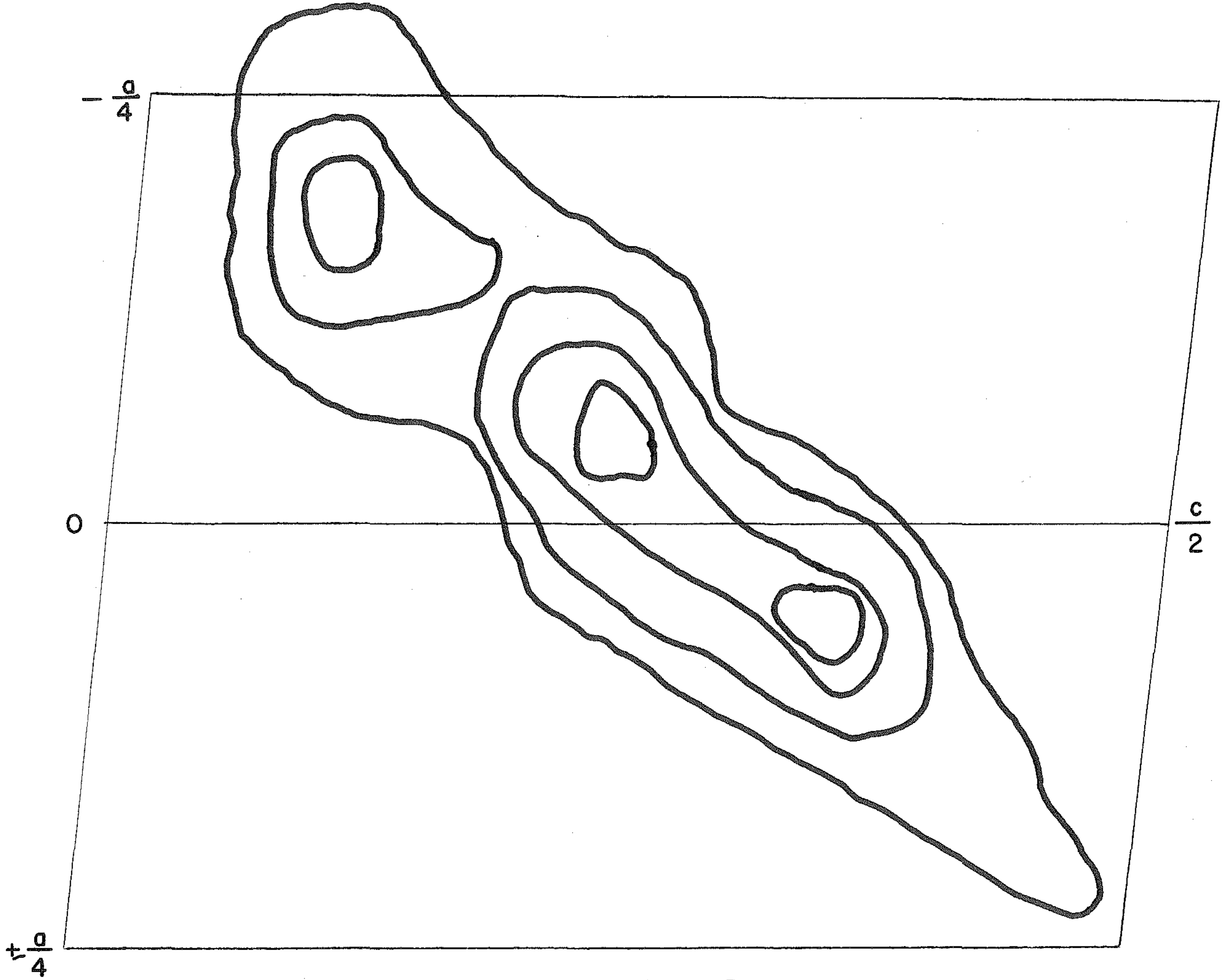

FIGURE 5

Electron density projection of cyclohex-1-enylcyclobutenedione onto (010). The contours are at arbitrary intervals.

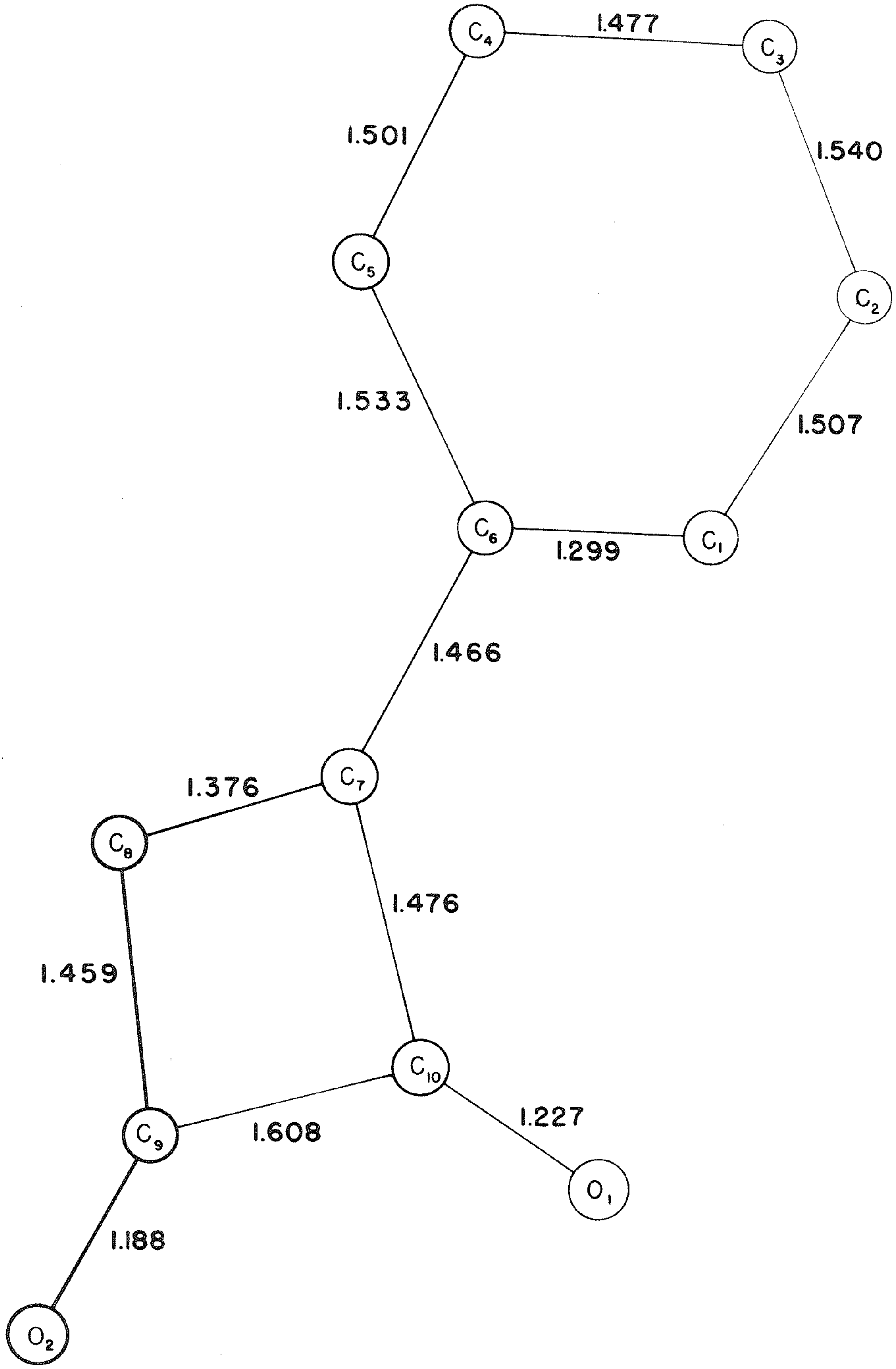

FIGURE 6

Interatomic distances within the molecule cyclohex-1-enylcyclobutenedione.

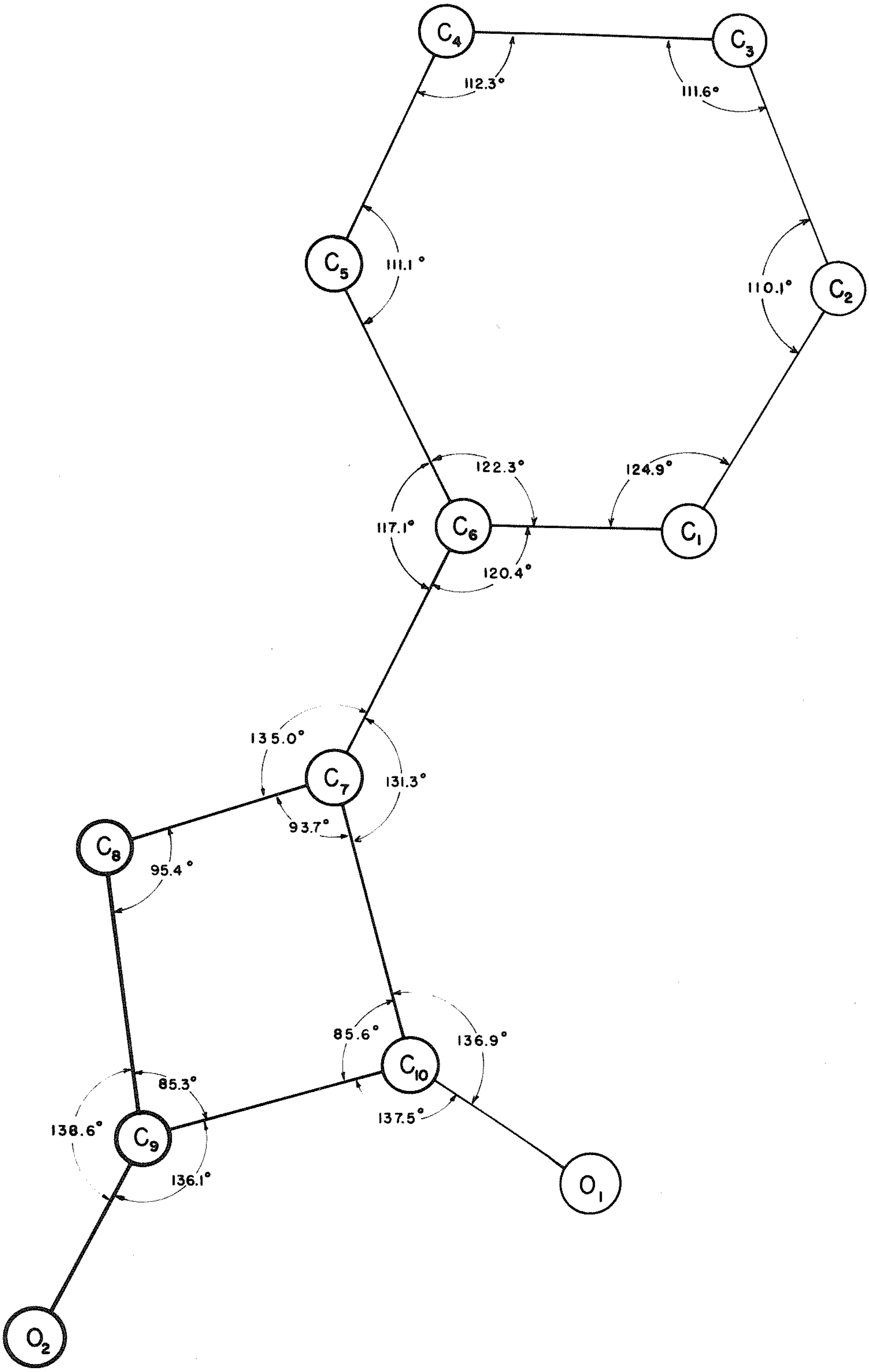

FIGURE 7

Bond angles within the cyclohex-1-enylcyclobutenedione molecule.

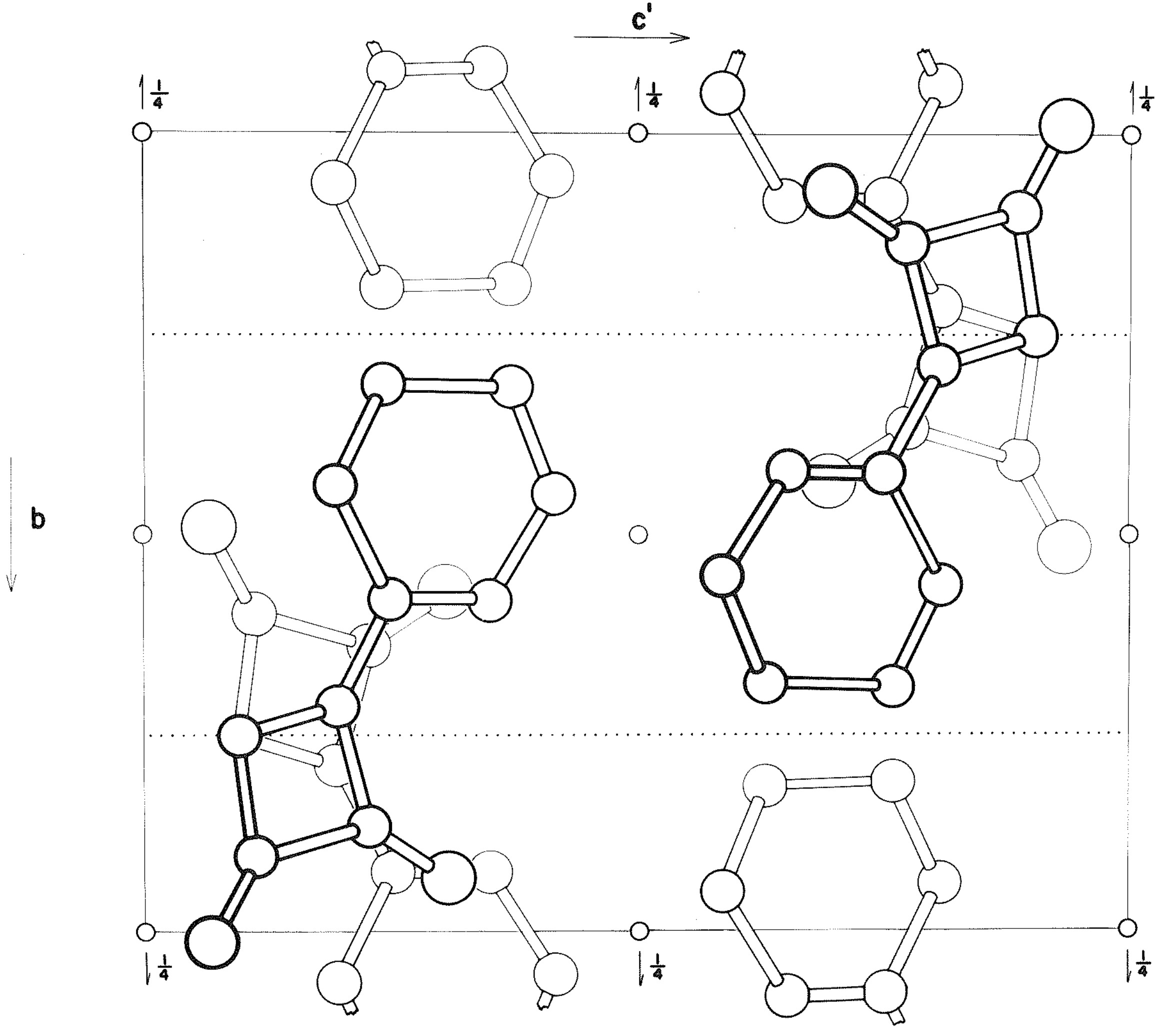

FIGURE 8

The structure of cyclohex-1-enylcyclobutenedione viewed along the a axis.

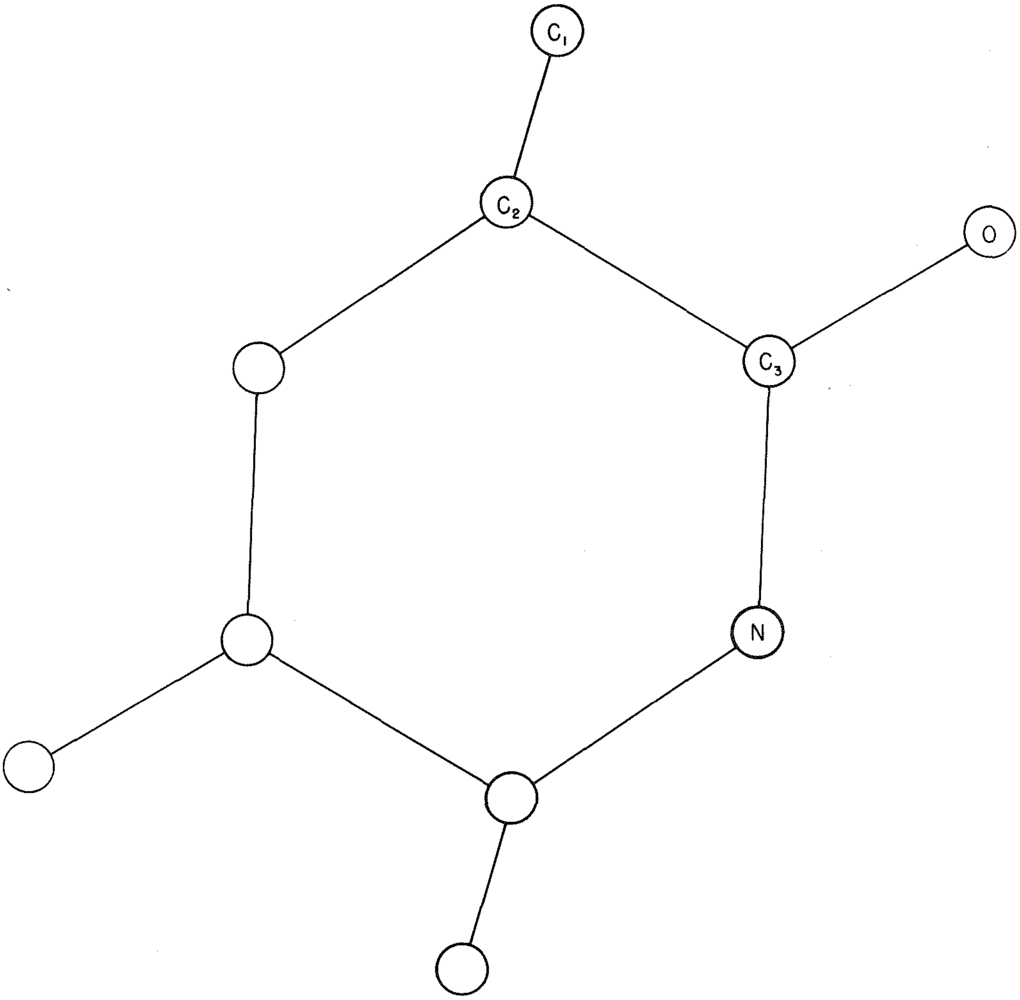

FIGURE 9

The molecule 3,6-dimethylpiperazine-2,5-dione.

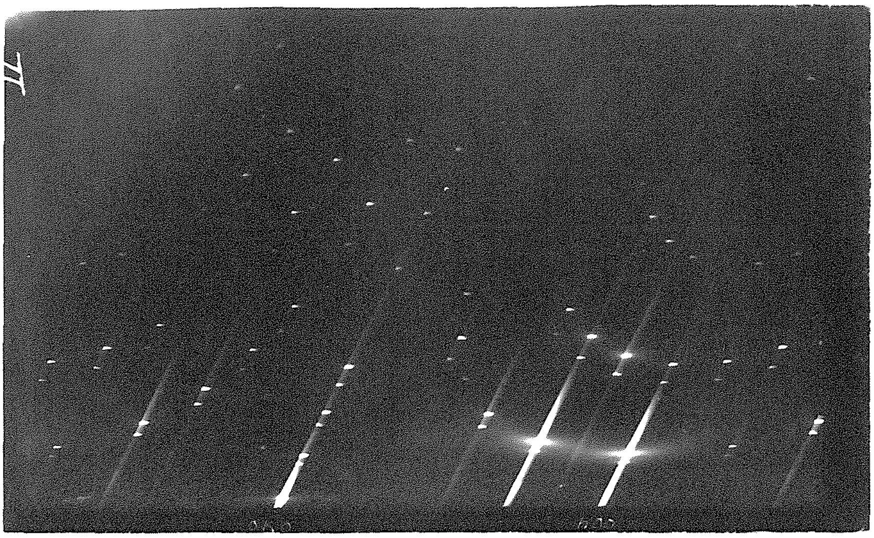

FIGURE 10a

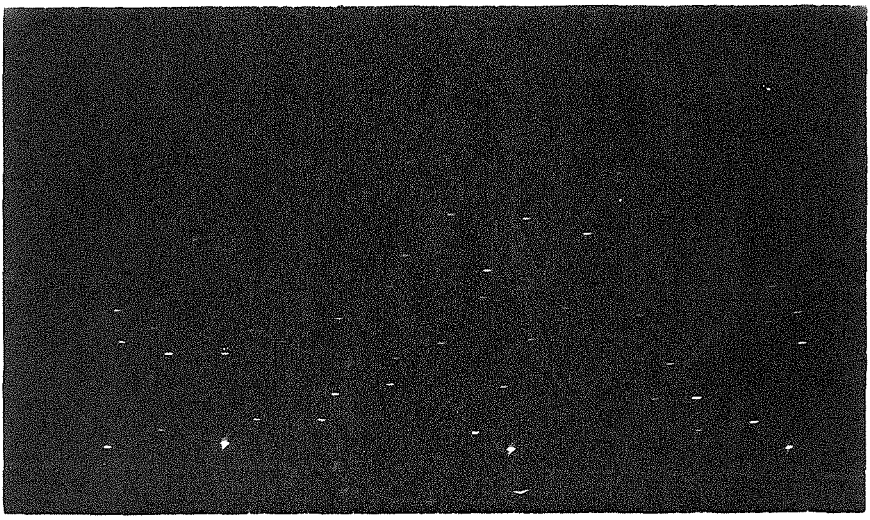

FIGURE 10b

(a) A zero-layer and (b) a first-layer Weissenberg photograph of 3,6-dimethylpiperazine-2,5-dione taken about the c axis. Doubling of the Weissenberg festoons due to twinning of the crystals can be seen in the first-layer photograph.

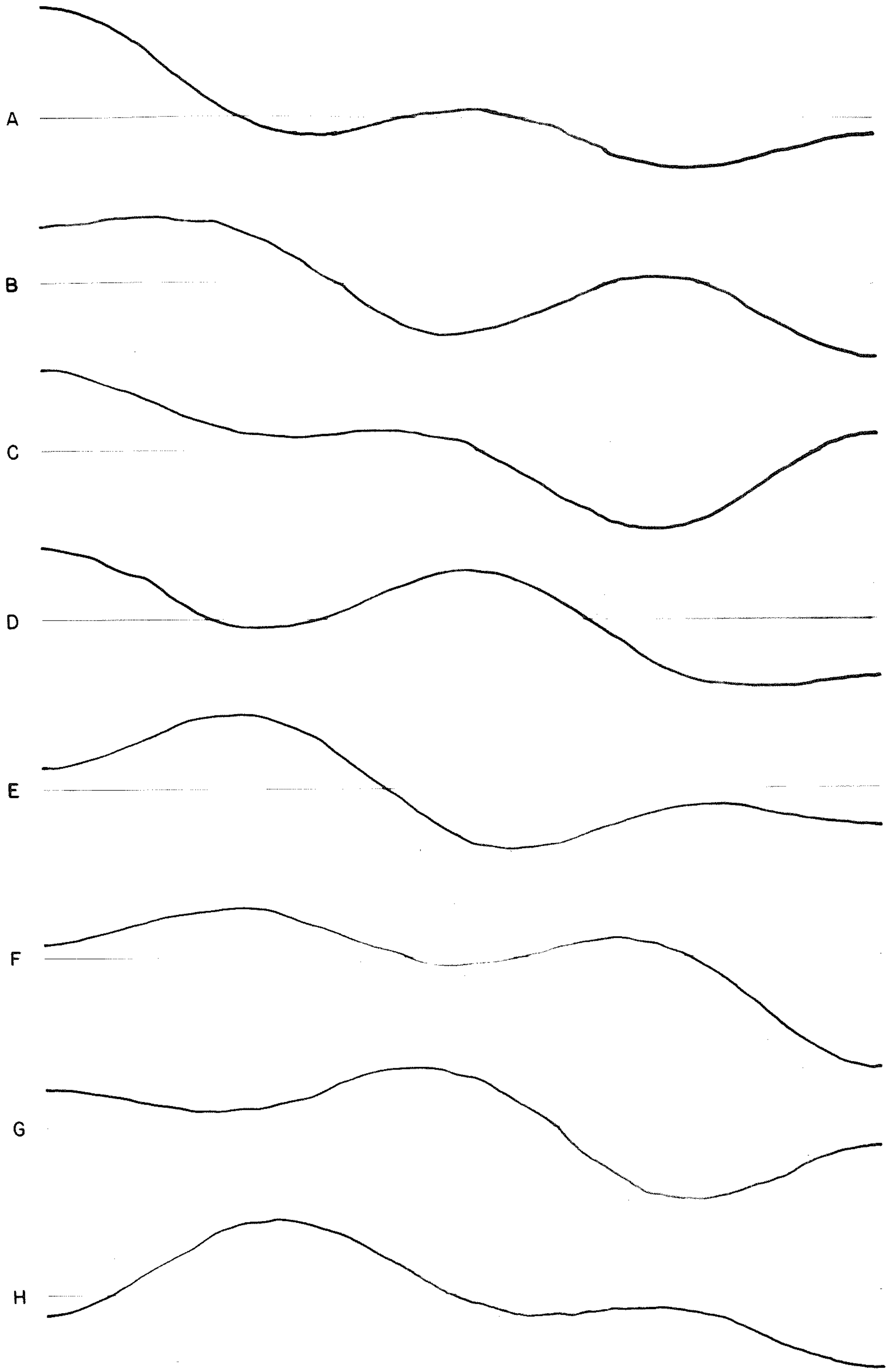

FIGURE 11

All possible line Fouriers for which F(010) is positive and F(020), F(030), and F(040) are either positive or negative. The Fouriers cover the range $y = 0$ to $y = 1/2$. See Table 14.

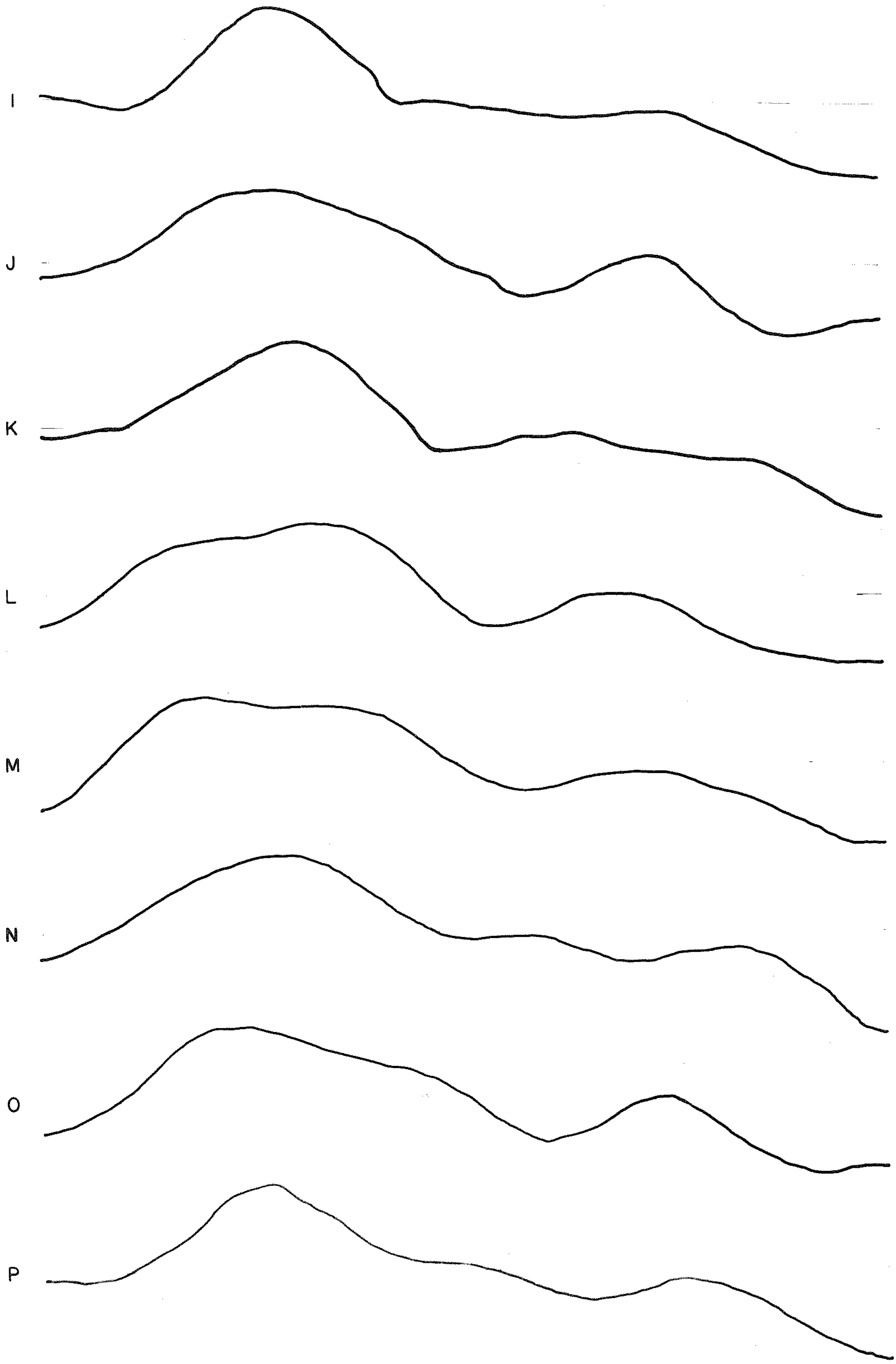

FIGURE 12

Line Fouriers from 0 to $\frac{1}{2}$b, computed from Fourier H of Figure 11 and all possible sign combinations of F(060), F(070), and F(080). See Table 15.

TABLE 14

Numerical Values and Signs of the Structure Factors Used in Calculating the Line Fouriers in Figure 11.

Index	Curve								
	A	B	C	D	E	F	G	H	F_o
010	+	+	+	+	+	+	+	+	101
020	+	+	+	-	+	-	-	-	44
030	+	+	-	+	-	+	-	-	35
040	+	-	+	+	-	-	+	-	60

TABLE 15

Numerical Values and Signs of the Structure Factors Used in Calculating the Line Fouriers in Figure 12.

Index	Curve								
	I	J	K	L	M	O	P	Q	F_o
010	+	+	+	+	+	+	+	+	101
020	-	-	-	-	-	-	-	-	44
030	-	-	-	-	-	-	-	-	35
040	-	-	-	-	-	-	-	-	60
060	+	+	+	+	-	-	-	-	14
070	+	-	+	-	-	+	-	+	22
080	+	+	-	-	-	-	+	+	15

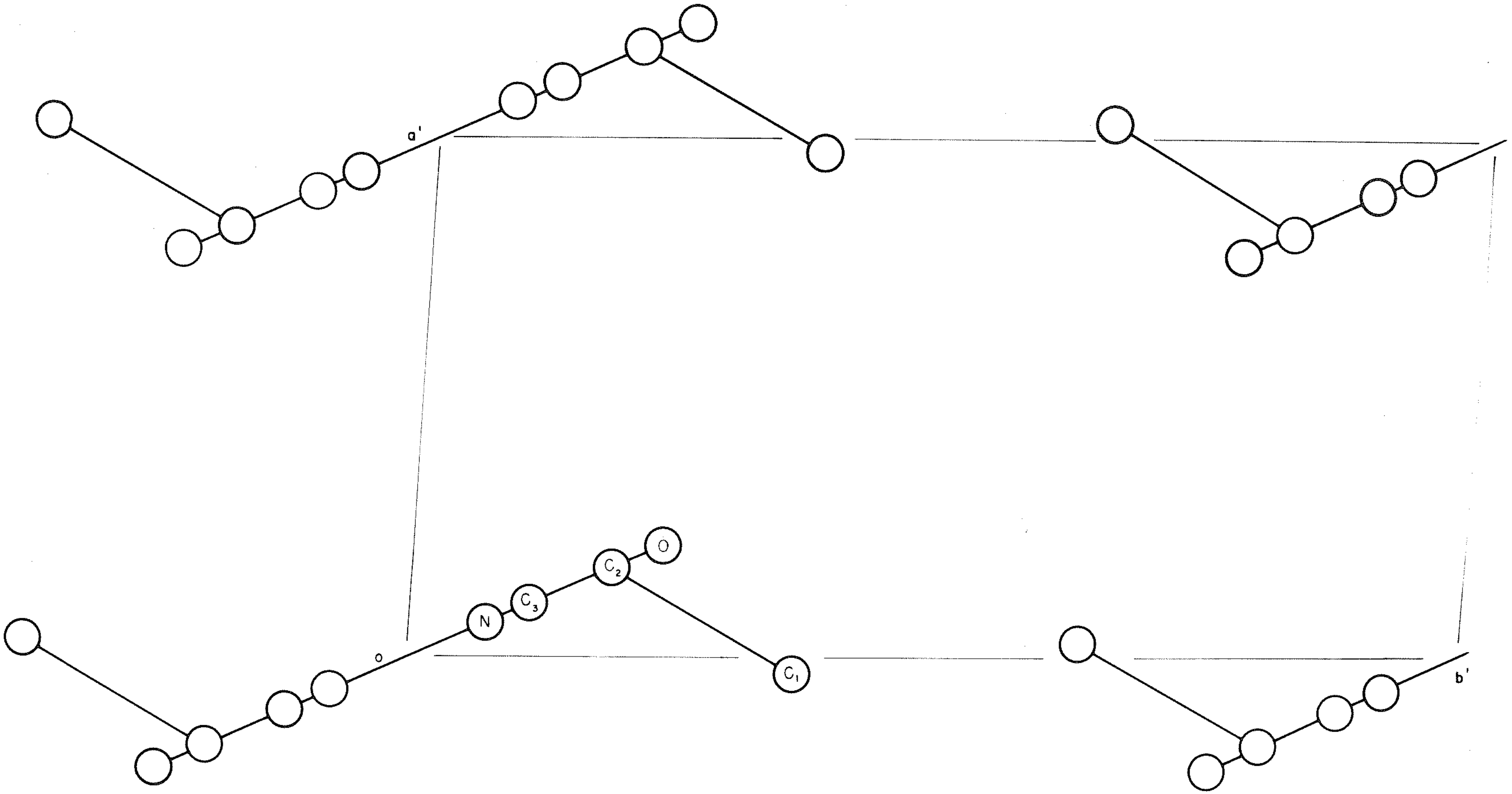

FIGURE 13

Projection of the trial structure of 3,6-dimethylpiperazine-2,5-dione down $\underset{\sim}{c}$.

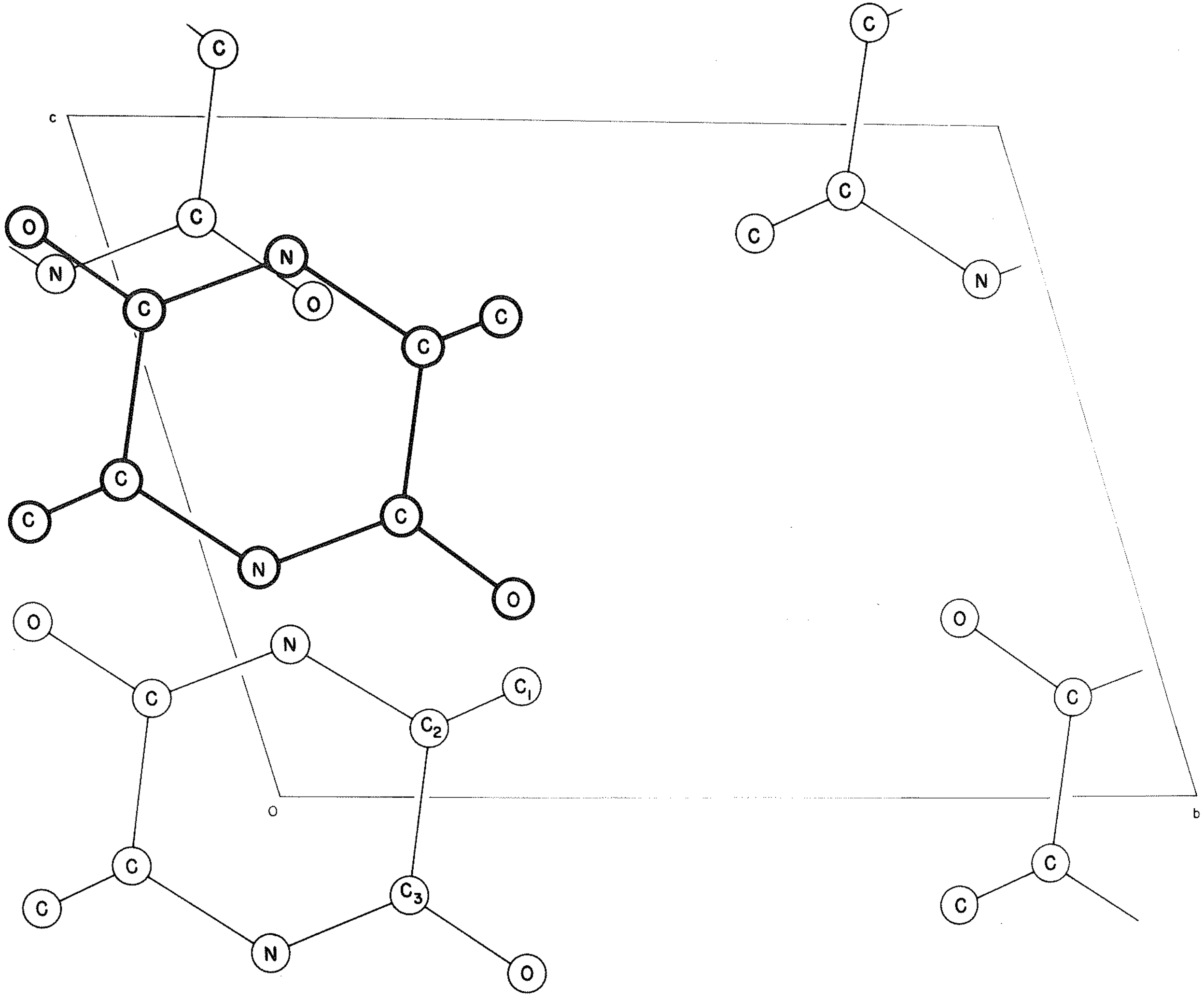

FIGURE 14

Projection of the trial structure of 3,6-dimethylpiperazine-2,5-dione onto (100).

TABLE 17

Observed and Calculated Structure Factors of Cyclohex-1-enylcyclobutenedione

The three columns in each group contain the values, reading from left to right, of k, $10F_o$, and $10F_c$. Reflections indicated by an asterisk (*) were given zero weight in the least-squares calculations

0,k,0

2	339	301
4	72	76
6	205	-182
8	129	-129
10	23	23

0,k,1

1	462*	-304
2	38	-36
3	375	-324
4	196	197
5	82	-94
6	19	25
7	194	195
8	100	116
9	17	20
10	16	13
11	18	22

0,k,2

1	570*	-439
2	139	129
3	419	373
4	274	256
5	73	76
6	133	136
7	33	35
8	114	121
9	17	-15
10	15	1
11	18	-19

0,k,3

0	43	25
1	41	33
2	192	196
3	380	294
4	27	-25
5	43	39
6	15	14
7	71	81
8	34	-34
9	17	14
10	15	16
11	11	8

0,k,4

0	139	-119
1	229	-197
2	22	18
3	317	-295
4	49	-58
5	193	-188
6	57	56
7	17	16
8	17	-3
9	33	42
10	15	-5
11	10	49

0,k,5

0	99	82
1	25	20
2	152	-138
3	33	40
4	34	-24
5	48	63
6	79	81
7	17	15
8	48	-57
9	19	-16
10	14	-3

0,k,6

0	367	-271
1	88	89
2	21	-19
3	94	93
4	44	-56
5	73	75
6	26	-22
7	17	20
8	32	-32
9	24	-22
10	13	4

0,k,7

0	278	-238
1	16	-18
2	50	46
3	56	56
4	96	-42
5	17	10
6	25	-27
7	57	-71
8	16	-9
9	19	17

0,k,8

0	18	-15
1	111	98
2	72	-74
3	19	18
4	87	-92
5	18	26
6	17	-9
7	37	-44

0,k,9

0	66	59
1	38	40
2	33	-30
3	140	-137
4	42	-49
5	27	-30
6	34	-51

0,k,10

0	47	42
1	22	-18
2	34	-36
3	34	-36
4	21	31
5	17	17
6	17	-27

0,k,11

0	17	15
1	21	-19
2	30	-37
3	22	26
4	25	22
6	17	-18

TABLE 17 (cont.)

0,k,12

0	16	12
1	25	-26
3	15	17

0,k,13

0	18	-23

1,k,0

1	148	188
2	115	-134
3	246	-228
4	70	74
5	192	142
6	172	-138
7	210	-180
8	59	-55
9	70	-51
10	15	-14
11	17	20

1,k,1

1	18	32
2	491	564
3	38	-58
4	127	108
5	32	37
6	14	14
7	39	-38
8	51	48
9	17	-6
10	42	-33
11	11	2

1,k,2

1	246	-267
2	47	54
3	100	106
4	73	59
5	129	-108
6	139	-118
7	196	165
8	30	-43
9	49	32
10	25	-19
11	23	-19

1,k,3

1	332	328
2	88	-96
3	47	47
4	11	13
5	55	-42
6	15	-14
7	75	57
8	58	-60
9	16	13
10	15	-14
11	23	26

1,k,4

1	115	94
2	125	-122
3	98	114
4	111	-95
5	33	25
6	57	60
7	25	-19
8	18	-17
9	44	43
10	14	15
11	31	28

1,k,5

1	350	345
2	34	-44
3	112	111
4	49	-53
5	114	92
6	16	-15
7	75	-66
8	15	22
9	16	-9
10	29	16
11	8	5

1,k,6

1	111	104
2	29	28
3	35	32
4	15	-14
5	54	56
6	16	12
7	30	31
8	75	62
9	19	15
10	11	-4

1,k,7

1	117	-116
2	62	-69
3	63	65
4	57	50
5	21	20
6	17	1
7	127	104
8	16	14
9	27	23
10	10	-2

1,k,8

1	27	33
2	22	24
3	27	40
4	76	73
5	17	23
6	38	36
7	16	8
8	15	-16
9	11	-17

1,k,9

1	16	-6
2	16	2
3	17	8
4	89	-85
5	17	9
6	16	9
7	19	-26
8	13	-1

1,k,10

1	25	-24
2	21	18
3	17	-0
4	17	-14
5	23	24
6	21	-15
7	14	4

1,k,11

1	17	2
2	47	47
3	31	-32
4	66	69
5	15	-5

1,k,12

1	22	23
2	19	-18
3	15	-2
4	14	4

TABLE 17 (cont.)

1,k,13

1	16	-15
2	15	-16
3	13	2
4	11	-14
5	24	-8

$\bar{1}$,k,1

1	635*	-515
2	287	239
3	40	35
4	62	-51
5	72	-73
6	21	-27
7	57	-41
8	55	60
9	17	-11
10	15	-9
11	37	-48

$\bar{1}$,k,2

1	224	-194
2	57	79
3	143	-134
4	396*	252
5	154	-101
6	99	-74
7	43	33
8	17	-11
9	39	-41
10	15	-9
11	35	-34

$\bar{1}$,k,3

1	789*	-588
2	24	19
3	347	-300
4	44	43
5	48	-62
6	15	15
7	87	75
8	54	-53
9	16	-4
10	27	-23
11	10	11

$\bar{1}$,k,4

1	14	-17
2	35	20
3	18	-34
4	73	-48
5	87	-81
6	20	-27
7	103	-105
8	94	-82
9	23	-21
10	14	-5
11	9	-1

$\bar{1}$,k,5

1	266	209
2	50	50
3	122	-104
4	155	-119
5	44	-53
6	29	-26
7	162	-142
8	17	-5
9	18	-22
10	13	10

$\bar{1}$,k,6

1	81	-70
2	89	-62
3	14	-30
4	131	-97
5	16*	-31
6	73	-63
7	21	28
8	14	26
9	25	23

$\bar{1}$,k,7

1	30	32
2	15	10
3	15	10
4	222	189
5	16	-15
6	17	9
7	51	39
8	15	-6
9	26	3

$\bar{1}$,k,8

1	75	59
2	64	-64
3	16	0
4	39	-35
5	17	-8
6	21	29
7	16	-9
8	14	2
9	11	-11

$\bar{1}$,k,9

1	32	-18
3	83	75
4	176	-133
5	51	38
6	16	1
7	15	18

$\bar{1}$,k,10

1	38	-29
4	27	39
5	56	58
6	15	5

$\bar{1}$,k,11

1	78	59

2,k,0

0	708	703
1	291	-331
2	178	-200
3	519	464
4	159	-133
5	114	115
6	108	-96
7	16	9
8	89	-77
9	17	-9
10	16	-5

2,k,1

0	295*	400
1	295*	-358
2	41	69
3	161	-160
4	157	-170
5	66	-74
6	72	- 77
7	178	155
8	144	-121
9	17	14
10	16	0

2,k,2

0	1011*	-1764
1	162	-173
2	202	-216
3	72	-69
4	52	-49
5	21	-23
6	155	144
7	80	73
8	90	72
9	17	15
10	16	-15

TABLE 17 (cont.)

2,k,3

0	697*	-597
1	257	277
2	16	9
3	188	195
4	90	-103
5	34	37
6	46	43
7	99	-89
8	40	-46
9	17	-25
10	15	-18

2,k,4

0	234	188
1	243	195
2	44	47
3	63	-65
4	160	-166
5	15	-0
6	104	-99
7	49	-47
8	105	-73
9	30	14
10	15	-0

2,k,5

0	42	52
1	37	-31
2	163	-173
3	156	-173
4	35	-29
5	25	-5
6	17	6
7	81	-55
8	17	-7
9	16	-9
10	14	-3

2,k,6

0	42	30
1	87	93
2	57	-38
3	70	68
4	19	20
5	86	68
6	17	-20
7	18	-9
8	17	-7
9	17	-30
10	11	1

2,k,7

0	72	-75
1	15	2
2	43	45
3	16	18
4	17	3
5	17	-2
6	58	-53
8	16	34
10	10	3

2,k,8

0	76	86
1	16	-5
2	21	17
3	34	-34
4	17	11
5	39	-26
6	18	-6
8	39	16

2,k,9

0	94	115
1	17	9
2	21	-14
3	33	-35
4	18	10
5	18	-8
6	17	-6
8	14	3

2,k,10

0	22	25
1	38	-46
2	18	-7
3	30	-35
4	35	40
5	17	-19
6	16	5

2,k,11

0	18	-24
1	18	-20
2	17	5
3	41	53
4	25	30
5	16	6

2,k,12

0	17	-16
1	17	-6
2	16	22
3	24	33
4	15	-10

2,k,13

3	14	-10

$\bar{2}$,k,1

0	176	-168
1	22	14
2	42	-16
3	193	-157
4	121	107
5	14	11
6	47	-40
7	68	-68
8	82	77
9	35	-28
10	30	-23
11	17	-21

$\bar{2}$,k,2

0	276*	174
1	17	8
2	46	51
3	556*	420
4	67	65
5	270	230
6	82	-75
7	27	-28
8	18	10
9	17	-19
10	15	11
11	11	-46

$\bar{2}$,k,3

0	194	180
1	37	-35
2	121	93
3	160	-128
4	71	55
5	183	-140
6	24	-33
7	17	8
8	42	43
9	30	24
10	15	3
11	46	6

$\bar{2}$,k,4

1	50	-52
2	11	-7
3	124	-104
4	99	84
5	97	-95
6	73	52
7	38	27
8	59	56
9	16	13
10	14	4
11	9	22

TABLE 17 (cont.)

$\bar{2}$,k,5

0	352*	235
1	44	-38
2	39	-34
3	63	-41
4	73	68
5	16	7
6	57	45
7	97	93
8	23	13
9	37	-23
10	13	17
11	21	19

$\bar{2}$,k,6

0	46	-31
1	197	-131
2	225	172
3	31	35
4	161	120
5	17	-14
6	18	24
7	49	51
8	17	-2
9	15	2

$\bar{2}$,k,7

0	122	-124
1	49	-46
2	41	41
3	253*	197
4	34	36
5	47	43
6	84	80
7	22	-10
8	16	-7

$\bar{2}$,k,8

0	39	-38
1	60	65
2	47	33
3	22	16
4	63	-61
5	38	-18
6	43	48
7	16	2

$\bar{2}$,k,9

0	17	-25
1	68	50
4	48	-31
5	32	14
6	16	12

3,k,0

1	140	135
2	19	21
3	147	143
4	193	205
5	66	58
6	60	-45
7	42	-40
8	16	-24
9	17	23

3,k,1

1	192*	284
2	70	82
3	11	-13
4	10	3
5	43	61
6	49	-64
7	16	-15
8	25	31
9	15	7

3,k,2

1	37	29
2	39	55
3	55	82
4	11	-38
5	50	-51
6	51	52
7	105	118
8	42	36
9	29	24

3,k,3

1	8	-10
2	72	-100
3	22	38
4	40	-41
5	21	-30
6	26	25
7	59	67
8	32	-30
9	15	11

3,k,4

1	91	100
2	46	-50
3	16	21
4	38	-45
5	14	8
6	58	63
7	73	-88
8	16	3
9	15	-2
10	21	11

3,k,5

1	76	-79
2	25	-37
3	17	-20
4	14	-16
5	44	56
6	16	10
7	46	-43
8	34	42
9	14	-6

3,k,6

1	44	-46
2	38	48
3	35	-48
4	23	18
5	31	33
6	23	-33
7	16	9
8	19	20

3,k,7

1	79	-79
2	24	24
3	17	-16
4	22	38
5	39	-48
7	34	36
8	14	-6

3,k,8

1	43	-51
5	22	-26
7	15	5
8	13	-24

3,k,9

1	22	30
7	35	-41
8	18	-13

TABLE 17 (cont.)

$\bar{3}$,k,1

1	228	297
2	25	-38
3	177	229
4	23	29
5	16	17
6	17	-21
7	19	-21
8	54	64
9	18	18
10	26	19

$\bar{3}$,k,2

1	75	-73
2	72	-79
3	41	-36
4	97	105
5	70	80
6	15	21
7	97	114
8	54	53
10	13	7

$\bar{3}$,k,2

1	130	-130
2	62	59
3	49	48
4	87	98
5	51	56
6	62	52
7	82	94
8	21	-11
9	19	-4
10	19	-18

$\bar{3}$,k,4

1	33	26
2	75	80
3	17	25
4	26	11
5	25	-4
6	52	55
7	47	-60
8	19	-24
9	14	-11
10	11	16

$\bar{3}$,k,5

1	72	-73
2	31	-35
3	13	-10
4	178	-186
5	15	8
6	46	-38
7	35	-30
8	15	3
9	13	0

$\bar{3}$,k,6

1	87	-64
2	83	94
3	39	-34
4	95	101
5	16	-11
6	27	-34
7	16	10

$\bar{3}$,k,7

1	71	54
2	76	36
3	91	-91
4	123	128
5	66	-66
6	16	1
7	32	-39

$\bar{3}$,k,8

2	56	-80
4	94	-92
5	51	-53
7	24	-21

4,k,0

0	152	-119
1	30	-25
2	41	-39
3	195	190
4	46	-38
5	105	92
6	49	47
7	21	-6
8	19	-6
10	16	-8

4,k,1

0	67	43
1	37	-26
2	23	36
3	29	13
4	83	-83
5	47	43
6	25	16
7	35	-34
8	58	-55
9	19	-16
10	16	13

4,k,2

0	225	-224
1	63	46
2	76	72
3	203	-201
4	33	14
5	42	-39
6	46	43
7	21	-7
8	21	12
9	18	12
10	16	6

4,k,3

0	306	-254
1	183	198
2	42	-36
3	14	3
4	68	61
5	18	31
6	78	67
7	79	-57
8	76	56
9	18	-8
10	15	-5

4,k,4

0	534*	370
1	169	132
2	71	41
3	58	50
4	17	13
5	19	22
6	78	-62
7	66	-55
8	21	-12
9	17	-16

4,k,5

0	392	296
1	100	-86
2	24	-19
3	74	-76
4	22	26
5	19	-6
6	64	-49
7	21	10
8	19	9

TABLE 17 (cont.)

4,k,6

0	16	-7
1	122	-71
2	57	-35
3	18	-10
4	74	57
5	21	-9
6	50	29
7	25	25
8	43	25
9	16	-4

4,k,7

0	66	-34
1	18	-7
2	64	48
3	73	56
4	38	22
5	33	-9
6	21	-5
7	43	19
8	17	10
9	14	-11

4,k,8

0	39	-11
1	25	-15
2	41	23
3	21	-2
4	21	-8
5	21	-17
6	21	2
7	18	7
8	16	6

4,k,9

0	46	29
1	21	-5
2	21	-6
3	21	-10
4	21	-0
5	21	-6
6	18	16
7	17	7
8	13	-11

4,k,10

0	21	0
1	21	-10
2	21	-10
3	21	1
4	19	2
6	24	6

4,k,11

0	44	-39

4,k,12

0	22	-18

$\bar{4}$,k,1

0	131	-164
1	9	7
2	35	-30
3	135	83
4	50	-46
5	163	124
6	19	1
7	30	-29
8	41	-25
9	18	-14
10	15	-2

$\bar{4}$,k,2

0	205*	-121
1	11	-3
2	25	16
3	65	53
4	60	-46
5	41	51
6	44	-31
7	56	-51
8	64	-51
9	18	7
10	15	-6

$\bar{4}$,k,3

0	154	-75
1	114	126
2	17	-21
3	16	1
4	67	-46
5	19	-17
6	41	-33
7	59	-61
9	18	9
10	14	-9

$\bar{4}$,k,4

0	57	57
1	106	107
2	153	-107
3	90	-75
4	138	-80
5	19	2
6	39	-54
7	25	-26
8	19	23
9	17	-4

$\bar{4}$,k,5

0	127	122
2	31	-40
3	183	-145
4	19	13
5	35	-22
6	79	-64
7	21	15
8	30	8
9	15	-1

$\bar{4}$,k,6

2	40	-43
3	19	21
4	71	72
5	21	4
6	26	-26
7	19	0
8	17	4

$\bar{4}$,k,7

0	25	23
1	54	-56
3	64	73
4	33	26
5	43	-26
6	19	-4
7	18	5
8	15	-9

5,k,0

1	50	45
2	15	-22
3	35	28
4	51	54
5	37	-33
6	13	14
7	62	-56
8	16	20
9	11	4

TABLE 17 (cont.)

5,k,1

1	39	-41
2	13	-11
3	46	-45
4	27	36
5	11	-13
6	13	-15
7	14	-20
8	34	36
9	11	-12

5,k,2

1	31	-30
2	8	-18
3	35	-48
4	56	-67
5	25	-26
6	13	4
7	21	23
8	18	18
9	11	-14

5,k,3

1	83	-97
2	19	-24
3	13	-14
4	14	-18
5	13	-6
6	39	36
7	17	35
8	13	-9
9	11	-0

5,k,4

1	22	-20
2	9	10
3	14	-13
4	11	17
5	13	14
6	14	8
7	34	-41
8	22	-22
9	11	-4

5,k,5

1	10	15
2	10	-8
3	11	-11
4	15	4
5	13	8
6	14	-21
7	37	-45
8	11	15
9	9	-5

5,k,6

1	38	-29
2	11	5
3	22	-17
4	17	11
5	14	17
6	31	-28
7	24	25
8	11	13
9	8	-3

5,k,7

1	13	-2
2	13	31
3	13	5
4	14	18
5	16	-21
6	13	-5
7	24	27
8	10	-18

5,k,8

1	13	16
2	33	-8
3	14	14
4	14	1
5	29	-27
6	13	13
7	11	-1
8	9	-12

5,k,9

1	23	14
2	14	-9
3	14	1
4	13	-16
5	13	10
6	11	8
7	10	-15

5,k,10

1	14	13
2	16	13
3	13	-3
4	14	-6
5	11	12
6	10	-5

$\bar{5}$,k,1

1	42	47
2	41	-51
3	18	-27
4	19	-21
5	13	-15
6	41	-39
7	17	-26
8	24	22
9	11	13

$\bar{5}$,k,2

1	8	6
2	22	-28
3	14	-19
4	22	28
5	26	22
6	14	-17
7	39	45
8	15	17
9	10	-0

$\bar{5}$,k,3

1	35	50
2	16	22
3	22	19
4	79	68
5	13	-14
6	42	39
7	14	14
8	13	-2

TABLE 17 (cont.)

$\bar{5}$,k,4

2	56	-66
3	43	55
4	86	-84
5	14	7
6	14	22
7	13	-7
8	11	6

$\bar{5}$,k,5

3	46	41
4	44	-46
5	52	59
6	14	-4
7	25	34
8	10	6

$\bar{5}$,k,6

4	72	82
5	14	29
6	13	1
7	11	7

TABLE 18

Observed Structure Factors of

3,6-dimethylpiperazine-2,5-dione

The three columns in each group contain, reading from left to right, the value of k, the unscaled value of F_o and a letter designating which of the two twin crystals produced this particular diffraction maximum.

0,k,0

1	1506	A+B
2	659	A+B
3	516	A+B
4	888	A+B
5	64	A+B
6	213	A+B
7	265	A+B
8	219	A+B

1,k,0

0	1557	A+B
1	249	A+B
2	1100	A+B
3	815	A+B
4	266	A+B
5	305	A+B
6	60	A+B
7	428	A+B
8	179	A+B

2,k,0

0	829	A+B
1	415	A+B
2	733	A+B
3	315	A+B
4	63	A+B
5	30	A+B
6	319	A+B
7	299	A+B

3,k,0

1	240	A+B
2	190	A+B
4	97	A+B
5	202	A+B
6	174	A+B
7	73	A+B

4,k,0

3	69	A+B
4	112	A+B
5	92	A+B

$\bar{1}$,k,0

1	1936	A+B
2	1125	A+B
3	144	A+B
4	534	A+B
5	234	A+B
6	69	A+B
7	92	A+B
8	112	A+B

$\bar{2}$,k,0

1	1494	A+B
2	1270	A+B
3	408	A+B
5	88	A+B
6	55	A+B
7	77	A+B
8	41	A+B

$\bar{3}$,k,0

1	218	A+B
2	384	A+B
3	308	A+B
4	148	A+B
5	291	A+B

$\bar{4}$,k,0

3	63	A+B
5	52	A+B

0,k,1

0	970	A
1	324	A
2	876	A
3	1585	A
4	1454	A
5	100	A
6	92	A
7	153	A
8	0	A

1,k,1

0	807	A
1	542	A
2	636	A
3	548	A
4	542	A
6	133	A
7	137	A

2,k,1

0	263	A
1	119	A
2	565	A
3	473	A
4	170	A
5	63	A
6	103	A
7	80	A

3,k,1

0	57	A
1	99	A
2	129	A
3	375	A
4	98	A
5	38	A
6	32	A

$\bar{1}$,k,1

0	2405	A
1	737	A
2	1679	A
3	84	A
4	1193	A
5	355	A
6	104	A
7	146	A
8	97	A

TABLE 18 (cont.)

$\bar{2},k,1$

0	435	B
1	410	A
2	909	A
3	500	A
4	164	A
5	229	A
6	170	A
7	87	A
8	69	A

$\bar{3},k,1$

0	104	B
1	39	B
2	312	B
3	318	A
4	94	A
5	53	A
6	94	B
7	97	B

$0,\bar{k},1$

1	1249	B
2	1016	B
3	263	B
4	1050	B

$1,\bar{k},1$

1	213	B
2	454	B
3	200	B
4	331	B
5	179	B
6	62	B

$2,\bar{k},1$

1	190	A
2	55	A
3	100	B
4	43	B
5	94	B
6	31	B

$3,\bar{k},1$

1	57	A
2	70	A
3	55	A
5	38	A
6	31	A

$1,k,\bar{1}$

1	58	B
2	1302	B
3	1333	B
4	953	B
5	35	B
6	283	B
7	130	B

$2,k,\bar{1}$

1	389	B
2	369	B
3	1017	B
4	260	B
5	77	B
6	187	B
7	63	B

$3,k,\bar{1}$

1	103	B
2	324	B
3	235	B
4	64	B
6	65	B
7	41	B

$0,k,2$

0	208	A
1	938	A
2	704	A
3	453	A
6	198	A
8	52	A

$1,k,2$

0	708	A
1	268	A
2	513	A
3	325	A
4	59	A
5	133	A
6	72	A
7	36	A
8	49	A

$2,k,2$

0	273	A
1	0	A
2	248	A
3	248	A
4	30	A
5	169	A
6	159	A

$3,k,2$

0	56	A
1	87	A
2	92	A

$\bar{1},k,2$

0	---	-
1	169	A
2	152	A
3	52	A
4	178	A
5	364	A
6	193	A
7	139	A
8	23	A
9	69	A

$\bar{2},k,2$

0	603	A
1	1427	A
2	367	A
3	52	A
4	144	A
5	109	A
6	51	A

$\bar{3},k,2$

0	258	B
1	543	A
2	314	A
3	89	A
4	51	A
6	26	A

TABLE 18 (cont.)

$\bar{4},k,2$

0	170	B
1	195	B
2	103	B
3	41	B

$\bar{5},k,2$

0	44	B
1	99	B
2	43	B

$0,\bar{k},2$

1	1175	B
2	325	B
3	296	B
4	179	B
5	310	B
6	140	B
7	284	B
8	276	B
9	94	B

$1,\bar{k},2$

1	255	B
2	523	B
3	222	B
4	354	B
5	185	B
6	61	B

$2,\bar{k},2$

1	211	A
2	59	A
3	105	A
4	43	A
5	90	A
6	28	A

$3,\bar{k},2$

1	51	A
2	62	A

$1,k,\bar{2}$

1	---	-
2	27	B
3	1202	B
4	451	B
5	408	B
6	235	B
7	748	B
8	309	B

$2,k,\bar{2}$

1	73	B
2	305	B
3	608	B
4	285	B
5	89	B
6	732	B
7	726	B
8	77	B

$3,k,\bar{2}$

1	48	B
2	270	B
3	291	B
4	87	B
5	463	B
6	574	B
7	271	B
8	47	B

$4,k,\bar{2}$

1	60	B
2	43	B
3	61	B
4	237	B
5	269	B
6	184	B

$5,k,\bar{2}$

1	45	B
2	58	B
3	100	B
4	66	B

$0,k,3$

0	1026	A
1	520	A
2	167	A
3	1111	A
4	926	A
5	103	A
6	76	A
7	38	A

$1,k,3$

0	311	A
1	79	A
2	553	A
3	631	A
4	281	A
6	54	A

$2,k,3$

0	41	A
1	199	A
2	237	A
3	132	A
4	40	A

$3,k,3$

0	58	A
1	54	A

$\bar{1},k,3$

0	953	A
1	1797	A
2	1752	A
3	176	A
4	106	A
5	191	A
6	104	A
7	100	A

$\bar{2},k,3$

0	527	B
1	754	A
2	791	A
3	290	A
4	476	A
5	410	A
6	133	A
7	66	A

$\bar{3},k,3$

0	169	B
1	200	A
2	316	A
3	241	A
4	58	A
5	129	A
6	95	A
7	108	A

$\bar{4},k,3$

0	277	B
1	89	B
2	84	B
3	101	B
4	26	B

$\bar{5},k,3$

0	193	B
1	100	B

TABLE 18 (cont.)

$0,\bar{k},3$

1	409	A
2	167	B
3	349	B
4	697	B
5	336	B
7	66	B
8	54	B
9	51	B

$1,\bar{k},3$

1	306	A
2	128	A
3	128	A
4	156	A
5	107	A

$2,\bar{k},3$

1	29	A
2	62	A
3	118	A
4	92	A
5	25	A

$3,\bar{k},3$

1	39	A

$1,k,\bar{3}$

1	972	B
2	1385	B
3	1030	B
4	587	B
5	332	B
6	1061	B
7	416	B
9	179	B

$2,k,\bar{3}$

1	514	B
2	763	B
3	2698	B
4	1078	B
5	367	B
6	317	B
7	290	B

$3,k,\bar{3}$

1	464	B
2	1177	B
3	1078	B
4	60	B
5	496	B
6	287	B
7	77	B
8	139	B
9	94	B

$4,k,\bar{3}$

1	450	B
2	374	B
3	40	B
4	255	B
5	276	B
6	57	B
7	62	B
8	210	B

$5,k,\bar{3}$

1	117	B
2	27	B
3	116	B
4	128	B
5	47	B
6	40	B

PART V

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PART VI

PROPOSITIONS

1. A statistical procedure is proposed for the testing of a set of analytical data for systematic errors of certain types.

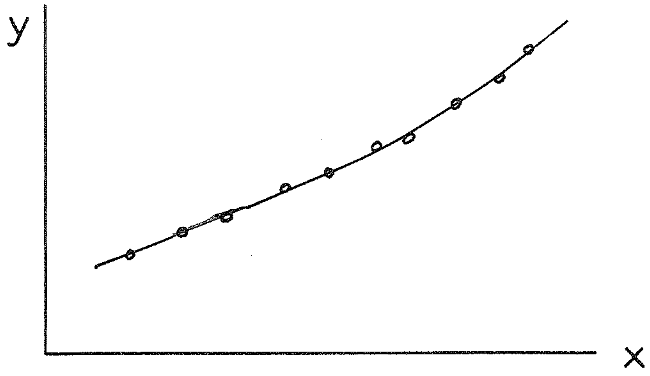
(1) Suppose, for example, that it is desired to determine the percentage of substance A in a mixture. Several samples of the mixture are weighed out, the sample weights being $x_1, x_2, \ldots, x_r$; the weight $y_1, y_2, \ldots, y_r$ of A in each sample is then measured by some means. If these measurements were all absolutely exact, the percentage of A in the original mixture could be calculated from the results of the $i^{\underline{th}}$ experiment by the formula

$$(\%A)_i = \frac{y_i}{x_i} \cdot 100.$$

The values of $(\%A)_i$ so calculated clearly should be identical for all i.

(2) If each of the above measurements is subject to only random errors, the best estimate of the percentage of A in the original mixture is the weighted mean of the values of %A calculated from each of the r measurements.

(3) The practical case is that which takes into account the possible existence of both random and systematic errors. The y_i are plotted as ordinates and the x_i as abcissas as follows



Then by some suitable technique (e.g. least squares) the "best" polynomial of, say, the second degree is fitted. The result is a set of values and estimated standard deviations for the coefficients of the polynomial

$$y \approx P(x) \equiv a_o + a_1x + a_2x^2 \cdot \cdot \cdot \cdot$$

The hypothesis that the data contain no constant bias, i.e. that a_o does not differ from zero by a significant amount is then tested at the p percentile level. Define

$$t_{a_o} \equiv \frac{a_o}{\sigma_{a_o}}$$

The value of t_{a_o} calculated from the estimates of a_o and σ_{a_o} may then be compared with a table of critical values of t, entering the table at M-3 degrees of freedom. If the value of t_{a_o} is less than the critical value, the above hypothesis is substantiated at the p percentile level of significance. If $t_{a_o} > t_{critical}$, the hypothesis fails.

The hypothesis that a_2 does not differ from zero by a significant amount can be tested in a similar fashion.

2. The function

$$G(n,\sigma,m) \equiv \frac{1}{\sigma\sqrt{2\pi}}\int_0^\infty x^n e^{-\frac{1}{2\sigma^2}(x-m)^2}\,dx,$$

which is closely related to the $n^{\underline{th}}$ moment of a normal distribution, occurs frequently in applied statistics. By means of the transformation $t \equiv \frac{x}{\sigma}$, $z \equiv \frac{m}{\sigma}$, it can be written as the product

$$G(n,\sigma,m) \equiv \sigma^n\psi_n(z),$$

where $\psi_n(z) \equiv \frac{1}{\sqrt{2\pi}}\int_0^\infty t^n e^{-\frac{1}{2}(t-z)^2}dt.$

The following relations can be proved:

(a) $\psi_{n+1}(z) = z\psi_n(z) + n\psi_{n-1}(z)$, $n \neq 0$,

(b) $\psi_n'(z) = \psi_{n+1}(z) - z\psi_n(z)$, $n \neq -1$,

(c) $\psi_n''(z) + z\psi_n'(z) - n\psi_n(z) = 0$, $n \neq -1$,

(d) $\psi_n(z) = \frac{1}{\sqrt{\pi}}\, 2^{\frac{n}{2}-1}\,\Gamma\left(\frac{n+1}{2}\right)\sum_{j=0}^{\infty}\frac{1}{(2j+1)!}\,z^{2j}\prod_{k=0}^{j}\frac{2k-n-1}{-(1+n)}$

(e) $\sum_{n=-\infty}^{+\infty}\psi_n(z)s^n = \frac{1}{\sqrt{\pi}}\,e^{\frac{z}{s}-\frac{1}{2}z^2}\sum_{n=-\infty}^{+\infty}2^{\frac{n}{2}-1}\,\Gamma\left(\frac{n+1}{2}\right)s^n$

(f) $\int_{-\infty}^{+\infty}\psi_n(z)\psi_m(z)dz = 0$ if $n \neq m$.

3. Neurosis is characterized(1) by the following symptoms:

   (a) Dissociation occurs between a set of symbols and the stimuli which they represent.

   (b) Response to such symbols is invariably compulsive, and subject to conscious change only with extreme difficulty.

   (c) Such responses are rationalized by the neurotic individual even when they are clearly inappropriate, and the rationalizations seemingly are believed.

   Completing the syndrome is the commonly-accepted mechanism for the induction of the neurotic state. This mechanism holds that:

   (d) Induction occurs during a state of heightened suggestibility, such as that induced by extreme stress.

   (e) Repression of the traumatic experience then occurs, resulting in the dissociation mentioned above.

   Inasmuch as the above syndrome characterizes both the phenomena of neurosis and of posthypnotic suggestion, it is proposed that these phenomena are identical.

4. A method is proposed for the measurement of the densities of very small crystals ($\sim 1\ \text{mm}^3$ in volume) which has the advantages over currently used methods that densities up to 13 $\frac{\text{gm}}{\text{cm}^3}$ are easily measurable, and extreme precision (1 part in 10^5) is obtainable.

A diver, the density of which is greater than that of mercury, is floated in a pool of mercury in a closed system (see Figure 15). An air bubble is introduced into the diver, and pressure is applied to the system (causing the volume of the bubble to decrease and the diver to sink) until the fiducial mark on the diver is at the meniscus of the mercury. A crystal is then introduced under the diver and the process is repeated. The density of the crystal may be calculated from the equation

$$\frac{1}{D_x} = \frac{1}{D_{Hg}} + \frac{c}{m_x}\left[1 - \frac{z_L P_{MT}}{z_{MT} P_L}\right],$$

where

$$c = \frac{m_d\left[\frac{1}{D_{Hg}} - \frac{1}{D_d}\right]}{1 - \frac{D_g}{D_{Hg}}},$$

and D_{Hg} is the density of mercury, D_d the density of the material from which the diver is made, and D_g is the density of the buoying gas. m_x is the mass of the crystal, P_{MT} and P_L are the pressures required to bring the diver to equilibrium before and after the crystal is introduced, and z_{MT} and z_L are the corresponding compressibility factors from the gas law

$$PV = nzRT.$$

Professor Niemann has pointed out that a somewhat similar method(2) is commonly used for measuring the densities of certain biological materials.

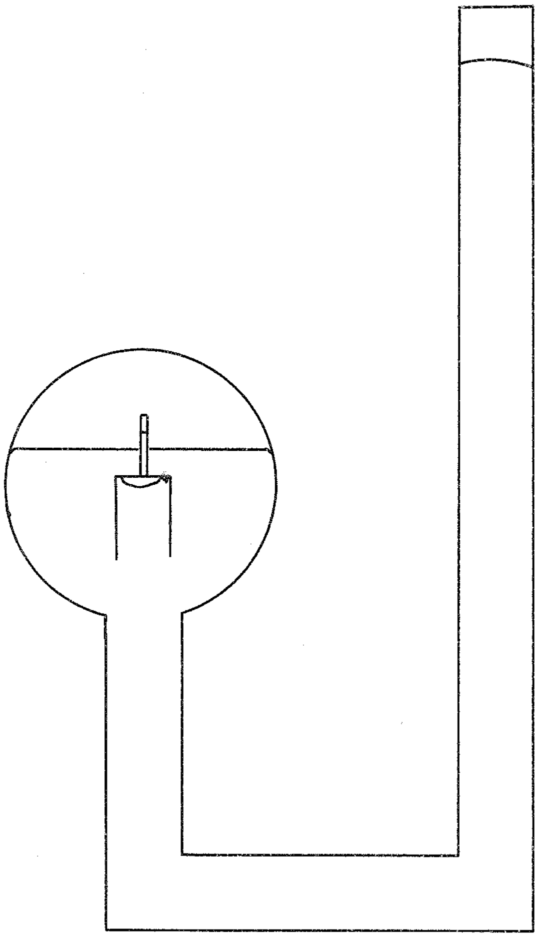


FIGURE 15

5. A new linear approximation to the cosine function within a small interval has been developed.

Let $y = y_o + \epsilon$, $0 \leq \epsilon \leq h$. Then if $f(y)$ is a continuous bounded function for all finite real y, $f(y)$ can be approximated within the small interval $0 \leq \epsilon \leq h$ by

$$f(y) \approx f(y_o) + \epsilon \sum_{n=1}^{\infty} \frac{\Delta^n f(y_o)}{n} .$$

For most $f(y)$, further approximation is necessary, such as including only a finite number of terms in the sum. However, when $f(y) = \exp(2\pi ix)$, evaluation of the sum in closed form is possible. Since

$$\Delta^r e^{2\pi ix} = (-1)^r \left[1-e^{2\pi i\Delta x}\right]^r e^{2\pi ix},$$

$$e^{2\pi iy} \approx e^{2\pi iy_o} + \epsilon\, e^{2\pi iy_o} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \left[1-e^{2\pi ih}\right]^n$$

$$= e^{2\pi iy_o} + \epsilon\, e^{2\pi iy_o}\left[-\ln(2-e^{2\pi ih})\right].$$

From the real part of the above equation,

$\cos 2\pi y \approx a + b\epsilon$, where $a = \cos 2\pi y_o$, and

$$b = \sin 2\pi y_o \tan^{-1}\left(\frac{\sin 2\pi h}{2-\cos 2\pi h}\right) - \tfrac{1}{2}\cos 2\pi y_o \ln(5-4\cos 2\pi h).$$

Similarly, the imaginary part yields an approximation to the sine function.

6. During the course of a crystal-structure investigation, the approximately correct structure which is found initially usually must be refined extensively in order to obtain accurate atomic coordinates. A very convenient procedure for carrying out such a refinement is afforded by the method of least squares. Unfortunately, the least-squares procedure commonly used by crystallographers(3) involves a linearization of the observational equations which imposes rather serious limitations on the refinement process. A variation of the least-squares method is proposed which circumvents this linearization.

Let us suppose, for the sake of concreteness, that the crystal structure to be refined is of $P\bar{1}$ symmetry. For this space group the structure-factor expression is

$$F(\underset{\sim}{h}) = 2 \sum_{n=1}^{N} f_n \cos 2\pi \underset{\sim}{h} \cdot \underset{\sim}{x}_n ,$$

where $\underset{\sim}{h} \equiv (h,k,\ell)$, and $\underset{\sim}{x}_n \equiv (x_n, y_n, z_n)$, and f_n is the scattering factor of the $n^{\underline{th}}$ atom, and the summation is over all of the atoms in the asymmetric unit.

Suppose further that the magnitudes of M structure factors, $|F_o(\underset{\sim}{h}_1)|$, $|F_o(\underset{\sim}{h}_2)|$, ..., $|F_o(\underset{\sim}{h}_M)|$ have been measured. Then the least-squares condition yields the system of equations

$$G_1(x) \equiv \frac{\partial}{\partial x_1} \sum_{m=1}^{M} \left(\left| F_o(\underset{\sim}{h}_m) \right|^2 - \left| F(\underset{\sim}{h}_m) \right|^2 \right)^2 = 0$$

$$G_2(x) \equiv \frac{\partial}{\partial y_1} \sum_{m=1}^{M} \left(\left| F_o(\underset{\sim}{h}_m) \right|^2 - \left| F(\underset{\sim}{h}_m) \right|^2 \right)^2 = 0$$

$$\vdots$$

$$G_{3N}(x) \equiv \frac{\partial}{\partial z_N} \sum_{m=1}^{M} \left(\left| F_o(\underset{\sim}{h}_m) \right|^2 - \left| F(\underset{\sim}{h}_m) \right|^2 \right)^2 = 0,$$

which may be more compactly written by means of the column matrix

$$\underset{\sim}{G}(\underset{\sim}{x}) \equiv (G_1(\underset{\sim}{x}),\ G_2(\underset{\sim}{x}),\ \ldots,\ G_{3N}(\underset{\sim}{x})) = 0.$$

Then if an initial set, $\underset{\sim}{x}^o$, of positional parameters is known which is reasonably close to the correct set, $\underset{\sim}{x}^*$, improved values of these parameters may be found by means of the iterative expression

$$\underset{\sim}{x}^{n+1} = \underset{\sim}{x}^n - J^{-1}(x^n)\underset{\sim}{G}(\underset{\sim}{x}^n),$$

where

$$J(\underset{\sim}{x}) = \left\| \begin{matrix} \dfrac{\partial G_1(\underset{\sim}{x})}{\partial x_1} & \dfrac{\partial G_1(\underset{\sim}{x})}{\partial y_1} & \cdots & \dfrac{\partial G_1(\underset{\sim}{x})}{\partial z_N} \\ \dfrac{\partial G_2(\underset{\sim}{x})}{\partial x_1} & & & \vdots \\ \vdots & & \cdots & \dfrac{\partial G_{3N}(\underset{\sim}{x})}{\partial z_N} \end{matrix} \right\| .$$

7. Attempts(4,5) have been made to solve one-dimensional crystal structures by solving systems of equations of the forms

$$|F(h00)|^2 = \sum_{n,m=1}^{N} f_n f_m \exp 2\pi ih(x_n - x_m) \quad \text{(acentric structure), or}$$

$$|F(h00)|^2 = 4\left[\sum_{n=1}^{N} f_n \cos 2\pi hx_n\right]^2 \quad \text{(centrosymmetrical structure).}$$

Moreover, the author has suggested(6) that attempts be made to solve the system of equations

$$\begin{aligned} g_1(\underset{\sim}{x}) &\equiv \left(\sum_{n=1}^{N} f_n \cos 2\pi h_1 x_n\right)^2 - \tfrac{1}{4}|F_o(h_1)|^2 = 0 \\ g_2(\underset{\sim}{x}) &\equiv \left(\sum_{n=1}^{N} f_n \cos 2\pi h_2 x_n\right)^2 - \tfrac{1}{4}|F_o(h_2)|^2 = 0 \qquad (1) \\ &\vdots \\ g_N(\underset{\sim}{x}) &\equiv \left(\sum_{n=1}^{N} f_n \cos 2\pi h_N x_n\right)^2 - \tfrac{1}{4}|F_o(h_N)|^2 = 0 \end{aligned}$$

by iterative procedures such as the Newton-Raphson method starting with a trial structure consisting essentially of randomly placed atoms.

Unfortunately, however, there are $2^N \prod_{i=1}^{N} h_i$ solutions of the above system of equations, and only 2^{N+1} congruent solutions of a one-dimensional structure, so that in general such a procedure would not converge to a physically meaningful solution.

It is now suggested that attempts be made to solve systems similar to (1) above, but containing $M > N$ observed structure-factor moduli.

8. If a crystal structure consists of N molecules per asymmetric unit and n atoms per molecule, the general structure-factor expression may be written

$$F(\mathbf{h}) = \sum_{j=1}^{N} \sum_{k=1}^{n} f_{jk}(\mathbf{h})\, e^{2\pi i \mathbf{h}\cdot\mathbf{r}_{jk}}, \qquad (1)$$

where $\mathbf{h} \equiv (h,k,\ell)$ and $\mathbf{r}_{jk} \equiv (x_{jk}, y_{jk}\ z_{jk})$, the position from the origin of the unit cell to the $k^{\underline{th}}$ atom of the $j^{\underline{th}}$ molecule. The basis vectors of the unit cell are $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$.

It frequently happens that the structure of the $j^{\underline{th}}$ molecule can be predicted <u>a priori</u> with respect to some vector triple $\mathbf{a}_j'$, $\mathbf{b}_j'$, $\mathbf{c}_j'$ which is congruent with the triple $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$. Then making use of the position vectors $\mathbf{r}_{jk}'$ with respect to this coordinate system, equation 1 becomes

$$F(\mathbf{h}) = \sum_{j=1}^{N} \sum_{k=1}^{n} f_{jk}(\mathbf{h}) \exp 2\pi i \left[\mathbf{R}_j + A_j \mathbf{r}_{jk}'\right] \cdot \mathbf{h}, \qquad (2)$$

where $\mathbf{R}_j \equiv (X_j, Y_j, Z_j)$ represents a translation of the origin of $\mathbf{a}_j'$, $\mathbf{b}_j'$, $\mathbf{c}_j'$, and the matrix A_j a rotation of $\mathbf{a}_j'$, $\mathbf{b}_j'$, $\mathbf{c}_j'$ with respect to $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$. Taking the first row of A_j to be

$$\cos\alpha_j \qquad \sin\alpha_j\cos\beta_j \qquad \sin\alpha_j\sin\beta_j,$$

and restricting consideration to the centrosymmetrical case and to structure factors of the type F(h00), equation 2 becomes

$$F(h) = 2\sum_{j=1}^{N} \sum_{k=1}^{n} f_{jk}(h)\cos 2\pi h\left[X_j + x_{jk}'\cos\alpha_j + y_{jk}'\sin\alpha_j\cos\beta_j + z_{jk}'\sin\alpha_j\sin\beta_j\right]. \qquad (3)$$

It is suggested that a second method for finding trial structures might be to solve, by the Newton-Raphson method, a system of equations of the form of equation 3. The parameters to be found--X_j, α_j, and β_j--are 3N in number rather than nN as is the case with the procedure suggested in proposition 7. For many molecules this represents a drastic decrease in the number of parameters sought, and perhaps as a consequence, a considerable increase in the radius of convergence of the iterative procedure.

9. In the precision determination of the lattice constants of orthorhombic crystals, it is common practice to fit by least squares the constants of the equation

$$H^2(hk\ell) \equiv \frac{4\sin^2\theta(hk\ell)}{\lambda^2} = Ah^2 + Bk^2 + C\ell^2$$

to several (say, N) observed values of $H^2(hk\ell)$. There results, in addition to three values of the constants A, B, and C, three estimates of the standard deviations σ_A, σ_B, and σ_C of these constants. The lengths of the basis vectors of the unit cell are then calculated from equations of the form

$$a = A^{-\frac{1}{2}}.$$

It is proposed that this last equation is correct only for the true value of A, and not for the mean value which emerges from the least-squares treatment. The best statistical estimate of a is given by the equation

$$\bar{a} = \frac{1}{2\sigma_A\sqrt{2\pi}}\int_0^\infty u^{-\frac{1}{2}}\, e^{\frac{1}{2\sigma_A^2}(u-A)^2}\, du,$$

and the best estimate of its standard deviation by

$$\sigma_a = \sqrt{\frac{\alpha_2 - \bar{a}^2}{N-3}}, \text{ where}$$

$$\alpha_2 = \frac{1}{2\sigma_A\sqrt{2\pi}}\int_0^\infty u^{-1}\, e^{-\frac{1}{2\sigma_A^2}(u-A)^2}\, du.$$

These results are applicable also to crystals having higher than orthorhombic symmetry.

10. R, the so-called "residual" or "reliability index", defined by the equation

$$R = \frac{\sum_j w(hk\ell)_j (F_o(hk\ell)_j - F_c(hk\ell)_j)^2}{\sum_j w(hk\ell)_j \left|F_o(hk\ell)\right|^2}$$

is used commonly by x-ray crystallographers as an indication of the correctness and of the degree of refinement of a crystal structure. That it is inadequate for these purposes has been recognized for some time.(7) A criterion is proposed which avoids the deficiencies of R.

From an analysis of the intensity data it is usually possible to obtain an empirical equation which expresses $\epsilon(|F_o|)$, the observed uncertainty in $|F_o|$, as a function of $|F_o|$. Such a relation might, for example, conveniently be expressed as a power series

$$\epsilon(|F_o|) = a_o + a_1|F_o| + a_2|F_o|^2 + \cdots$$

In the analysis which follows, and usually in current crystallographic practice, it is assumed that terms of second and higher degree are negligible.

It has been shown(8,9) that the probability that the value of $|F_o|$ be less than or equal to some number z is given by

$$N_c(z) = \sqrt{\frac{2}{\pi\langle I\rangle}}\int_0^z e^{-\frac{t^2}{2\langle I\rangle}}\,dt$$

for centrosymmetric structures and by

$$N_a(z) = \frac{2}{\langle I\rangle^{\frac{1}{2}}}\int_0^z te^{-\frac{t^2}{\langle I\rangle}}\,dt$$

for acentric ones.

The frequency functions which represent the statistical distribution of $\epsilon(|F_o|)$ are given by

$$f_c(y) = \frac{1}{a_1}\sqrt{\frac{2}{\pi\langle I\rangle}}\; e^{-\frac{(y-a_o)^2}{2a_1{}^2\langle I\rangle}},$$

and

$$f_a(y) = \frac{2}{a_1{}^2\langle I\rangle^{\frac{1}{2}}}(y-a_o)\; e^{-\frac{(y-a_o)^2}{a_1{}^2\langle I\rangle^{\frac{1}{2}}}}.$$

It is proposed that, after the empirical constants a_o and a_1 have been found for a particular crystal, the appropriate theoretical frequency function should be plotted. Then if a structure is refined until its positional parameters are nearly correct, the values of F_o-F_c should approximate closely the theoretical frequency law.

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