I. MOLECULAR STRUCTURE INVESTIGATIONS

II. A THEORY OF MOLECULAR COMPOUNDS

Thesis by

Arthur James Stosick

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Introduction

In part I of this thesis there are presented the results of investigations of molecular structures by means of electron diffraction by gases, and by x-ray experiments with crystals.

The electron diffraction studies were made on a group of related molecules of the fifth group elements. The molecules of this class are the trioxides of phosphorus and arsenic, the pentoxide and sulfoxide of phosphorus, and hexamethylene tetramine. The observed interatomic distances are discussed in terms of single-double and double-triple bond resonance, and the valence angles in terms of bond orbital hybridization.

The remaining substance investigated by the electron diffraction method is tetranitromethane. In order to obtain a satisfactory interpretation of the data it was necessary to assume a rotatory oscillation of nitro groups about C-N bonds. In addition to this it was found necessary to include in the approximate intensity formula the usually omitted temperature factor.

The x-ray investigations included the determination of the space group and unit cell for three crystals; these are the potassium salt of nitroform, $KC(NO_2)_3$, phenylpropiolic acid, $C_6H_5C{\equiv}C-COOH$, and the molecular compound between naphthalene and p-dinitrobenzene.

In part II an attempt has been made to provide a theory of molecular compounds. The class of complexes discussed is that for which the well-understood hydrogen bond or coordination type of bond cannot possibly be postulated. It is suggested that van der Waals forces are the source of complex stabilization, and arguments in support of this view are given. There follows next a brief discussion of the color of the complexes with a suggestion as to the origin of the color. Part II concludes with a summary of the available x-ray data for several crystalline complexes.

Part I

MOLECULAR STRUCTURE INVESTIGATIONS

The Molecular Structure of Arsenious Oxide, As₄O₆, Phosphorus Trioxide, P₄O₆, Phosphorus Pentoxide, P₄O₁₀, and Hexamethylenetetramine, (CH₂)₆N₄, by Electron Diffraction

BY G. C. HAMPSON AND A. J. STOSICK

In a recent paper,[1] which was published while this work was in progress, there were reported the results of an electron diffraction investigation of the structures of phosphorus trioxide, phosphorus pentoxide and arsenious oxide. The values which we have obtained for P_4O_6 and As_4O_6 are in good agreement with those of Maxwell, Hendricks and Deming. On the other hand, the latter authors were unable to deduce a structure for P_4O_{10} and came to the conclusion that the molecule probably has lower symmetry than that of the point group T_d. The reason for their failure probably lies in the fact that the molecule has an abnormally short P–O distance and we were led to our final structure, which gives an excellent fit with the photographs, only after very many models had been shown to be wrong.

The visual method of measurement was used, the results being compared in the usual way with the approximate scattering formula

$$I = \Sigma_{ij} Z_i Z_j \frac{\sin s r_{ij}}{s r_{ij}}$$

in which r_{ij} is the distance between the ith and jth atoms, $Z_i Z_j$ their atomic numbers and $s = (4\pi \sin \theta/2)/\lambda$, where θ is the scattering angle and λ the wave length of the electrons. Radial distribution curves[2] were also calculated and interatomic distances deduced from them. When a molecule contains several approximately equal distances, the radial distribution method fails to resolve the closely spaced maxima and very little information can be obtained from the curve. A modification of the method, suggested by Dr. V. Schomaker of these Laboratories, in which the estimated intensities are multiplied by a factor

(1) Maxwell, Hendricks and Deming, *J. Chem. Phys.*, **5**, 626 (1937).

(2) Pauling and Brockway, THIS JOURNAL, **57**, 2684 (1935).

Table I

Max.	Min.	I	c	s_0	s(VII)	s(VIII)	s_{VII}/s_0	s_{VIII}/s_0
	1			1.602	1.41	1.45	(0.881))	(0.905)
1		20	3	2.365	2.33	2.34	.986	.989
	2			3.273	3.19	3.20	.975	.978
2		30	20	4.239	4.25	4.26	1.002	1.005
	3			5.434	5.39	5.37	0.992	0.988
3		6	12	6.240	6.24	6.23	1.000	.998
	4			7.055	6.95	6.94	0.986	.984
4		10	50	8.121	7.95	7.99	.979	.984
	5			9.213	9.20	9.18	.999	.996
5		4	25	10.278	10.42	10.35	1.014	1.007
	6			11.261	11.00	10.90	0.977	0.968
6		4	35	12.353	11.84	11.89	.959	.963
	7			13.292	13.12	13.11	.987	.986
7		4	45	14.218	14.33	14.36	1.007	1.010
	8			15.347	15.37	15.41	1.002	1.004
8		1	12	16.309	16.15	16.18	0.991	0.992
	9			17.298	17.05	17.09	.986	.988
9		2	25	18.212	18.13	18.17	.996	.998
	10			19.246	19.17	19.22	.996	.999
10		2	25	20.224	20.08	20.03	.993	.990
	11							
11		1	10	22.087	21.84	21.89	.990	.991
					Mean	.9909	Mean	.9909

$s^3e^{-as^2}$, with a chosen such that the exponential factor is equal to one-tenth for the last measured ring, gave a satisfactory resolution of most of the distances, and was invaluable in fixing the model for P_4O_{10}.

As_4O_6, P_4O_6, P_4O_{10}, and $(CH_2)_6N_4$ were measured in Oxford using the apparatus described by de Laszlo;[3] for his assistance in operating the electron diffraction camera we are greatly indebted to Dr. A. H. Gregg. The measurements on As_4O_6, P_4O_6, and P_4O_{10} were then repeated in Pasadena using the apparatus described by Brockway,[4] and the two sets of results were found to agree to within 1%. With the latter apparatus two or three extra outer rings were obtained, but the longer jet-to-camera distance employed in the de Laszlo apparatus enabled some inner fine structure to be resolved which was of great help in the P_4O_{10} investigation.

Experimental

The As_4O_6 used was the C. P. arsenious oxide of commerce which was not further treated.

The P_4O_6 was prepared by the method of Wolf and Schmager,[5] a modification of the older method of Thorpe and Tutton.[6] The trioxide so prepared contains 1 to 2% of free yellow phosphorus even after repeated vacuum distillation. The greater share of this free phosphorus was removed by irradiating the impure oxide for two days with a mercury vapor lamp. This treatment largely converts the yellow form into the much less volatile red form permitting separation by a subsequent distillation *in vacuo*.

The P_4O_{10} used was commercial C. P. phosphorus pentoxide which was sublimed in a stream of oxygen to remove lower oxides. This treatment is necessary since the lower oxides are all more volatile.

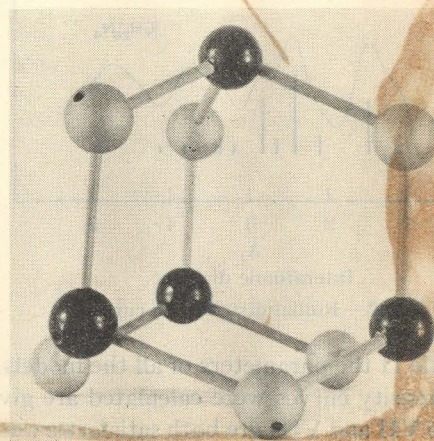The hexamethylenetetramine was a commercial sample purified by vacuum sublimation.

(3) De Laszlo, *Proc. Roy. Soc.* (London), **A146**, 672 (1934).
(4) Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).
(5) Wolf and Schmager, *Ber.*, **62**, 771 (1929).
(6) Thorpe and Tutton, *J. Chem. Soc.*, **57**, 545 (1890).

Fig. 1.—Photograph of model of As_4O_6, P_4O_6, or $(CH_2)_6N_4$. The black balls represent As, P, or N; the silver balls represent O or CH_2.

Arsenious Oxide.—The models tried for As_4O_6 consist of four As atoms at the positions (v,v,v), $(\bar{v},\bar{v},v)$, $(\bar{v},v,\bar{v})$ and $(v,\bar{v},\bar{v})$ and six O atoms at the positions $(\pm u,0,0)$, $(0,\pm u,0)$ and $(0,0,\pm u)$ (Fig. 1).

The photographs of As_4O_6 show thirteen maxima, eleven of which were measurable. The first, second and fourth maxima are strong. Preceding the fifth maximum and following the sixth maximum there are deep minima of about equal depth. The fifth and sixth maxima are of equal intensity. The values of s_0 for the maxima and minima and the estimated intensities of the maxima are given in Table I together with the weighted intensity values, c, used in the modified radial distribution method. The corresponding values of s for models VII and VIII are also given.

VI is not satisfactory because the sixth maximum has become weaker than the fifth.

TABLE II

Model	u	v	As–As	As–O	O–As–O	As–O–As
I	2.310	1.155	3.26 Å.	2.00 Å.	109°28′	109°28′
II	2.057	1.308	3.70	2.00		
III	1.890	1.160	3.27	1.79		
V	1.890	1.142	3.23	1.78	97°20′	130°14′
VI	2.038	1.142	3.23	1.84	102°34′	121°58′
VII	1.981	1.142	3.23	1.82	100°39′	125°6′
VIII	1.959	1.142	3.23	1.81	99°54′	126°20′

Models VII and VIII lead to the following values of the interatomic distances and valence angles

Model VII	Model VIII
As–As = 3.20 Å.	As–As = 3.20 Å.
As–O = 1.80 Å.	As–O = 1.79 Å.
O–As–O = 100°39′	O–As–O = 99°54′
As–O–As = 125°6′	As–O–As = 126°20′

The radial distribution method applied to the As_4O_6 photographs gives a curve with maxima at 1.82 and 3.21 Å. corresponding to the values given above for the distances in the molecule. The curve for this calculation is given in Fig. 2. In Fig. 3 the theoretical intensity curves for As_4O_6 are
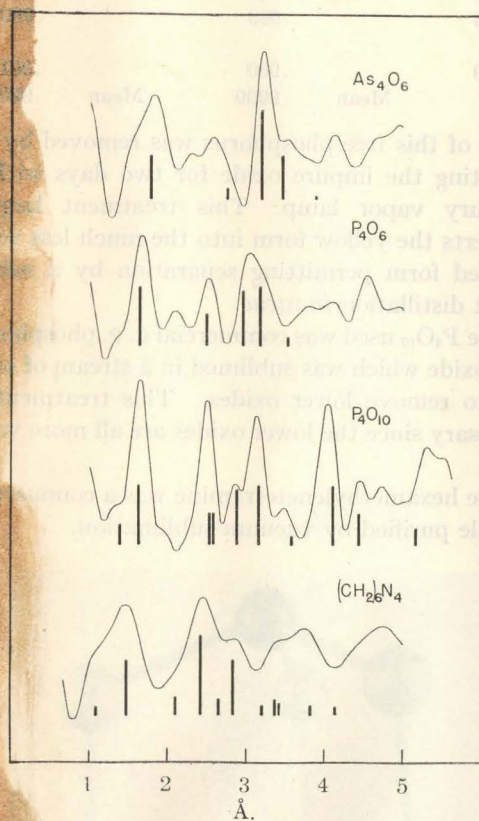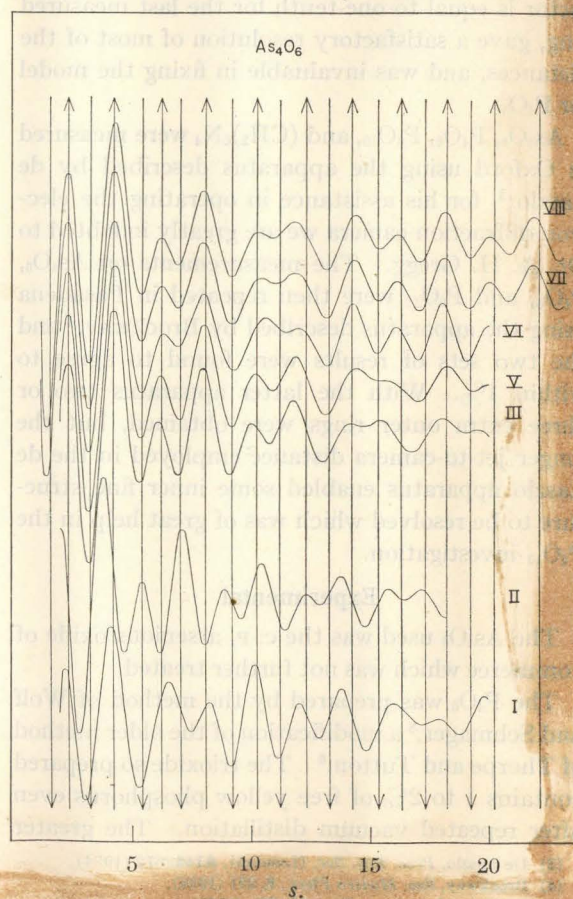
Fig. 2.—Radial distribution curves.

In Table II the parameters of all the models for which intensity curves were calculated are given.

Models VII and VIII are both satisfactory since both are in qualitative agreement with the photographs. Model V is not satisfactory because for it the eighth maximum becomes a shelf, and model

Fig. 3.—Calculated intensity curves for As_4O_6.

TABLE III

Max.	Min.	I	c	s_0	$s(VI)$	$s(VIII)$	s_{VI}/s_0	s_{VIII}/s_0
1				1.803	1.60	1.62	(0.887)	(0.899)
	1	12		2.659	2.49	2.47	(.936)	(.929)
	2			3.581	3.40	3.39	.949	.947
2		10	8	4.591	4.57	4.56	.995	.993
	3			5.623	5.86	5.91	(1.042)	(1.051)
3		1	2	6.641	6.30	6.30	0.949	0.949
	4			7.542	7.08	7.02	.939	.931
4		5	20	8.514	8.39	8.37	.985	.983
	5			9.634	9.70	9.68	1.007	1.005
5		1	6	10.687	10.72	10.71	1.003	1.002
	6			11.820	11.23	11.19	0.950	0.947
6		2	16	12.863	12.49	12.42	.971	.966
	7			14.319	14.09	14.05	.984	.981
7		2	18	15.548	15.69	15.62	1.009	1.005
	8				16.95	16.84		
8		1			17.70	17.58		
	9				18.52	18.44		
9		2	16	19.90	19.71	19.63	0.990	0.9866
						Mean	.9802	Mean .9769

given. As final values of the distances the following are given:

As–As = 3.20 ± 0.03 Å.   As–O–As = 126 ± 3°
As–O = 1.80 ± 0.02 Å.   O–As–O = 100 ± 1.5°

Maxwell, Hendricks and Deming[1] give As–As = 3.20 ± 0.05 Å. They were unable to fix the oxygen parameter because of the much greater scattering power of the As atoms. Fair agreement was found with the oxygen valence angle As–O–As equal to 120°, 127.5° or 140°.

Phosphorus Trioxide.—The models used for P_4O_6 are of the same type as for As_4O_6. The four P atoms are at positions (v,v,v), $(\bar{v},\bar{v},v)$, $(\bar{v},v,\bar{v})$, and $(v,\bar{v},\bar{v})$, and the six O atoms at $(\pm u,0,0)$, $(0,\pm u,0)$, and $(0,0,\pm u)$.

The photographs of P_4O_6 show nine maxima, eight of which are measurable. The first, second and fourth maxima are strong; the second maximum is followed by a weak, almost shelf-like maximum; the sixth and seventh maxima are strong, of nearly equal intensity, separated by a broad and deep minimum; and the minimum following the weak eighth maximum is slightly deeper than that which precedes.

The values of s_0 for the maxima and minima and the estimated intensities of the maxima are given in Table III. Values of the parameters of models for which theoretical intensity curves were calculated are listed in Table IV.

Models VI and VIII were found to be in satisfactory qualitative agreement with the photographs. Model VII is unsatisfactory because the minimum following the eighth maximum has

become weaker than that which precedes. Also any model with the value of the parameter u greater than that of model VIII would make this same minimum too deep in comparison with the preceding one.

TABLE IV

Model	u	v	P–P	P–O	O–P–O	P–O–P
IV	1.600	1.064	3.010	1.597	90°11′	140°48′
I	1.664	1.064	3.010	1.620	93°10′	136°31′
V	1.750	1.064	3.010	1.654	96°53′	130°59′
VII	1.780	1.064	3.010	1.666	98°6′	129°6′
VI	1.800	1.064	3.010	1.675	98°50′	127°52′
VIII	1.820	1.064	3.010	1.684	99°41′	126°39′
III	1.900	1.064	3.010	1.721	102°36′	121°53′
II	2.128	1.064	3.010	1.843	109°28′	109°28′

Models VI and VIII lead to the following values of the interatomic distances:

Model VI
P–P = 2.95 Å.
P–O = 1.64 Å.
O–P–O = 98°50′
P–O–P = 127°52′

Model VIII
P–P = 2.94 Å.
P–O = 1.65 Å.
O–P–O = 99°41′
P–O–P = 126°39′

A final choice of model must lie between models VI and VIII, possibly favoring model VI. This leads to the final values of the distances:

P–P = 2.95 ± 0.03 Å.
P–O = 1.65 ± 0.02 Å.
O–P–O = 99° ± 1°
P–O–P = 127.5 ± 1°

The results given by Maxwell, Hendricks and Deming[1] are:

P–P = 3.00 ± 0.05 Å.
P–O = 1.67 ± 0.03 Å.
P–O–P = 128.5 ± 1.5°

Radial distribution calculations result in a curve (Fig. 2) with maxima corresponding to interatomic distances of 1.66 and 3.03 Å. The theoretical intensity curves for P_4O_6 are given in Fig. 4.
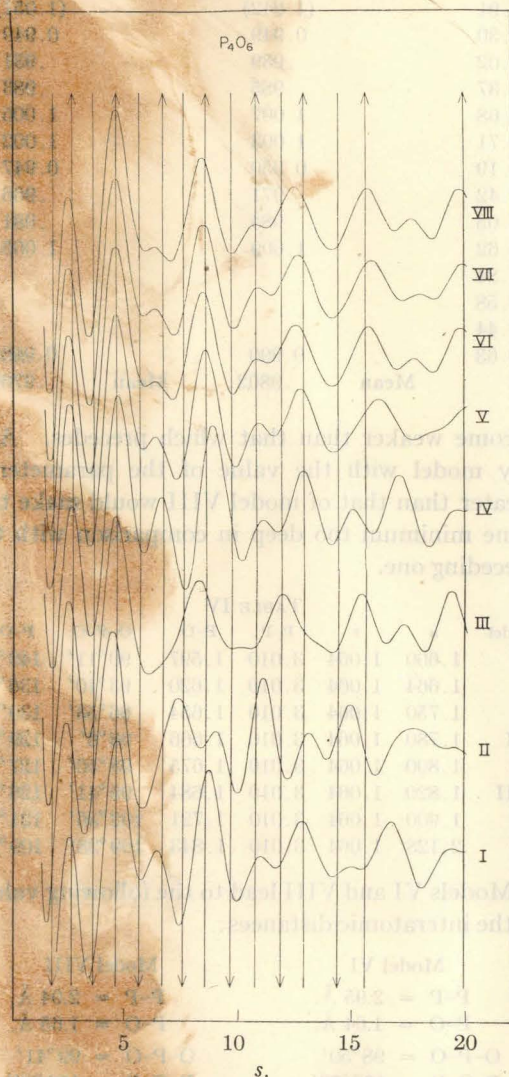

Fig. 4.—Calculated intensity curves for P_4O_6.

Phosphorus Pentoxide.—The photographs taken show eleven measurable maxima. The second maximum is the strongest and is followed by a shelf with no observable minimum interposed; and the third maximum is moderately strong and is followed by a broad shelf-like region. On photographs which were taken using a longer jet-to-camera distance (28.0 cm.) this shelf appears as two very weak maxima with poorly marked minima interposed. With the shorter camera distance (10.85 cm.) the doublet is not resolved. Following the eighth measured maximum there is another doublet of which only the outer ring is measurable. The second ring of this doublet is followed by a fairly pronounced minimum and a much stronger maximum. The last measured maximum is broad, and is preceded by a well marked minimum. The minima immediately preceding and following the weak seventh maximum are both weak, the outermost being possibly a little deeper. The measured values of s_0 of the maxima and minima and the estimated intensities of the maxima are listed in Table V. In Table VI the models for which theoretical intensity curves were calculated are listed.

TABLE V

Max.	Min.	I	c	s_0	s (XIV)	s_{XIV}/s_0
1		10	2	2.823	2.82	(0.999)
	1			3.965	3.75	(.946)
2		15	17	5.015	4.91	.979
	2	Absent				
3		5	10	6.300	6.20	.984
	3			7.215	7.05	.977
4		8	35	8.345	8.50	1.019
	4			9.86		
	2		16	11.102	11.00	0.991
	5			12.097	11.72	.969
6		3	31	12.922	12.76	.988
	6			13.730	13.72	.999
7		1	12	14.491	14.25	.983
	7			15.351	14.84	.967
8		2	27	16.043	15.86	.989
	8	Not measurable				
9		1	14	18.645	18.46	.990
	9			19.662	19.24	.979
10		2	27	20.470	20.23	.988
	10			21.525	21.38	.993
11		1	12	22.943	23.00	1.003
					Mean	0.9873

TABLE VI

Model	a	b	c	P-P	P-O	P-O'	OPO	POP
I	1.064	1.820	2.011	3.01	1.68	1.64	99°41'	126°39'
III	0.910	1.820	1.926	2.57	1.58	1.76	109°28'	109°28'
IV	.903	1.867	1.919	2.56	1.60	1.76	111°12'	106°4'
V	.923	1.785	1.943	2.61	1.57	1.77	107°24'	112°50'
VI	1.030	1.785	1.830	2.91	1.64	1.39	100°38'	125°24'
VII	1.018	1.805	1.844	2.88	1.64	1.43	102°18'	122°40'
VIII	0.992	1.720	2.008	2.81	1.58	1.76	100°36'	125°15
IX	.993	1.840	1.795	2.81	1.64	1.39	104° 0'	117°46'
X	1.045	1.750	1.830	2.96	1.64	1.36	98° 0'	129°14'
XI	1.022	1.795	1.829	2.89	1.64	1.40	101°30'	123°42'
XII	1.040	1.795	1.829	2.94	1.65	1.40	100°18'	125°39'
XIII	1.020	1.800	1.836	2.88	1.64	1.41	101°49'	123°12'
XIV	1.018	1.792	1.827	2.88	1.63	1.40	101°39'	123°28'

All of the models are for the four P atoms at positions (a,a,a), ($\bar{a}$,$\bar{a}$,a), ($\bar{a}$,a,$\bar{a}$), and (a,$\bar{a}$,$\bar{a}$), six O atoms at positions ($\pm$b,0,0), (0,$\pm$b,0), and (0,0,$\pm$b), and the remaining four O atoms at the positions (c,c,c), ($\bar{c}$,$\bar{c}$,c), ($\bar{c}$,c,$\bar{c}$), and (c,$\bar{c}$,c). Models XI, XIII and XIV are all satisfactory in

their qualitative agreement with the photographs. Model XIV is roughly the mean of models XI and XIII, and it has been used for the final calculations of the interatomic distances of the molecule. The following distances result from these calculations:

P–P	= 2.84 ± 0.03 Å.	OPO	= 101.5 ± 1°
P–O	= 1.62 ± 0.02 Å.	POP	= 123.5 ± 1°
P–O′	= 1.39 ± 0.02 Å.	OPO′	= 116.5 ± 1°

The angle designated by OPO′ is the angle formed by the P atom at (a,a,a) and the O atoms at (b,0,0) and (c,c,c) (Fig. 5). It may be seen from an inspection of the models listed that the valence angles are very closely limited. Model XII differs from model XI only in the phosphorus coördinates, causing a change in the P valence angle of only about one degree, but it is not in qualitative agreement with the photographs in that for it the shelf-like region following the fourth maximum has become a real maximum with a preceding minimum. The short P–O′ distance is also fixed closely by the disagreement of model VII. This model differs from the satisfactory models only in that the coördinates of the outer four O atoms are changed by a very small amount.
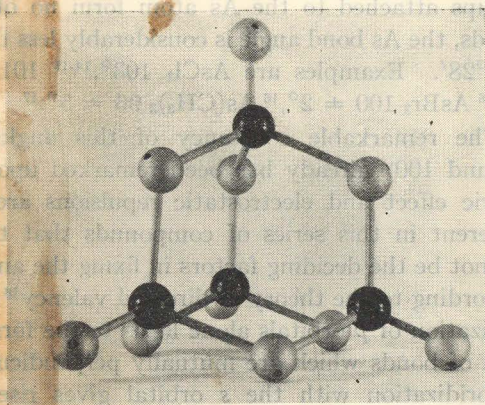
Fig. 5.—Photograph of model of P_4O_{10}. The black balls represent P; the silver balls represent O.

The modified radial distribution method suggested by Dr. Schomaker gave a remarkably good resolution of the various peaks, nearly all the interatomic distances in the molecule appearing as separate maxima. The curve is shown in Fig. 2. From the data which it provided, the three parameters could be determined within narrow limits, these parameters agreeing well with those chosen for the final model.

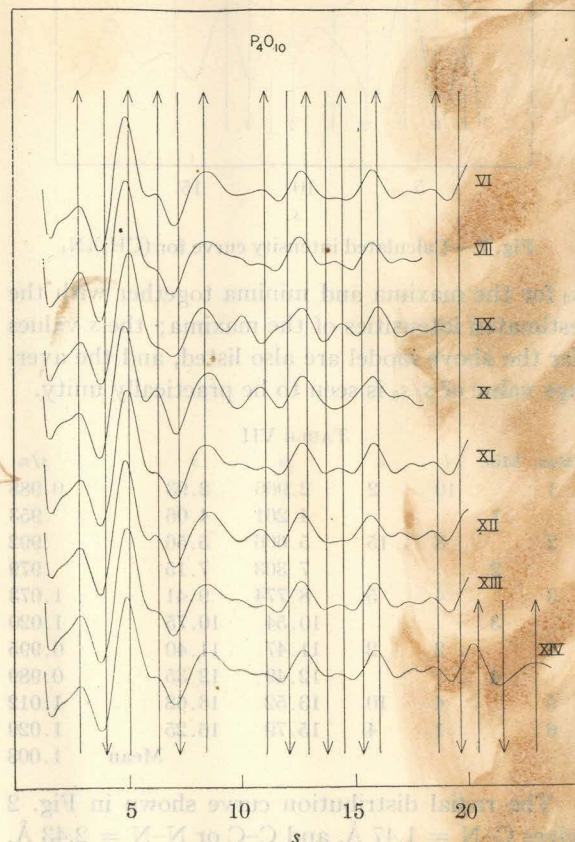The theoretical intensity curves for the models of Table VI are shown in Fig. 6.

Fig. 6.—Calculated intensity curves for P_4O_{10}.

Hexamethylenetetramine.—The photographs of this substance were taken using a long jet-to-camera distance and show six maxima. The first two are strong, the third broad and diffuse, the fourth very weak, the fifth fairly strong and the sixth very weak.

The hexamethylenetetramine model is essentially the same as that for P_4O_6 and As_4O_6. Four N atoms are in positions (v,v,v), $(\bar{v},\bar{v},v)$, $(\bar{v},v,\bar{v})$ and $(v,\bar{v},\bar{v})$, six C atoms in positions $(\doteq u,0,0)$, $(0,\doteq u,0)$ and $(0,0,\doteq u)$ and the twelve H atoms in positions $(x,\bar{x},z)$, $(\bar{x},x,z)$, etc. The hydrogen parameter could not be deduced from the photographs and an assumed value of 1.09 Å. for the C–H distance was used in computing the theoretical intensity curves. A model in which all the angles had the regular tetrahedral value of 109.5° and with a C–H distance of 1.48 Å. (N–N or C–C = 2.42 Å.) was found to agree well with the photographs. The curve for this model is shown in Fig. 7. Table VII gives the measured values of
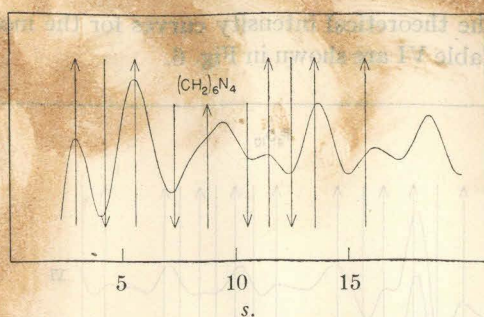
Fig. 7.—Calculated intensity curve for $(CH_2)_6N_4$.

s_0 for the maxima and minima together with the estimated intensities of the maxima; the s values for the above model are also listed, and the average value of s/s_0 is seen to be practically unity.

TABLE VII

Max.	Min.	I	c	s_0	s	s/s_0
1		10	2	2.966	2.93	0.988
	1			4.261	4.06	.953
2		8	15	5.606	5.56	.992
	2			7.303	7.15	.979
3		4	5	8.774	9.41	1.073
	3			10.54	10.75	1.020
4		2	2	11.47	11.40	0.995
	4			12.49	12.35	0.989
5		4	10	13.52	13.68	1.012
6		1	4	15.79	16.25	1.029
					Mean	1.003

The radial distribution curve shown in Fig. 2 gives C–N = 1.47 Å. and C–C or N–N = 2.43 Å. agreeing well with the above model.

Discussion of Results

Of the substances reported in this paper, two, hexamethylenetetramine and arsenious oxide, have been studied in the solid form. Hexamethylenetetramine crystallizes in a body-centered cubic lattice, Dickinson and Raymond[7] reporting a regular tetrahedral arrangement of valences with C–N = 1.44 Å. Gonell and Mark[8] gave C–N = 1.48 Å. and C–C = 2.58 Å., and this same type of structure has also been confirmed by Wyckoff and Corey,[9] who give C–N = 1.42 ± 0.08 Å. The sum of the covalent single-bond radii[10] of carbon and nitrogen is 1.47 Å. in good agreement with the value which we find here.

Arsenolite, cubic As_4O_6, was reported by Bozorth[11] to be a lattice of As_4O_6 molecules in a diamond-type arrangement. Both the As and the O

valence angles are tetrahedral in this solid, the As–As distance 3.28 Å. and the As–O distance 2.01 Å. There are two strong bonds for each O atom to two As atoms in the same molecule, and two weak bonds to two As atoms of a neighboring molecule. This attraction between neighboring molecules apparently draws the O atom out, increasing the As–O distance and decreasing the oxygen valence angle from the values observed for the vapor molecule to those observed in the solid. To a smaller extent this applies to the As atoms too, since each forms three strong bonds to oxygens in the same molecule and three weak bonds to oxygens of adjacent molecules. A redetermination of the crystal parameters was made by Harker and Eskijian[12] in these Laboratories confirming the older values but fixing them more closely (to within about 0.03 Å.).

Arsenic apparently has a tendency to form bonds at angles smaller than the tetrahedral angle, as As_4O_6 is not unique in this respect. In this compound where the atoms form closed rings it might be thought that the As valences are strained into taking up this angle because of the tendency of the oxygen angle to expand beyond the tetrahedral value[13] but even in compounds where the groups attached to the As atom form no other bonds, the As bond angle is considerably less than 109°28′. Examples are $AsCl_3$ 103°,[14,15] 101 ± 4°,[16] $AsBr_3$ 100 ± 2°,[16] $As(CH_3)_3$ 96 ± 5°.[17]

The remarkable constancy of this angle of around 100° already has been remarked upon.[16] Steric effect and electrostatic repulsions are so different in this series of compounds that they cannot be the deciding factors in fixing the angle. According to the theory of directed valency[18] the utilization of p orbitals alone leads to the formation of bonds which are mutually perpendicular. Hybridization with the s orbital gives rise to stronger bonds which, if hybridization is complete, as with carbon compounds, are at an angle of 109°28′. If, however, there are unshared electrons, as in the case we are considering, hybridization may not be complete, for there are two opposing tendencies. On the one hand, hybridization tends to stabilize the bonds but at the same

(7) Dickinson and Raymond, THIS JOURNAL, **45**, 22 (1923).
(8) Gonell and Mark, Z. physik. Chem., **107**, 181 (1923).
(9) Wyckoff and Corey, Z. Krist., **89**, 462 (1934).
(10) Pauling and Huggins, ibid., **87**, 205 (1934).
(11) Bozorth, THIS JOURNAL, **45**, 1621 (1923).

(12) Unpublished work.
(13) Sutton and Hampson, Trans. Faraday Soc., **31**, 945 (1935).
(14) Brockway and Wall, THIS JOURNAL, **56**, 2373 (1934).
(15) Pauling and Brockway, J. Chem. Phys., **2**, 867 (1934).
(16) Gregg, Hampson, Jenkins, Jones and Sutton, Trans. Faraday Soc., **33**, 852 (1937).
(17) Springall and Brockway, THIS JOURNAL, **60**, 996 (1938).
(18) Pauling, ibid., **53**, 1367 (1931).

time this means that the unshared electrons also tend to become hybridized between the s and p orbitals, whereas the unshared pairs of electrons are always most stable when they occupy the s orbitals. As usual the actual configuration taken up is that which gives the lowest energy.

The sum of the covalent single-bond radii[10] of arsenic and oxygen is 1.87 Å. The decrease from the sum of the radii to the observed value of 1.80 Å. may be explained as the result of double bond character caused by unshared pairs from the oxygen atoms forming double bonds with the As atoms.[14-16] The value $126 \pm 3°$ which is observed for the oxygen angle is close to $125°16'$, the angle between a double and a single bond on the regular tetrahedral model.

Phosphorus, like arsenic, shows a tendency to form bond angles less than the tetrahedral angle. In P_4O_6 it is found to be 99°. In other substances where the groups attached form no other bonds the same behavior is noted. Examples are PF_3 $99 \pm 4°$,[14] PCl_3 $100 \pm 2°$,[14] PBr_3 $100 \pm 2°$,[16] PI_3 $98 \pm 4°$,[16] $POCl_3$ $104°$,[19] $P(CH_3)_3$ $100 \pm 4°$.[17]

The sum of the covalent radii[10] for phosphorus and oxygen is 1.76 Å. Again the observed value is lower presumably because of double-bond character, as with As_4O_6.

In P_4O_{10} the phosphorus angles are 101.5 and 116.5°. The latter angle is that between an outer oxygen atom and one within the P_4O_6 "kernel." Addition of this outer oxygen atom has had very little effect on the other bond angles and this might have been anticipated from the values given for PCl_3 and $POCl_3$. The most startling feature of the P_4O_{10} molecule is the unusually short distance of 1.39 Å. between each P atom and the "extra" O atom. The value found is about 79% of the sum of the single bond radii (1.76 Å.) and is approximately that expected for a triple bond between the two atoms. A similar anomaly has been observed in thiophosphoryl chloride, $PSCl_3$,[20] where the P–S distance is found to be 1.94 Å. instead of the normal single bond distance of 2.14 Å. It is clear that double bond character in a structure such as $O=P\diagdown\overset{O-}{\underset{O-}{}}$, I, is not sufficient to explain such a large shortening as is observed. The addition of four extra oxygen atoms to P_4O_6 has very little effect on the dimensions of this P_4O_6 "kernel," and since we have

postulated single-double bond resonance in P_4O_6, it seems reasonable to conclude that it also occurs in P_4O_{10}. The important systems are probably II and III in resonance with I.
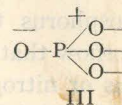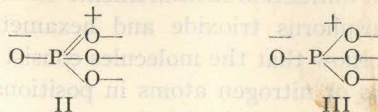
There is another piece of evidence which favors this conclusion. In P_4O_6 the contribution of a double-bonded structure IV was postulated to explain the short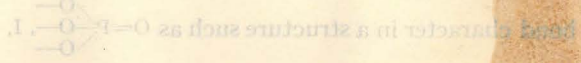ening of the P–O bond below the single bond value. In this structure the phosphorus and oxygen atoms carry opposite charges and so there is no "formal charge effect"[21] influencing the bond length. On the other hand, in structures II and III of P_4O_{10} the positive charge on the oxygen or phosphorus atom is not compensated by a negative charge within the P_4O_6 "kernel" and hence because of the increased effective nuclear charge we should expect the bond length to be diminished. The P–O distance in P_4O_6 is 1.65 Å. and the corresponding distance in P_4O_{10} is indeed shorter, being 1.62 Å. The difference may be due to experimental error, although in view of the above argument it may be of some significance. As regards the other P–O distance having the extremely low value of 1.39 Å., the "formal charge effect" in structure II (negative charge on the oxygen, no charge on the phosphorus) would lead one to expect an increase rather than a decrease. One is forced to conclude that the predominant factor here must be the polar character of the bond. In discussing $PSCl_3$, Beach and Stevenson[20] ruled out any effect of ionic character and formal charges on the length of the bond, but concluded that the shortening of the P–S distance must be due to a considerable (about one half) contribution of $S-P\diagdown\overset{Cl^+}{\underset{Cl}{-Cl}}$ without, however, giving any reasons. The short P–O distance in P_4O_{10} is in accord with the chemical properties of this molecule. Such short bonds are presumably extremely stable, and the thermal stability and resistance to reduction of P_4O_{10} are well known.

We wish to express our thanks to Professor Brockway, Professor Pauling and Professor Sidgwick for their help and interest in this work,

(19) Brockway and Beach, THIS JOURNAL, **60**, 1836 (1938).
(20) Beach and Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).
(21) Elliott, THIS JOURNAL, **59**, 1380 (1937).

and the Commonwealth Fund for a Fellowship to one of us (G. C. H.).

Summary

Electron diffraction measurements on arsenious oxide, phosphorus trioxide and hexamethylenetetramine show that the molecules consist of four phosphorus or nitrogen atoms in positions (vvv) ($\overline{v}\overline{v}v$) ($v\overline{v}\overline{v}$) and ($v\overline{v}v$) and six oxygen atoms or methylene groups in the positions ($\pm$u00) (0$\pm$u0) and (00$\pm$u). In phosphorus pentoxide there are four additional oxygen atoms in the positions (www) ($\overline{w}\overline{w}w$) ($\overline{w}w\overline{w}$) and ($w\overline{w}\overline{w}$).

The interatomic distances and angles are: for As_4O_6, As–O = 1.80 $\pm$ 0.02 Å., O–As–O = 100 $\pm$ 1.5°, As–O–As = 126 $\pm$ 3°, for P_4O_6, P–O = 1.65 $\pm$ 0.02 Å., O–P–O = 99 $\pm$ 1°, P–O–P = 127.5 $\pm$ 1°, for $N_4(CH_2)_6$, C–N = 1.47 $\pm$ 0.02 Å., C–N–C = N–C–N = 109.5°, for P_4O_{10}, P–O = 1.62 $\pm$ 0.02 Å., P–O' = 1.39 $\pm$ 0.02 Å., O–P–O = 101.5 $\pm$ 1°, P–O–P = 123.5 $\pm$ 1° and O–P–O' = 116.5 $\pm$ 1°.

The shortening of the bond distances in As_4O_6, P_4O_6 and P_4O_{10} below the theoretical single-bond values is attributed to single-bond double-bond resonance. It is concluded that the abnormally low value of 1.39 Å. for the P–O' bond in P_4O_{10} is due to the polar character of the bond.

THE DETERMINATION OF THE MOLECULAR STRUCTURE OF TETRANITROMETHANE
BY THE ELECTRON DIFFRACTION METHOD

Because of the unusual properties of tetranitromethane and the conflicting views with regard to its structure, it was felt that an electron diffraction investigation of it would be desirable.

The samples of the compound used in this investigation came from two sources; one sample was purchased from Kahlbaum, and the other sample was made according to the method of Chattaway.[1] Both samples were subjected to successive vacuum fractionations until the first, last, and middle fractions had the same vapor pressure, in agreement with the values found by Menzies.[2]

The electron diffraction photographs showed seven measurable rings. The measured values of $s_o = \frac{4\pi}{\lambda} \sin \frac{\Theta}{2}$ for the maxima and minima, the estimated visual intensities, and the coefficients of the modified radial distribution function are listed in Table I. In the above expression for s_o, λ is the de Broglie wave length of the electrons, and Θ is the scattering angle. The coefficients c_o were obtained from the estimated visual intensities I_o by multiplying the latter by $s_k^2 e^{-a s_k^2}$, where s_k is the value of s_o for the k'th ring, the value of "a" being chosen such that the exponential factor is equal to 0.1 for the last ring.

In all of the assumed models for which intensity curves were calculated, there are four nitro groups attached to the central carbon atom at tetrahedral angles, i.e. $\angle N_1 C N_2 = 109°28'$. The assumed values of C-N = 1.46 Å, N-O = 1.21 Å, and the $\angle$ O-N-O = 127° are those found by Brockway, Beach and Pauling[3] for nitromethane.

Table I

Max.	Min.	I	c_0	s_0	s_{VII}/s_0
	1			1.76	(0.920)
1		8	4	2.79	(0.903)
	2			4.50	1.000
2		10	24	5.83	1.033
	3			7.02	1.027
3		3	12	7.81	1.001
	4			8.63	1.008
4		3	15	9.43	1.027
	5			10.45	0.996
5		4	25	11.71	0.997
	6	Not accurately measurable			
6		2	15	17.20	0.994
	7			19.10	1.021
7		1	6	21.70	1.018
				Mean	1.011

After assuming the previous dimensions and configuration of the nitro groups and the disposition of the C-N bonds, there remains the possibility of twisting the nitro groups about their respective C-N bond directions. In all models the nitro groups were twisted in phase, i.e. in such a manner as to keep the oxygen atoms of adjacent nitro groups as far apart as possible, all groups being given the same angle of twist φ . Figure I is a sketch of the molecule for $\varphi = 0°$. Figure II shows the equilibrium configuration of the molecule which is finally accepted as the result of this investigation.

Models I to III are static models, the nitro groups remaining at a fixed angle φ . In models IV and V the nitro groups were assumed to be in rotatory oscillation about the position $\varphi = 0°$ with oscillation amplitudes of 30° and 40° respectively. The character of the oscillation was assumed to be of the form $\varphi = \varphi_0 \sin 2\pi t$, an obviously idealized formulation, which however is probably as good as any other simple
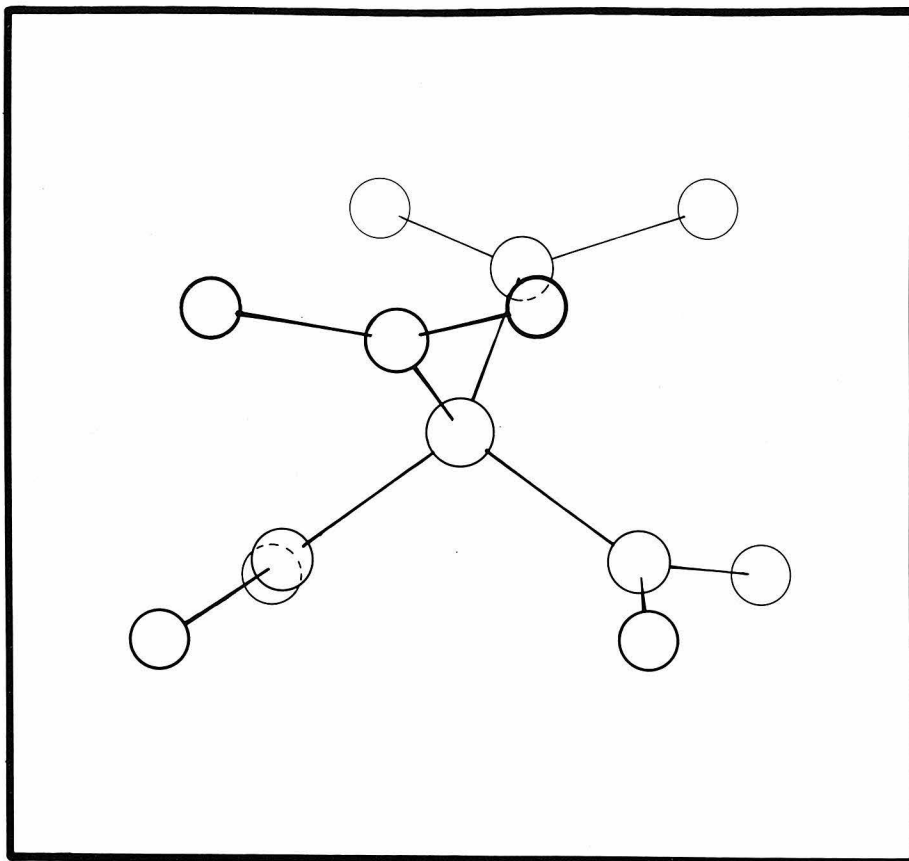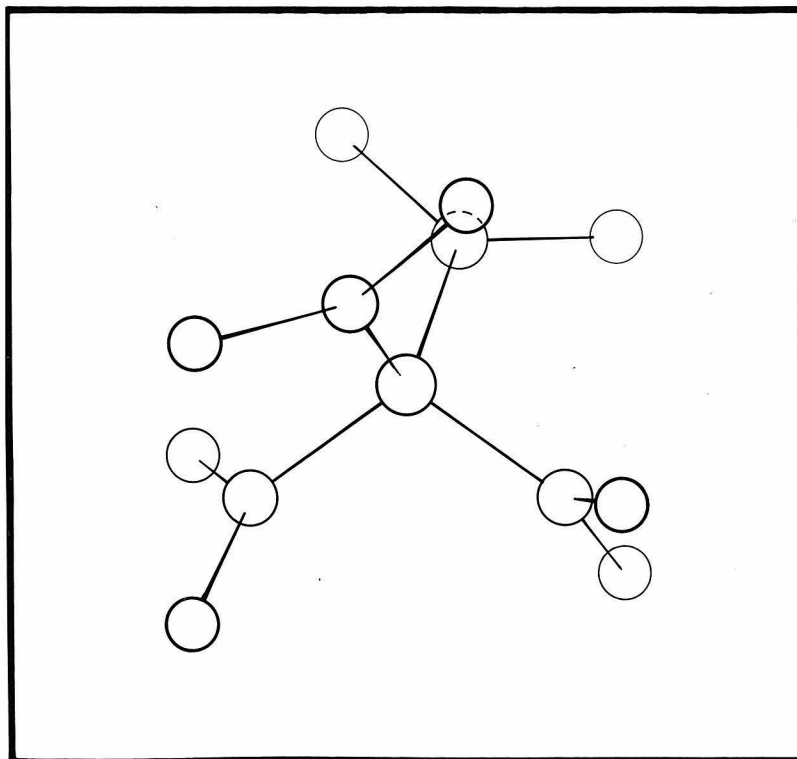
FIG. I

FIG. II

approximation that can be made. The range of oscillation was divided into three "time equal" sub-intervals: $-\varphi_o$ to $-\varphi_o/2$, $-\varphi_o/2$ to $+\varphi_o/2$, and $+\varphi_o/2$ to $+\varphi_o$. In accordance with the assumed character of the oscillation the group spends equal times in each of these ranges. Time average values of φ were calculated for each of these intervals, and interatomic distances were calculated for each range using the average φ for the range. It is to be noted that the distances so calculated are not time average distances, but distances calculated from a time average angle. In making the intensity curve calculation by the approximate formula $I = \sum_i \sum_j Z_i Z_j \dfrac{\sin sl_{ij}}{sl_{ij}}$, the coefficients for the φ dependent distances were divided equally among the three ranges of φ.

It became apparent that models I to V all showed more maxima and minima in the region beyond $s_o = 10$ than the photographs did, and that no obvious change in the above type of model would alter this. It was suggested by Dr. Schomaker of these laboratories that the usually discarded temperature factor e^{-A} in the intensity formula ought to be retained for molecules with changing distances. The intensity formula including the temperature factor is[4]:

$$I = \sum_i \sum_j Z_i Z_j \frac{\sin sl_{ij}}{sl_{ij}} e^{-A_{ij}}$$

in which $A_{ij} = 1/2 \overline{(\delta r_{ij})^2} s^2$, and $\overline{(\delta r_{ij})^2}$ is the mean square variation of the distance r_{ij}. The effect of the temperature factor is to make the widely varying distances increasingly less important as the scattering angle increases.

In order to test this suggestion an intensity calculation was made in which only the φ invariant distances were included. If thermal motion of the nitro groups is great, such a calculation should show better agreement with the photographs in the region of large s_o values

since the temperature factor makes all φ dependent distances un-
important for large values of s_0. The curve resulting from this
calculation (Model VI) is shown in Figure III, and is in excellent
qualitative agreement with the photographs beyond $s_0 = 10$.

Since Model III showed the best qualitative agreement in the region
out as far as $s_0 = 10$, a model was assumed in which the nitro groups
oscillated with an amplitude of $20°$ about the position of $30°$ twist;
i.e. $\varphi = 30° + 20° \sin 2\pi t$. For the calculation of approximate values
of $\overline{(\delta r_{ij})^2}$ the oscillation range was divided into three time equivalent
ranges as before. A time average φ was calculated for each range as
before, and interatomic distances calculated from these average angle
values. The deviations from the $\varphi = 30°$ distances were then squared
and the mean taken. The approximation involved in this calculation of
mean square deviations is probably no more objectionable than is the use
of a temperature factor derived for small displacements. In making the
intensity calculation the l_{ij} values (interatomic distances) used were
those for the equilibrium configuration of $\varphi = 30°$, and the coefficients
including the temperature factor were calculated for each integral value
of s_0. No detectable discontinuities in the curves are caused by these
changes of coefficients. The model just described appears as Model VII
in Figure III.

In a similar manner Models VIII and IX were calculated for angles
of twist of $0°$ and $25°$ and oscillation amplitudes of $30°$ and $20°$
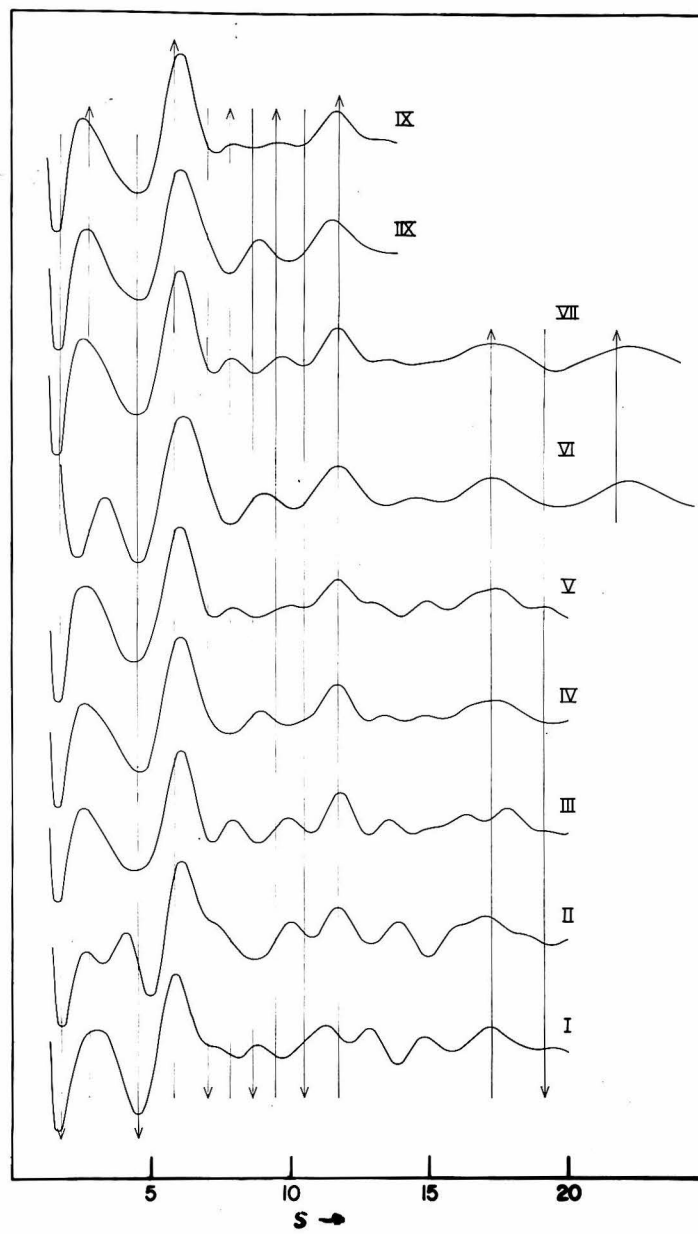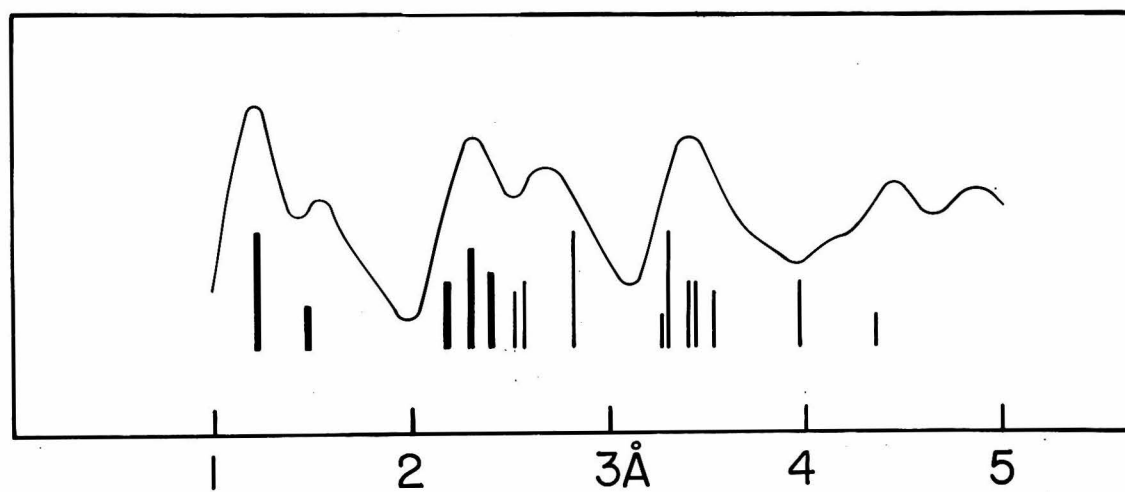respectively. Table II is a list of the various assumed models.

FIG. III

S →

FIG. IV

Table II

Model	Type	Equil. Pos'n.	Amplitude
I	Static	0°	0°
II	Static	90°	0°
III	Static	30°	0°
IV	Oscillating; no temperature factor	0°	30°
V	Oscillating; no temperature factor	0°	40°
VI	Independent distances only	-	-
VII	Oscillating; temperature factor	30°	20°
VIII	Oscillating; temperature factor	0°	30°
IX	Oscillating; temperature factor	25°	20°

In all models C-N = 1.46 Å, N-O = 1.21 Å, $\angle$ O-N-O = 127°, and $\angle$ N-C-N = 109°28'.

The curve for Model VII best reproduces the observed data with regard to qualitative features. On the photographs the minimum following the fourth maximum appeared slightly deeper than the curve for Model VII indicates, but the over-all agreement is very satisfactory.

A quantitative comparison was next made; the values of s_{calc}/s_0 for Model VII are listed in Table I. After making the small change of scale the values of the interatomic distances and valence angles are:

$$C-N = 1.47 \pm 0.02 \text{ Å} \qquad \angle \text{ O-N-O} = 127°$$
$$N-O = 1.22 \pm 0.02 \text{ Å} \qquad \angle \text{ N-C-N} = 109°28'$$

Discussion:

The two oxygen atoms bonded to the same nitrogen atom are 2.18 Å apart, whereas the closest approach of oxygen atoms of different nitro groups varies from 2.48 Å to 2.73 Å as the angle of twist varies, the equilibrium distance being 2.57 Å. If it is remembered that 2.5 Å

is approximately the distance of closest approach of oxygen atoms not bonded to the same third atom as is indicated by numerous crystal structure investigations the reason for the nitro groups oscillating rather closely in phase about the apparent equilibrium position is evident.

Another model proposed by Mark and Noethling[5] on the basis of admittedly incomplete x-ray data had three nitro groups and a linear nitrite group, the molecule exhibiting point group symmetry C_{3v}, the three-fold axis coinciding with the linear axis of the nitrite group. The molecule which this investigation indicates as the correct one belongs to the tetragonal point group S_4. It is possible that the S_4 molecule is in a condition of almost free rotation in the crystal lattice at temperatures close to the melting point, thereby assuming a statistical symmetry which will meet the symmetry requirements of the space group determined by Mark and Noethling. Moreover, a linear nitrite group is very unlikely in the light of other structure deter- minations of nitrites, all of which indicate non-linear groups.

Another piece of evidence in favor of the symmetrical structure proposed in this paper is the zero dipole moment of the molecule. The investigations of Williams[6], and of Weissberger and Sangewald[7] both indicate a zero moment to within the accuracy of the experimental measurement.

The modified radial distribution method gave very little information. The only peak which was of much value was that at 1.21 $\overset{\circ}{A}$, which indicated the N-O distance quite accurately. The curve is shown in Figure IV. The heavy vertical lines indicate φ -independent distances, the thinner lines indicate φ -dependent distances. The lengths of the lines

indicate their relative importance at $s_o = 0$, the importance of the φ-dependent distances falling off rapidly with increasing s_o. In all cases the position is that of the equilibrium position for Model VII.

The observed C-N distance is just the sum of the covalent radii of carbon and nitrogen atoms, that is, 1.47 Å. The value 1.22 Å found for the N-O distance is considerably less than the sum of the single bond radii for nitrogen and oxygen which is equal to 1.36 Å. This value found in this investigation is within 0.01 Å of 1.23 Å, the value expected for 50% double bond character for the bond on the basis of resonance between the structures I and II below. There is apparently no pronounced additional shortening of the N-O bond caused by the formal charge of the nitrogen atom.

Summary:

A structure for tetranitromethane is proposed which is in agreement with electron diffraction data. In the model there are four nitro groups attached to the carbon atom at tetrahedral angles, the C-N distance is 1.47 ± 0.02 Å, the N-O distance is 1.22 ± 0.02 Å, and the angle O-N-O in the nitro group is 127°. In order to obtain satisfactory intensity agreement it was necessary to assume the nitro groups to be undergoing rotatory oscillation about the C-N bonds in such a way as to keep the oxygen-oxygen repulsions essentially minimized, and to include the usually omitted temperature factor in the approximate intensity formula.

THE ELECTRON DIFFRACTION INVESTIGATION OF
PHOSPHORUS SULFOXIDE, $P_4O_6S_4$

Phosphorus sulfoxide, $P_4O_6S_4$, was first reported by Thorpe and Tutton[8] in a paper giving the method of preparation of the compound and the results of vapor density measurements. Its mode of formation by direct reaction of P_4O_6 and the stoichiometric equivalent of free sulfur (a reaction paralleling the reaction of P_4O_6 and O_2) suggests that $P_4O_6S_4$ should be structurally similar to P_4O_{10}. The $P_4O_6S_4$ used in this investigation was prepared by the method referred to above, and was purified by a vacuum distillation, crystallization from CS_2, and a second vacuum distillation.

Electron diffraction photographs of the compound were made in the usual way, and were found to be excellent, showing thirteen measurable rings. The measured values of $s_o = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$ for the maxima and minima (in which λ is the de Broglie wave length of the electrons (about 0.06 Å), and θ the scattering angle), the visual intensities I_o, and the coefficients c_o of the modified radial distribution function are listed in Table I. These coefficients are the visually estimated intensities multiplied by $s_k^3 e^{-as_k^2}$, where s_k is the s_o value for the k'th ring, and "a" is chosen such that e^{-as^2} is equal to 0.1 for the last ring. The resulting numbers are normalized to one hundred for ease of computation. The radial distribution curve is presented in Figure I, the vertical lines indicating the distances found in the final model and their relative importance. The large peaks at 1.61 Å and 2.87 Å were immediately recognized as due to the bonded P-O distance and the non-bonded P-P distance respectively, since these are within a few hundredths of an Angstrom of the values found in a previous investigation of P_4O_{10}[9].
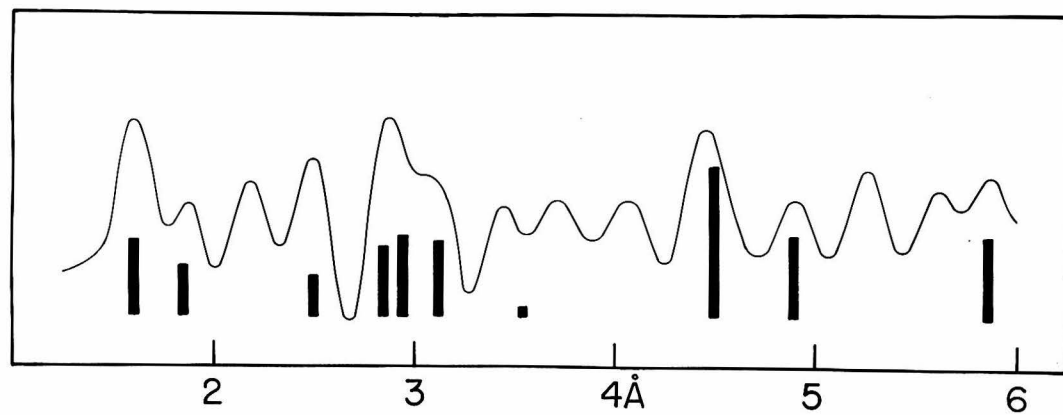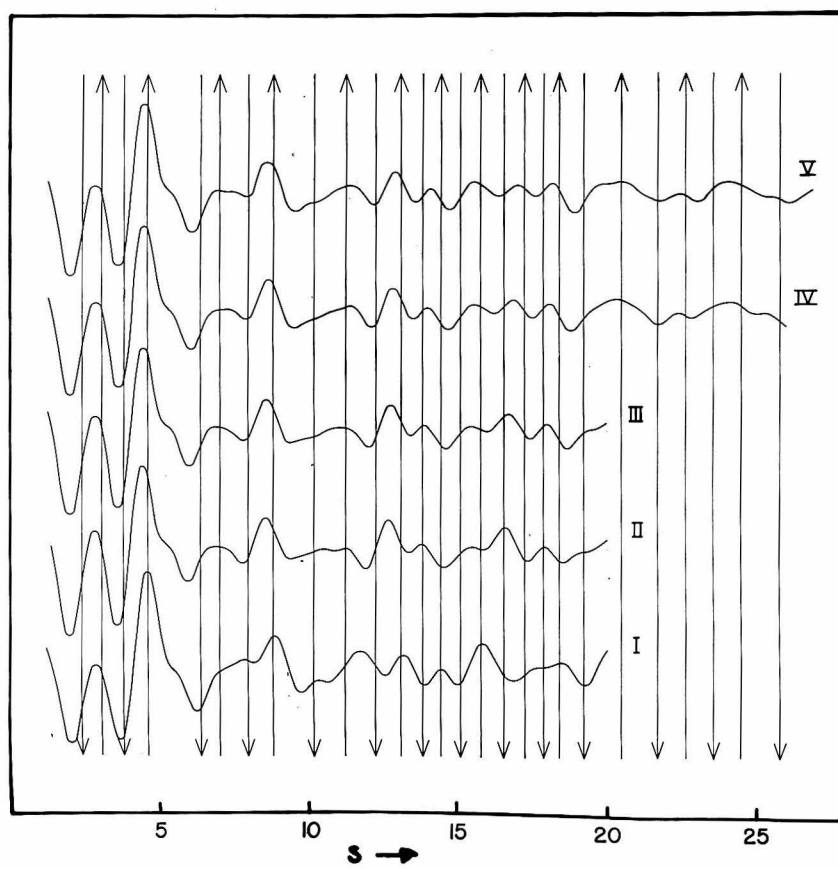
FIG. I

FIG. II

Table I

Max.	Min.	I_o	c_o	s_o	s_c/s_o
	1			2.43	(0.827)
1		10	1	3.10	(0.929)
	2			3.83	(0.948)
2		15	4	4.64	0.974
	3			Absent	
3				Shelf; not measured	
	4			6.45	0.960
4		5	4	7.09	0.994
	5			8.01	0.986
5		10	14	8.87	0.991
	6			10.21	0.979
6		4	9	11.26	0.995
	7			12.28	0.998
7		5	16	13.14	0.987
	8			13.87	0.984
8		2	7	14.49	0.977
	9			15.12	0.979
9		5	20	15.81	0.992
	10			16.55	0.995
10		3	14	17.26	0.989
	11			17.90	0.987
11		4	19	18.43	0.989
	12			19.24	0.986
12		5	24	20.49	0.991
	13			21.73	1.002
13		1	5	22.68	0.988
	14			23.57	0.977
14		2	8	24.46	0.984
	15			25.77	0.999

Mean 0.9867

Making use of the information obtained from the radial distribution curve, a series of models were calculated using the values of the P and O parameters for the P_4O_6 "kernel" as found in P_4O_{10} and varying only the S parameter. These models have four P atoms at (a,a,a), $(a,\bar{a},\bar{a})$, $(\bar{a},\bar{a},a)$, and $(\bar{a},a,\bar{a})$; six O atoms at $(\pm b,0,0)$, $(0,\pm b,0)$, and $(0,0,\pm b)$; and four S atoms at (c,c,c), $(c,\bar{c},\bar{c})$, $(\bar{c},\bar{c},c)$, and $(\bar{c},c,\bar{c})$. In $P_4O_6S_4$ the four S atoms are substituted for four O atoms in similar positions in P_4O_{10}, the molecule exhibiting symmetry T_d. A list of the models for which intensity calculations were made is presented in Table II. In making

Table II

Model	a	b	c	P-S	P-O	P-P
I	1.018	1.792	2.040	1.77	1.63	2.88
II	1.018	1.792	2.155	1.97	1.63	2.88
III	1.018	1.792	2.132	1.93	1.63	2.88
IV	1.018	1.792	2.115	1.90	1.63	2.88
V	1.018	1.792	2.098	1.87	1.63	2.88

In all models $\angle$ O-P-O = 101.5°, $\angle$ P-O-P = 123.5°,

$\angle$ O-P-S = 116.5° .

the intensity calculations the approximate intensity formula

$$I = \sum_i \sum_j z_i z_j \frac{\sin sr_{ij}}{sr_{ij}}$$

was used. The curves resulting from these calculations are shown in Figure II, the vertical arrows indicating the measured positions of the maxima and minima.

Characteristic features of the photographs are: a weak shelf following the second maximum; a marked broadness and asymmetry of the third, fifth, eleventh, and thirteenth maxima; a relatively closely spaced "triplet" between s_o = 15 and 19, with the middle ring slightly weaker than the outer two; and a very weak but measurable twelfth ring. It may be seen from the curves that model V best reproduces these features. The quantitative comparison of $s_{calc.}$ and s_o was made for model V, the values of s_c/s_o being listed in Table I. After changing the scale of the model as indicated by the s_c/s_o ratio the following distances are found for $P_4O_6S_4$:

P-O = 1.61 $\pm$ 0.02 Å $\qquad$ $\angle$ O-P-O = 101.5° $\pm$ 1°

P-P = 2.85 $\pm$ 0.03 Å $\qquad$ $\angle$ P-O-P = 123.5° $\pm$ 1°

P-S = 1.85 $\pm$ 0.02 Å $\qquad$ $\angle$ O-P-S = 116.5° $\pm$ 1°

Discussion:

The bonded distances P-O and P-S at 1.61 $\overset{\circ}{A}$ and 1.85 $\overset{\circ}{A}$ are both less than the respective covalent single bond values[10] of 1.76 $\overset{\circ}{A}$ and 2.14 $\overset{\circ}{A}$. The shortening of the P-O distance to 1.61 $\overset{\circ}{A}$ is to be ascribed to partial double bond character of the bond. Since the octet rule need not rigorously apply to elements beyond the first row of the periodic table, the following structures are permissible. It may be seen that none of them is in disagreement with the adjacent charge rule[11]. Since the P-S distance is considerable less than the double bond value

  I   II   III   IV

  V   VI   VII
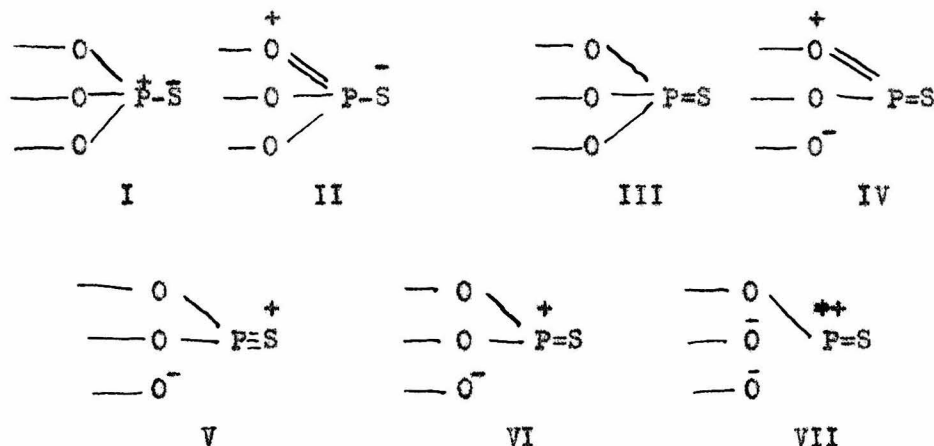
of 1.95 $\overset{\circ}{A}$, and since the P-O distance is also considerably shorter than the single bond value of 1.73 $\overset{\circ}{A}$ [10], it is probable that structure III represents to the first approximation the bonding arrangements, with considerable contributions of structures such as IV and V. Structures such as I and II probably do not contribute appreciably since these would tend to increase the P-S distance to the single bond value. It would appear that structure V must contribute to the resonance system if the shortening of the P-S bond below the double bond value is to be simple explained. Structures VI and VII could also result in a shortening of the P-S distance by a formal change effect.

A comparison of the P=O and P=S distances in various other phosphorus compounds is instructive.

Compound	P=O	Compound	P=S
P_4O_{10}	1.39^9	$P_4O_6S_4$	1.85
$POCl_3$	1.58^{12}	$PSCl_5$	1.94^{13}
$POFCl_2$	1.54^{12}		
POF_2Cl	1.55^{12}		
POF_3	1.56^{12}		

It is evident from the above table that the P=O and P=S bond type in P_4O_{10} and $P_4O_6S_4$ respectively is different from that in the phosphoryl and thiophosphoryl halides, and the inclusion of structure V may be considered justifiable.

The O-P-O valence angle of 101.5° is close to the value of the phosphorus angle in several other compounds, the decrease below the tetrahedral value of 109°28' being explainable by a greater degree of p orbital character than in normal sp^3 tetrahedral bonds. The change of the O-P-O angle from 99° in P_4O_6 [9] to 101.5° in $P_4O_6S_4$ and P_4O_{10} indicates that increasing the coordination of the phosphorus atom from three to four tends to make the valence angles become more like those of the tetrahedral PO_4^{---}.

Summary:

The structure of $P_4O_6S_4$ has been determined by electron diffraction in the gas phase. The molecule consists of four P atoms at (a,a,a), $(a,\bar{a},\bar{a})$, $(\bar{a},\bar{a},a)$, and $(\bar{a},a,\bar{a})$; six O atoms at $(\pm b,0,0)$, $(0,\pm b,0)$, and $(0,0,\pm b)$; and four S atoms at (c,c,c), $(c,\bar{c},\bar{c})$, $(\bar{c},\bar{c},c)$, and $(\bar{c},c,\bar{c})$. The valence angles and the principal interatomic distances are: P-O = 1.61 ± 0.02 Å, P-S = 1.85 ± 0.02 Å, P-P = 2.85 ± 0.03 Å, ∠O-P-O = 101.5° ± 1°, ∠P-O-P = 123.5° ± 1°, and ∠O-P-O = 116.5° ± 1°. Single-double bond and double-triple bond resonance is considered to

be the cause of the shortening of the P-O and P-S bond distances below the single and double bond values respectively.

Acknowledgment

The author wishes to acknowledge the helpful criticisms of Professor Linus Pauling.

THE SPACE GROUP AND UNIT CELL OF THE POTASSIUM
SALT OF NITROFORM

Potassium aci-nitroform, $KC(NO_2)_3$, was prepared from tetra-nitromethane and potassium ferrocyanide by the method of Chattaway and Harrison[14]. The yellow crystals obtained from water solutions are tetragonal bipyramids showing four prism faces.

Laue photographs taken with the x-ray beam parallel to a_3 and a_1 indicated that the crystals belong to the D_{4h} Laue class.

Rotation and oscillation photographs were taken with copper $K\alpha$ radiation (filtered through a 27μ nickel filter) with $[001]$, $[100]$, and $[110]$ vertical and normal to the x-ray beam. Layer line measurements on these photographs furnished approximate lengths for the axes. These values were refined by more precise measurements of equatorial reflections on the various photographs. The following unit cell was thereby determined:

$$a_1 = 11.31 \pm 0.01 \text{ Å}$$
$$a_3 = 8.77 \pm 0.01 \text{ Å}$$
$$Z = 8 .$$

The density of the crystals measured by flotation in a mixture of methylene iodide and benzene was found to be 2.23 ± 0.01. This density requires that there be 8.01 molecules in the unit found above.

The following reflection forms appeared on rotation, oscillation, or Laue photographs only under the following conditions :

hkl	$h + k + l = 2n$;	
$0kl$	$k + l = 2n$;	
$hk0$	$h + k = 2n$;	
hhl	(a) $l = 2n$;	
	(b) $2h + l = 4n$.	
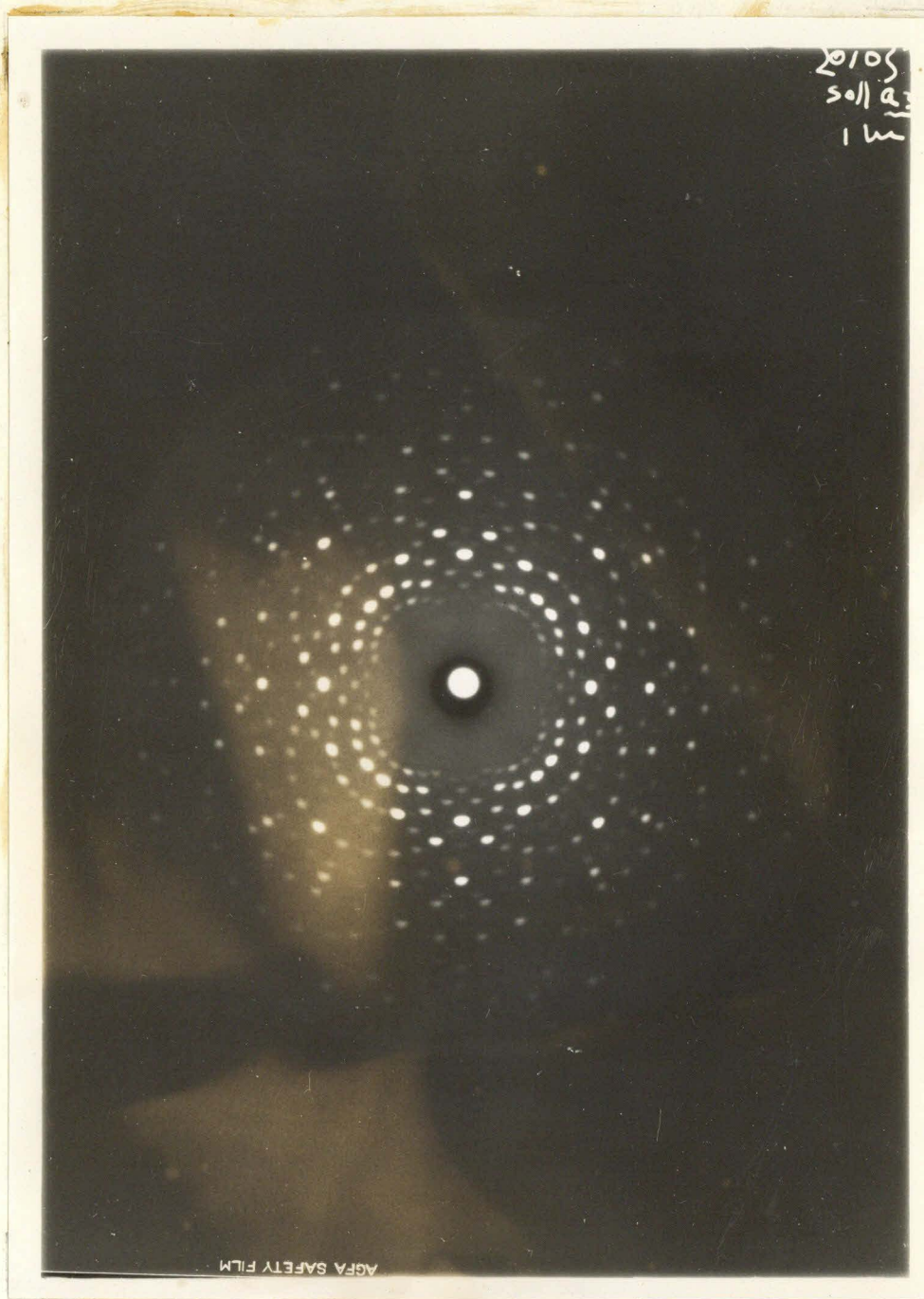
Laue photograph of $KC(NO_2)_3$ taken
with the x-ray beam parallel to $\underline{a}_3$
and with $\underline{a}_1$ vertical. Fluorazure in-
tensifying screens were used.

For the form hhℓ the condition that $\ell = 2n$ is included in $h + k + \ell = 2n$. The greater restrictions of condition (b) appear to exist inasmuch as no reflexions disobeying this rule were found, although numerous planes not obeying it were in position to reflect on one or more of the photographs.

Probable space groups then are D_{2d}^{12} - I $\bar{4}$ 2d and C_{4v}^{11} - I 4 md. In order to distinguish between these space groups the crystal was tested for pyroelectricity with none (or at best very little) being observed. The methods used to test for pyroelectricity were: (1) suspending a crystal in liquid air in a silvered Dewar flask to test for image forces; (2) bringing a suspended crystal just cooled in liquid air near a massive metal object to test for image forces; (3) attempting to observe ice "fibers" forming on a freshly cooled crystal suspended in air on a silk fiber.

From the smallness (or absence) of pyroelectricity it was concluded the space group is probably D_{2d}^{12} - I $\bar{4}$ 2d.

Further experiments with the compound were discontinued since the crystals exhibited the undesirable property of exploding after several hours in the x-ray beam.

It was hoped, when this investigation was begun, that some information about the resonance structures of the nitroform ion could be obtained. It is possible that this information has been obtained without a complete structure determination. An examination of the point symmetry of the various available positions in which to place the eight $C(NO_2)_3^-$ ions shows that the only satisfactory positions are the eight-fold positions for which the point symmetry is C_2 - 2. The four-fold positions have the point symmetry S_4 - $\bar{4}$, and these can be dismissed at once since the ion could not possibly exhibit this symmetry except by being in a state
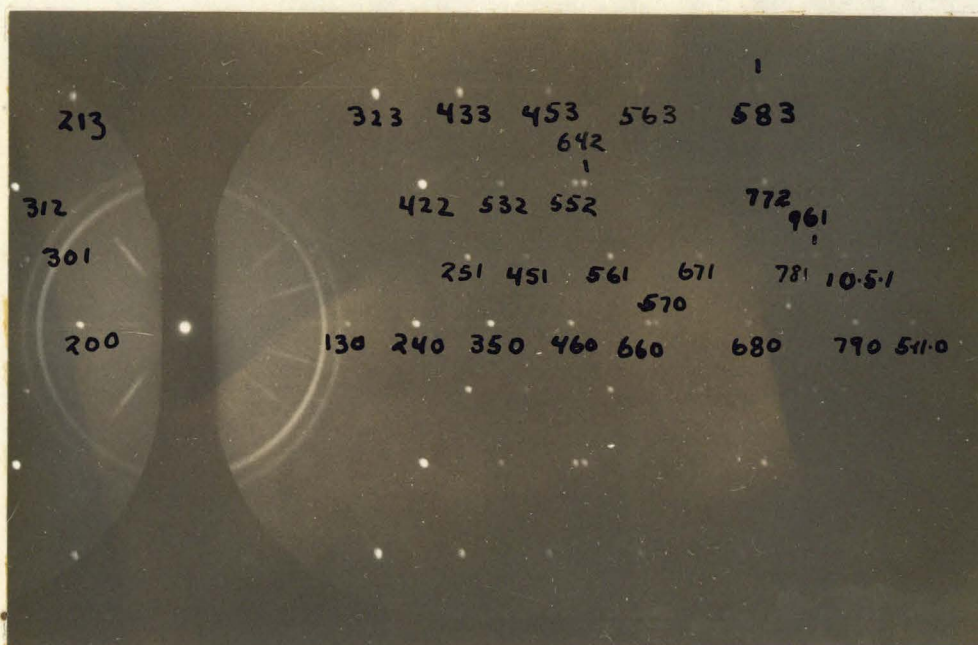
Oscillation photograph of $KC(NO_2)_3$. $\underline{a}_3$ vertical.
Filtered copper radiation. Camera radius: 5.0 cm.

Oscillation photograph of $KC(NO_2)_3$. $\underline{a}_1$ vertical.
Filtered copper radiation. Camera radius: 5.0 cm.

of rotation. There appears to be no evidence for rotation inasmuch as the x-ray photographs do not show an abnormally large "temperature factor" decline in intensities which ion rotation would cause.

It follows therefore that the ion must possess the symmetry $C_2 - 2$, that is that the skeleton of carbon and the three nitrogen atoms are co-planar. Since this is just what would be expected from resonance of the structures:

I   II   III
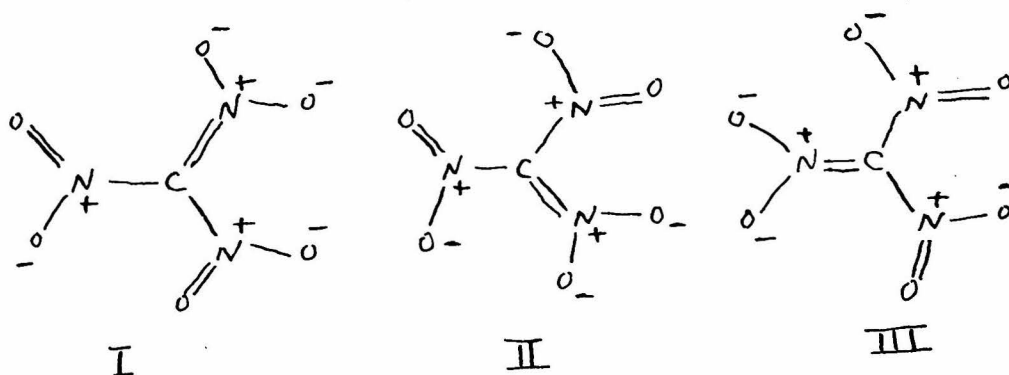
with resonance of the type and in each of the single bonded nitro groups, we can conclude that such resonance does indeed occur. The ion is probably not completely planar, since this would require oxygen atoms of adjacent nitro groups to be closer than the van der Waals radii would permit. The two forces, the repulsion of oxygen atoms, which tends to twist the C-N bonds and destroy coplanarity, and the stabilizing effect of resonance, which requires coplanarity, are in competition. The effect of resonance has presumably made the CN_3 skeleton planar.

This investigation indicates that similar resonance may take place in other asymmetric nitro ions, probably to a lesser extent. This accounts for the observed racemization of optically active nitro ions.

THE SPACE GROUP AND UNIT CELL OF PHENYLPROPIOLIC ACID

The phenylpropiolic acid used in this study was crystallized from water in the form of long needle-like prisms showing in general only one prism form.

A cursory optical examination of the crystals showed that the crystals were birefringent with parallel extinction. A goniometric examination gave the following angles between normals to the prism faces: 67°4', 112°49', 67°13', and 112°54'. These data place the crystal in either the orthorhombic or the monoclinic system.

Attempts to take Laue photographs were unsuccessful because of the smallness of the crystals available and because of the hardness of the x-rays.

A series of oscillation and rotation photographs were taken with copper $K\alpha$ radiation (filtered through a 27 μ nickel filter). In taking these photographs the crystal was mounted in the following ways: (1) the needle axis vertical, (2) the needle axis horizontal and the bisectrix of the acute prism angle vertical, and (3) the needle axis horizontal and the bisectrix of the obtuse prism angle vertical. Layer line measurements established an orthorhombic unit cell, which was refined by measurement of the equatorial reflections on several photographs. The unit cell so determined is:

$$a_1 = 9.61 \pm 0.01 \text{ Å}$$
$$a_2 = 15.08 \pm 0.01 \text{ Å}$$
$$a_3 = 5.12 \pm 0.01 \text{ Å (needle axis)}$$
$$z = 4.$$

For the determination of the space group a series of Weissenberg equi-inclination photographs were made. The reflections observed
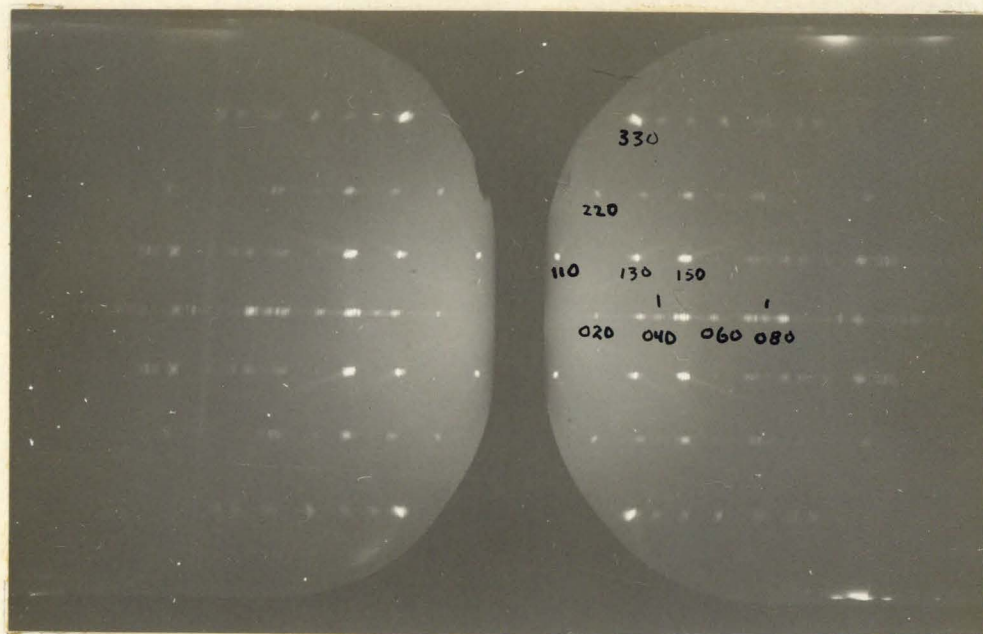
Rotation photograph of phenylpropiolic acid taken with
filtered copper radiation in a camera of 5.0 cm. radius.
The axis a₁ is vertical (needle horizontal).
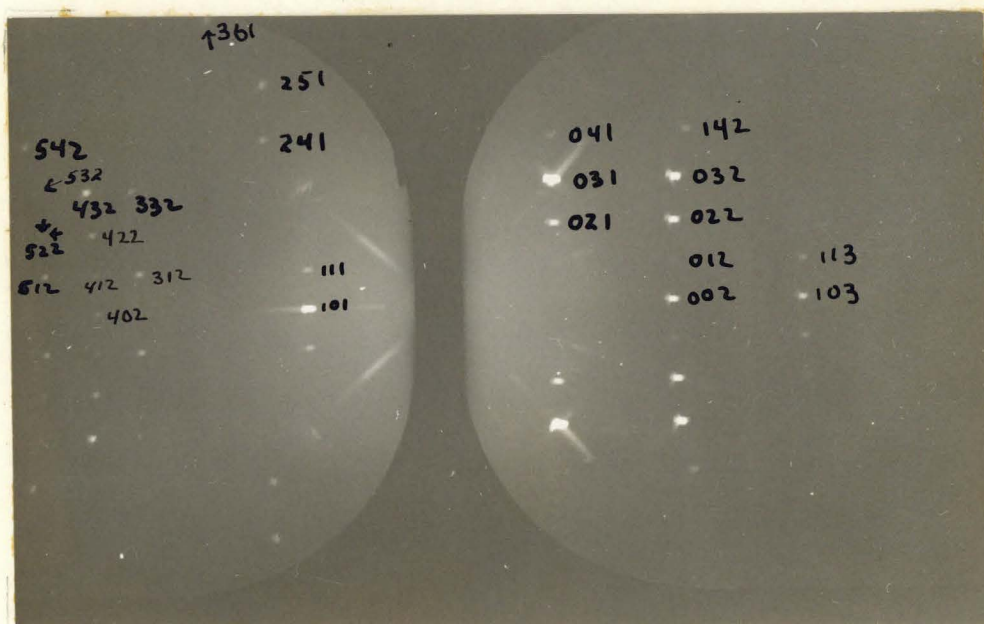
Oscillation photograph of phenylpropiolic acid taken
with filtered copper radiation in a camera of 5.0 cm.
radius. The axis a₂ is vertical (needle horizontal).
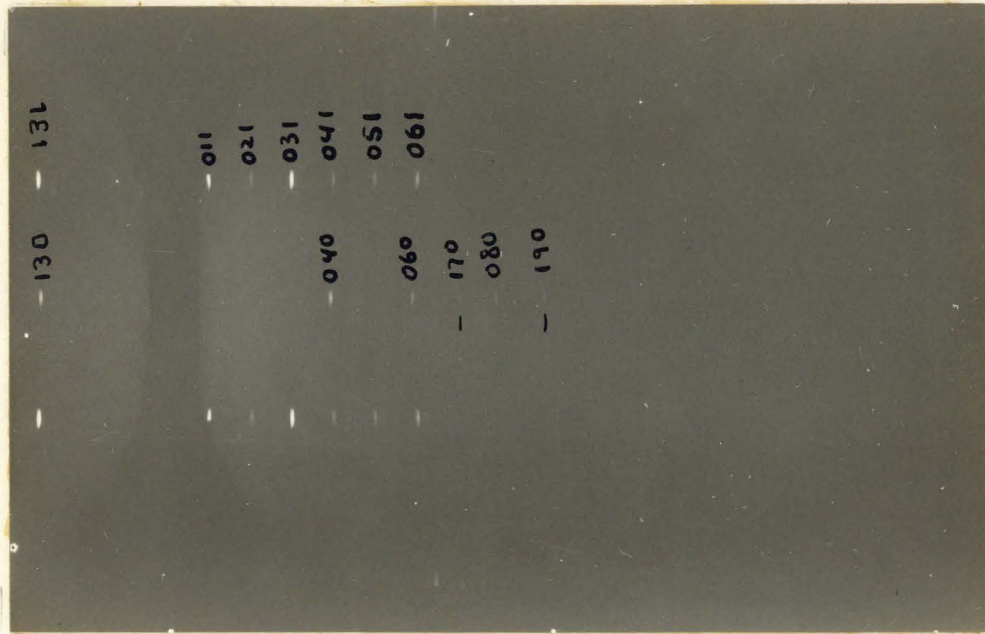
Oscillation photograph of phenylpropiolic acid taken with filtered copper radiation in a camera of 5.0 cm. radius. The axis a_3 (needle axis) is vertical.
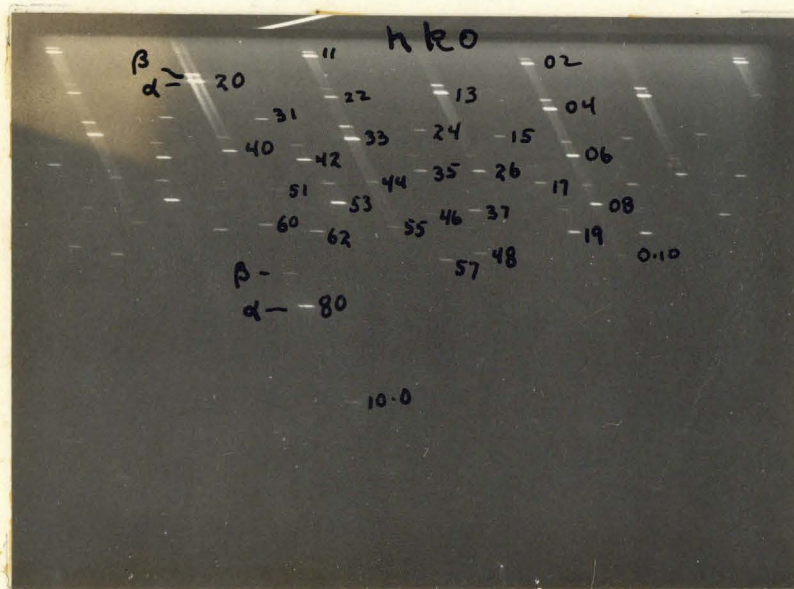
Weissenberg photograph of the hk0 reflections of phenylpropiolic acid taken with unfiltered copper radiation in a camera of 2.86 cm. radius.
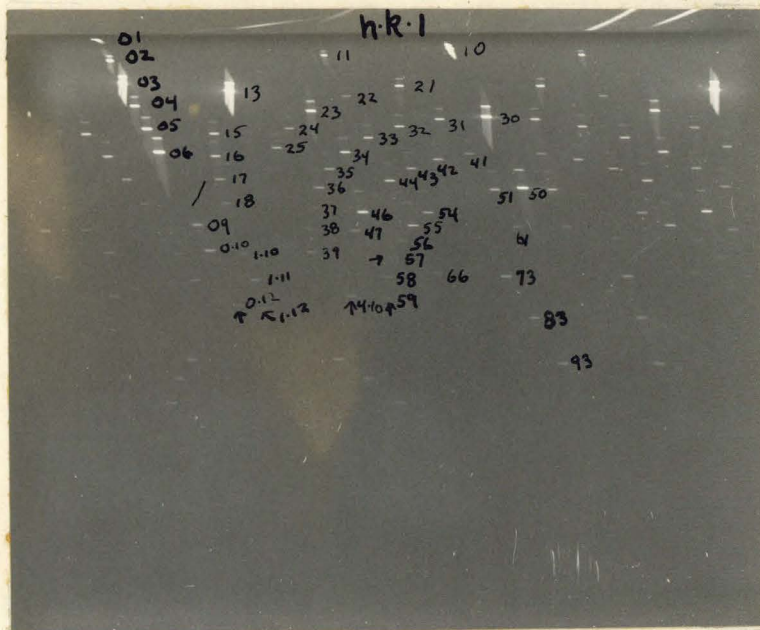
Weissenberg equi-inclination photograph of the
hkl (ℓ = 1) reflections of phenylpropiolic acid
taken with unfiltered copper radiation in a
camera of 2.86 cm. radius.
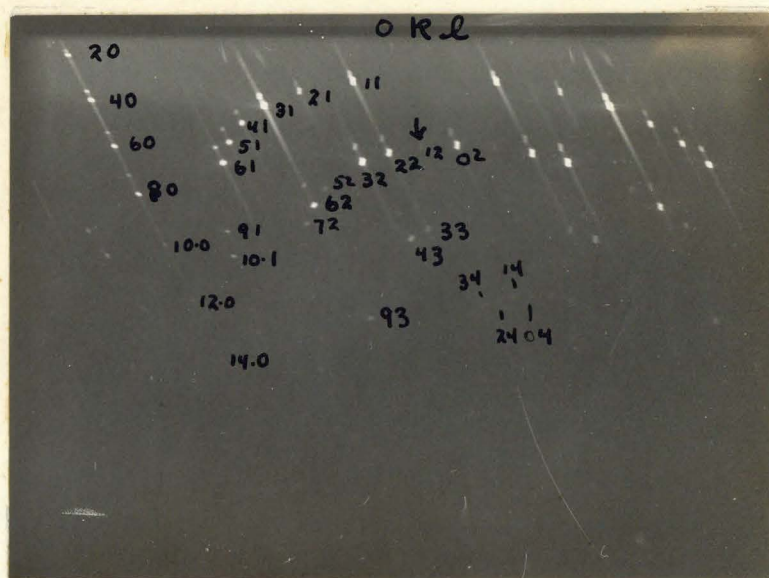
Weissenberg photograph of the Okℓ reflections
of phenylpropiolic acid taken with unfiltered
copper radiation in a camera of 2.86 cm. radius.

(expressed in terms of the above axes) appeared under the following conditions:

$hk\ell$ present for $h + k + \ell$ even or odd;

$hk\ell$ present for $h + k$, $k + \ell$, $h + \ell$ even or odd;

$h0\ell$ present only for $h + \ell$ even;

$0k\ell$ present for $k + \ell$ even or odd;

$hk0$ present only for $h + k$ even.

On the basis of this information the unit is simple, with two $\underline{n}$ type glide planes. There are only two orthorhombic space groups which require only the observed absences (after a suitable interchange of axes). These are $C_{2v}^{10} - P\ n\ n$ and $D_{2h}^{12} - P\ n\ nm$. Since the crystals were not sufficiently well developed to distinguish morphologically between the C_{2v} and the D_{2h} point symmetries, the crystals were tested for pyroelectricity by the methods enumerated in the previous discussion of $KC(NO_2)_3$. A rather weak effect was observed, which indicated that the space group to be $C_{2v}^{10} - P\ n\ n$; this conclusion is however not completely certain, and the space group $D_{2h}^{12} - P\ n\ n\ m$ must not be dismissed.

The interchange of axes referred to in the last paragraph is the following:

a_1 changed to A_3

a_2 "   " A_2

a_3 "   " A_1 .

Further study of the crystal with the hope of obtaining a complete structure determination is being made. The purpose of the investigation is to obtain information concerning the resonance conjugation of the benzene ring, the triple bond, and the carboxyl group. The amount of such resonance can be estimated from the values observed for interatomic distances in the molecules.

THE SPACE GROUP AND UNIT CELL OF THE MOLECULAR COMPOUND
## NAPHTHALENE: p-DINITROBENZENE

Crystals of the molecular compound naphthalene:p-dinitrobenzene
(1:1) were obtained as yellow prismatic needles by slow evaporation
of the solvent from solutions containing the two components. Solvents
best suited for preparing the complex are those in which the two com-
ponents have comparable solubilities. The solvent which seemed best for
this particular pair of substances is ethyl acetate. The crystals melted
at 118°C., in agreement with the value given by Pfeiffer[15].

An optical examination showed that the crystals were birefringent.
Goniometric measurements around the needle axis gave the following
interfacial angles: 80°13', 99°52', 80°19', and 99°47'. The crystal
was therefore monoclinic or orthorhombic.

A Laue photograph was taken with the x-ray beam perpendicular to
the needle axis and bisecting the obtuse prism angle. This photograph
showed a two-fold symmetry axis. Another Laue photograph with the x-ray
beam parallel to the needle axis and with the two-fold axis vertical
showed a horizontal symmetry plane. These observations indicated that
the crystal belonged to the C_{2h} Laue class, and was therefore monoclinic.
The gnomonic projection made from the photograph with the two-fold axis
indicated a monoclinic angle of approximately 70°.

Oscillation and rotation photographs using copper $K\alpha$ radiation
(filtered through a 27 μ nickel filter) were next made with a_3 (the
needle axis) or a_2 (the two-fold axis) vertical and perpendicular to the
x-ray beam. These photographs were successfully indexed on the basis of
the following unit cell:

$$a_1 = 9.85 \pm 0.02 \text{ Å}$$
$$a_2 = 10.78 \pm 0.02 \text{ Å}$$
$$a_3 = 6.97 \pm 0.02 \text{ Å}$$
$$\beta = 69°57'$$
$$Z = 2.$$
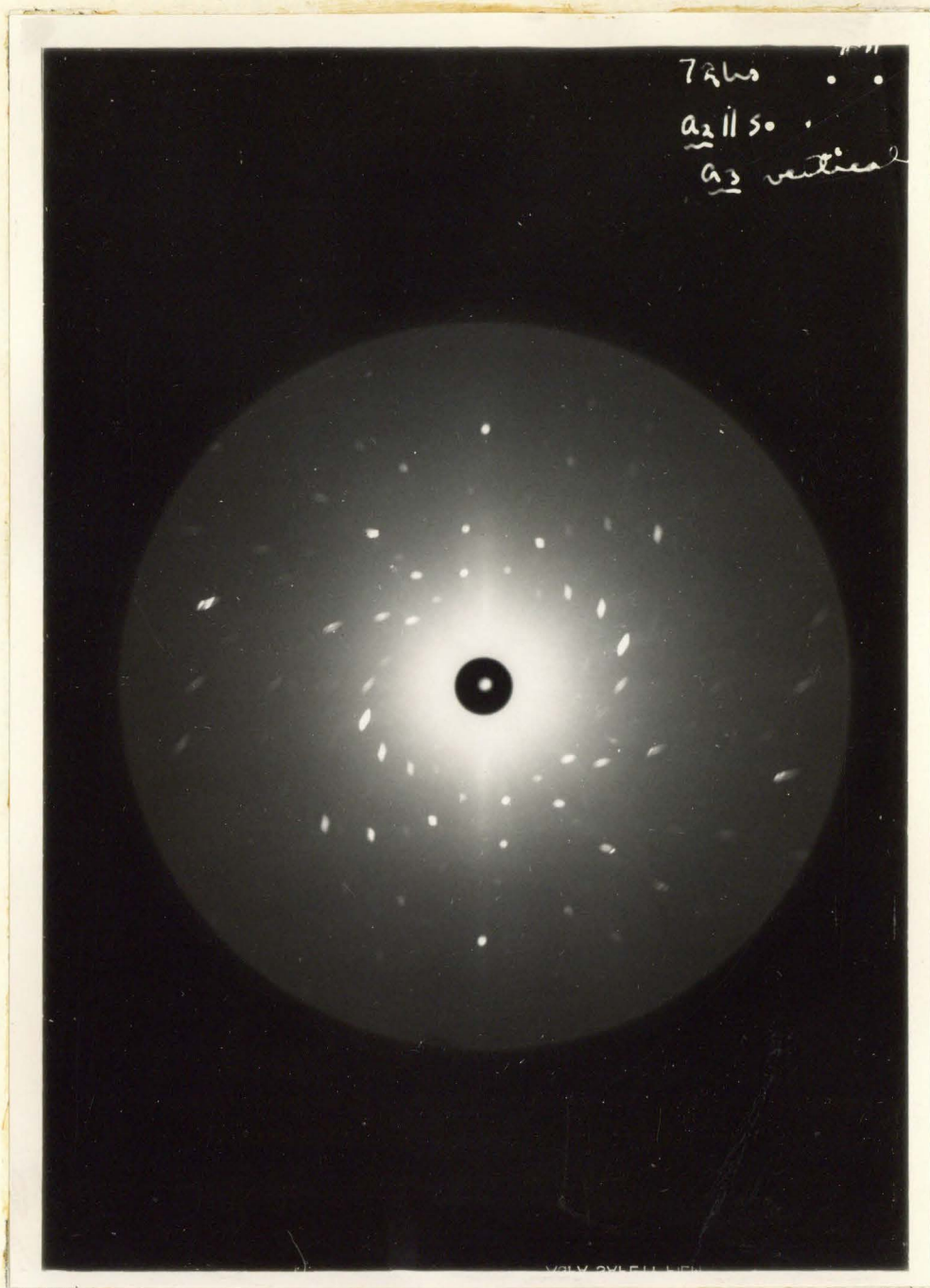
Laue photograph of the molecular compound. The x-ray
beam is parallel to $\underline{a}_2$ and with $\underline{a}_3$ vertical.
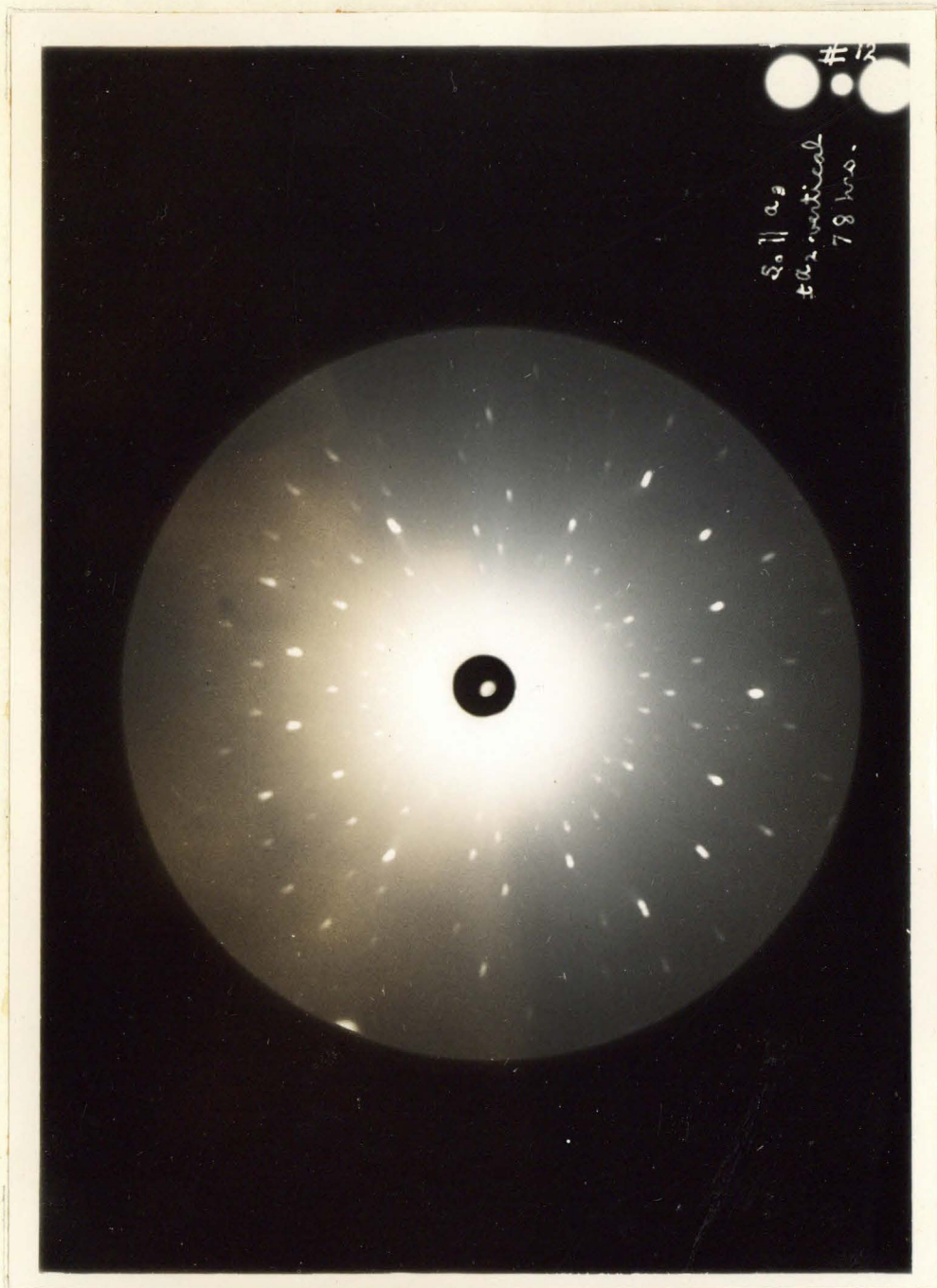
Laue photograph of the molecular compound. The x-ray
beam is parallel to a_3 with a_2 vertical.
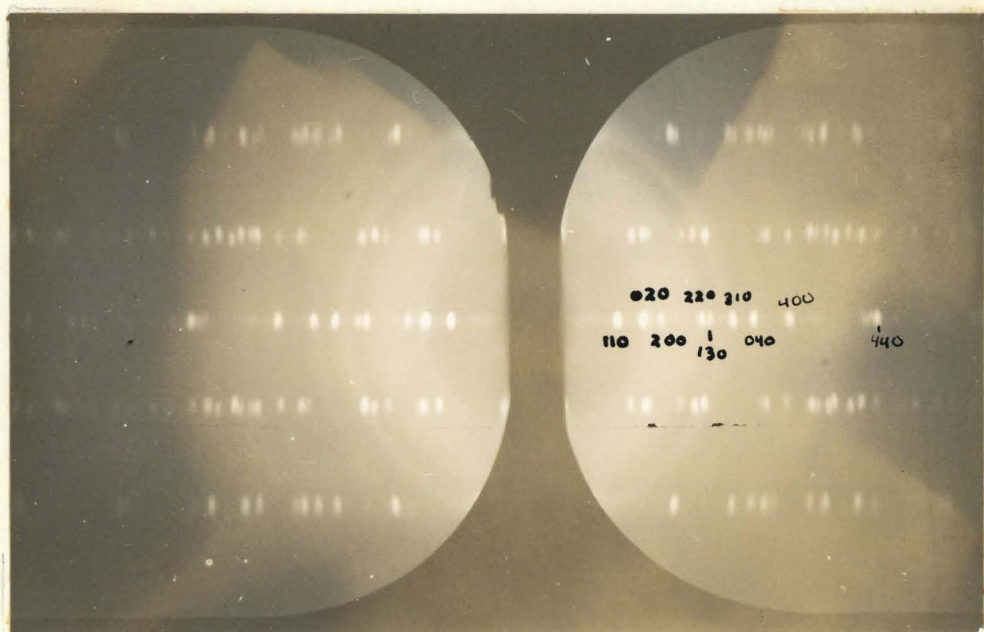
Rotation photograph of the molecular compound taken
with filtered copper radiation using a camera of 5.0
cm. radius. The needle axis (a₃) is vertical. The
powder pattern is caused by the wax to which the
crystal was attached.

The above unit cell was tested for correctness by means of a series of Laue photographs asymmetric with respect to the previously mentioned orientations of the crystal. None of the first order spots, which numbered about one hundred, necessitated a change in the axes.

The density of the crystals was next determined by flotation in calcium chloride solutions, and was found to be 1.39 ± 0.02. This density corresponds to 1.98 molecules of the complex in the unit cell listed above.

No systematic absences were observed except for the planes OkO which appeared only for $k = 2n$. Hence the probable space groups are $C_2^2 - P \, 2_1$ or $C_{2h}^2 - P \, \frac{2_1}{m}$. The morphology of the crystal specimens did not permit a choice to be made between the point symmetries $C_2 - 2$ or $C_{2h} - \frac{2}{m}$, and therefore the crystals were tested for pyroelectricity by the methods already described. It was not possible to make a definite decision as to whether the effect was present or not, and until a more refined technique for observing pyroelectricity is available both space groups are to be regarded as possible ones.

Inasmuch as the only practical method of attacking a crystal of this degree of complexity is by the Fourier projection technique further investigation of the complex was stopped. The only available projection direction is down the two-fold axis. Since this axis is over ten Angstroms long it was felt at the time that the results would not justify the effort involved.

The goal of the investigation was to obtain information as to the nature of molecular compounds (see part II of this thesis). This particular complex was chosen because the structures of the component molecules were thought to be sufficiently well known to be of aid in determining the structure of the complex.

PART II

A THEORY OF ORGANIC MOLECULAR COMPOUNDS

Introduction

By a molecular compound one means a stoichiometric complex of molecules, each of which exists separately and may be recovered from the complex unchanged. In a strict sense one should speak of a compound only if it can be isolated as a pure substance with definite physical properties; however, there are numerous unisolated complexes which give characteristic evidence of their existence and hence may also be considered.

The existence of complexes has been inferred in a variety of ways. The simplest and most definite evidence is the isolation of a substance of definite properties the stoichiometry of which can be represented by a formula $mA \cdot nB \cdots$, in which A, B, $\cdots$ are the molecular formulae of the component molecules and m, n $\cdots$ are integers.

In other cases less definite evidence has been used as an indication of the existence of a complex. Maxima, minima, or non-additivity in a plot of some physical property of a mixture as a function of composition have been used. Such physical properties are the melting point, viscosity, mole refractions, solubility, etc.

Still another type-of evidence is the appearance of a strong color on mixing colorless or weakly colored solutions of the components.

This discussion will restrict itself to the compounds in which at least one component is either an aromatic or an olefinic molecule. In certain of these complexes only one of the components is organic, the other being an inorganic halide; while in others both components are organic.

Isolation of crystalline molecular compounds. - Early in the history
of organic chemistry molecular compounds were known and came to be used
as a means of identifying substances. One need only mention the hundreds
of compounds in which one component is picric acid as a single example
of this use of these complexes. For the preparation of such complexes
the simplest of procedures was used, namely, the picric acid and the
second substance were placed in a solvent (not in excess), heated, cooled,
and the crystals filtered off and identified. If one solvent failed
others were tried. This simple method in the hands of able experimenters
added hundreds of new complexes to those already known.

In 1924 Dimrath and Bamberger[16] showed that the following expression
was valid for the molecular species in solutions from which complexes
could be formed:

$$\frac{S_C}{S_A \, S_B} = G$$

In this expression A and B are the components of a complex C; S_A, S_B, and
S_C are the saturation quotients (sättigungsgraden) of species A, B, and C;
and G is a constant independent of the solvent. For $G > 1$ the complex is
stable relative to its components, and for $G < 1$ it is unstable and will
completely decompose (if prepared in some other way such as by fusion of
its components in proper proportions) when placed in any solvent. The
relation of this expression to the association constant is the following

$$K = \frac{[C]}{[A][B]} = \frac{\{C\}}{\{A\}\{B\}} \times G \quad ; \quad S_A = \frac{[A]}{\{A\}} \quad ; \text{ etc.}$$

in which square brackets denote ordinary concentrations and curly brackets
the solubilities, each in mols per liter.

Hence the only way in which the solvent enters is by way of the
solubilities of the various species. These authors propounded a set of

working rules for the choice of a solvent to be used in preparing a complex. Most important of the rules for stability of the complex in a solvent is:

$$\frac{\text{Solubility of more soluble component}}{\text{Solubility of less soluble component}} < G.$$

In simpler terms it means that suitable solvents are those in which the two solubilities are nearly the same, the restriction being less rigorous with increasing G, the "stability constant."

In the course of preparation of numerous complexes of aromatic hydrocarbons with aromatic nitro compounds I have found the following solvents useful: methyl and ethyl alcohol; acetic acid; ethyl, propyl, butyl, and amyl acetates; and acetone. If well defined crystals suitable for x-ray studies are desired slow evaporation of the solvent (mixed solvents are generally not suitable for this technique) at a nearly constant temperature is necessary.

Examples of typical complexes. - At this point it may be well to list a few of the many hundreds of complexes which have been isolated in crystalline form:

Toluene : antimony trichloride	1:1
Toluene : antimony trichloride	1:2
Benzene : antimony tribromide	1:2
Benzene : antimony trichloride	1:2
Durene : carbon tetrabromide	1:1
Naphthalene : p-dinitrobenzene	1:1
Anthracene : s-trinitrobenzene	1:1
Hexamethylbenzene : s-trinitrobenzene	1:1
Benzene : triphenylmethane	1:1
Anthracene : picric acid	1:1
Benzene : platinum tetramethyl	1:1 (?)

Although the 1:1 complexes are by far the most numerous they are not the only type found. As two examples of other ratios one might list:

Fluorene : s-trinitrobenzene	2:3
Stilbene : s-trinitrobenzene	1:2

Next in importance are the complexes which have been postulated on the basis of color reactions. In numerous cases the admixture of two substances each dissolved in an inert solvent produces a more or less intense and characteristic color without permanent chemical changes appearing in the molecules of either substance. A few examples will suffice as illustrations of this type of complex:

Substances	Solvent	Color
Benzene + Tetranitromethane	CCl_4	yellow
Perylene + H_2SO_4	H_2SO_4 (conc.)	red-violet
1,1'di-p-tolyl ethylene + $SnCl_4$	C_6H_6	yellow
1,1'di-p-tolyl ethylene + H_2SO_4	H_2SO_4 (conc.)	yellow
1,1'di-p-methoxyphenyl ethylene + $SnCl_4$	C_6H_6	red-orange
Naphthalene + p-dinitrobenzene	$CH_3COOC_2H_5$	yellow
Triphenylethylene + $SnCl_4$	C_6H_6	orange-yellow
Triphenylethylene + $SnBr_4$	C_6H_6	orange
Ethylenic hydrocarbons + $C(NO_2)_4$	CCl_4	yellow to orange

In numerous cases the only information available concerning these complexes is the existence of a color reaction. In other cases more thorough investigations of the nature of the complex and its stability have been made.

Stability and energy effects in complex formation. - With regard
to the question of stability of complexes the existent data are rather
meager and disconnected. The early investigators of complex formation
were primarily interested in preparing new complexes and usually started
with substances of great complexity. Accordingly the greater part of the
data do not permit an easy analysis of what is relevant and essential
for the existence of a complex. In many cases the data are taken from
long-forgotten doctorate theses, and equilibrium constants are given
with no mention of what the equilibrium measured is.

The following table taken from an article by Hamilton and Hammick[17]
contains the most recent and reliable data available. The complex
stability was determined by colorimetric determinations of the association
constants in CCl_4 at several temperatures. The substances are s-trinitro-
benzene and the substance in the first column of the table.

Table I

Substance	$-\Delta H$	Substance	$-\Delta H$
o-Toluidine	2.0 kcal/mole	o-Chloroaniline	2.1 kcal./mole
m-Toluidine	2.0	m-Chloroaniline	2.0
p-Toluidine	1.7	p-Chloroaniline	1.9
Aniline	1.9	Methylaniline	2.3
o-Bromoaniline	2.5	Dimethylaniline	2.7
m-Bromoaniline	2.0	Diphenylamine	1.8
p-Bromoaniline	2.1	Triphenylamine	1.1
		α Naphthylamine	3.8

In each the complex is assumed to be 1:1.

The following table taken from Davies and Hammick[18] is from a similar
study of complexes between tetranitromethane and various aromatic hydro-
carbons in CCl_4 solution.

Table II

Substance	$-\Delta H$	Substance	$-\Delta H$
Durene	1.4 kcal./mol	Triphenylmethane	0.66 kcal./mol
Pentamethylbenzene	1.7	Ethylbenzene	1.08
Hexamethylbenzene	1.5	i-Propylbenzene	1.15
Diphenylmethane	0.5	t-Butylbenzene	0.98

In addition to these may be added the results of Hammick and Young[19] for tetranitromethane and various other substances in CCl_4.
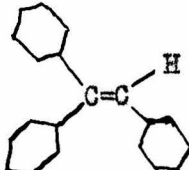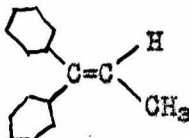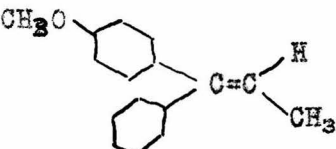
Table III

Substance	$-\Delta H$	Substance	$-\Delta H$
p-Xylene	0.72 kcal/mol	2,4-Dimethylnaphthalene	0.58 kcal/mol
Diphenyl ether	1.55	β Naphthol	0.86
Naphthalene	0.60	α-Nitronaphthalene	1.69
β Methyl naphthalene	0.71	Anthracene	1.59

Probably the only completely tenable conclusion that can be reached from these data is that in all cases the heat effect is small and of the same magnitude. Minor fluctuations among isomers may or may not be of significance because of the method used for the determination of the equilibrium constants. Experiments performed by myself with tetranitromethane and naphthalene in CCl_4 show that not only does the color intensity increase with increase in the concentration of the components, but the color also changes in character from a "chromate" yellow to a "dichromate" orange. This change may be sufficient to invalidate colorimetric methods for high concentrations.

Further data in the form of dissociation constants of complexes in benzene solution are given by the following table from Pfeiffer[15] .

Table IV

	SnCl$_4$	SnBr$_4$
6.74 orange-yellow	23.8 orange
2.75 yellow	12.8 orange-yellow
0.0251 orange	0.114 red-orange

The nature of the complexes. - From the smallness of the heats of formation of the complexes it can be stated with definiteness that the bonds formed cannot be covalent bonds. The stabilization must therefore be of a van der Waals type. Since complexes can form between molecule pairs only one of which contains a group to which a permanent dipole may be attributed, dipole-dipole interactions between permanent dipoles do not provide the answer. In all cases in which a complex does form one of the molecules must be an aromatic or ethylenic substance and the second molecule must possess one or more dipole groups of large or moderately large strength.

Hence one form of stabilization may be the polarization of the aromatic or ethylenic substance by the second molecule with subsequent dipole-dipole interaction. The fact that in general only olefins and aromatics, in which the average carbon atom polarizability is some 35% greater than in aliphatic compounds, form complexes lends support to this view.

In addition to this and possibly of greater importance are the London dispersion forces which also depend on the atomic polarizabilities.

Unfortunately a direct calculation of these effects is too difficult to make even with only approximate reliability. To have significance such a calculation would have as a necessary prerequisite the knowledge of the configuration of the complex. Since none of the complexes has received such thorough study this avenue of attack is at least temporarily closed.

Nevertheless pertinent arguments in favor of the essential correctness of the van der Waals stabilization can be given.

As a starting point we may examine the experimentally determined arrangement of molecules in the crystals of p-dichlorobenzene[20], p-chlorobromobenzene[20], p-dibromobenzene[20], quinone,[21] and p-dinitrobenzene[22]. In all of these substances the substituent groups of one molecule are located at a point near the perpendicular to the center of the ring of a second molecule. In p-dinitrobenzene and quinone the molecules are arranged in strings of the type:
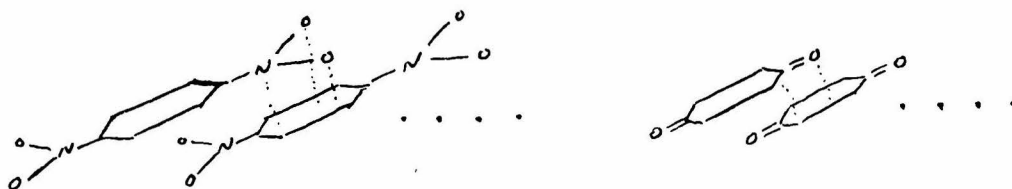
It will be noticed that these are just the positions which would be expected to lead to a large van der Waals stabilization, with the polarizing group close to the center of maximum polarizability. Obviously in an approach of such intimacy the idealization of a dipole can no longer be maintained and the dipole must now be thought of as an

asymmetrical charge distribution. It is not surprising that the "dipole" of the nitro group is not normal to the ring. Indeed it is in a position of maximum effectiveness since the benzene ring must certainly have a higher polarizability parallel to its plane than normal to it.

On the basis of the preceding discussion we may postulate that in a benzenoid or olefinic complex the molecules will be in similar configurations. For the complex of naphthalene and p-dinitrobenzene one might expect some arrangement as:

Further we may postulate that the stability of the complex will decrease if for steric reasons such an approach is not permitted. The existence of only a few crystalline complexes of aliphatic nitro compounds with aromatic molecules may be explained in this way. By the geometry of the aliphatic molecule such as $C(NO_2)_4$ the nitro groups cannot be both close and parallel to the ring simultaneously and hence a decrease in stability results. Similar remarks will apply to complexes involving other tetrahedral molecules, such as $SnCl_4$, $SnBr_4$, etc.

Another type of steric effect which can be operative in the molecule containing the nitro group is one affecting the nitro groups of a molecule such as trinitromesitylene as compared with s-trinitrobenzene. In the former compound the nitro groups will be pushed out of co-planarity with the rest of the ring by the intervening methyl groups.

This will have two effects: first there will be a decrease in the nitro moment (Birtles-Hampson effect), and second the nitro group will not be able to achieve as close an approach to a second molecule as in the methyl-free compound. In support of these arguments there are the observations that all attempts to prepare a complex containing tri-nitromesitylene have failed, although the corresponding s-trinitro-benzene complexes exist.

We may next consider the effect of substituents in the other molecule of the complex, i.e. the aromatic or olefin. In the discussion only aromatic molecules will be mentioned with the assumption that similar arguments will apply to olefins. An examination of the heats of formation of the complexes of $C(NO_2)_4$ with various benzene derivatives may be used as the basis of the arguments (cf Tables I, II, III). About all that can be said is that substituents exercise no great influence (in addition to steric effects) on the stability of the complex. In general addition of methyl or amino groups promotes stability, the effect being more pro-nounced for amino groups either simple or substituted. This may be attributed to slight increases in the polarizability of the ring by resonance of such structures as

and
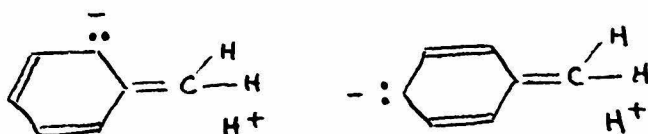
Such resonance would be greatest for amino groups, and hence the correlation with stability increases may be regarded as satisfactory. Another way in which a substituent can operate is by the inductive effect, whereby

electrons are removed from the ring with a loss of polarizability and hence of complex stability. This can be correlated with the existence of only a few complexes between different nitro compounds.

As a rough rule one might say that the ortho-para directing substituents stabilize a complex while the meta directing groups destabilize, the effect in either case being not very great.

Another piece of evidence for the van der Waals stabilization can be obtained from Table IV. In all cases a complex of $SnBr_4$ is less stable (as shown by the equilibrium constant) than the $SnCl_4$ complex with the same substance. This may be explained by the smaller van der Waals radius of Cl as compared to Br and the resultant more intimate approach of $SnCl_4$ as compared to $SnBr_4$. Also there is probably a small decrease in the group "dipole" moment of Sn-Br as compared to Sn-Cl which would further destabilize the complex.

Another complex which can be explained only on a van der Waals basis is that from benzene and platinum-tetramethyl observed by Mr. Rundle and myself of these laboratories. It was observed that when platinum-tetramethyl crystallizes out of benzene, birefringent needle-like crystals are formed, which disintegrate to an isotropic powder when the solvent is completely evaporated. The powder gave a cubic x-ray pattern, just as did single crystals or powders from other solvents, such as carbon disulfide and dibutyl ether. The anisotropic crystals stable in the presence of benzene were undoubtedly those of a complex.

The color of molecular compounds. - In the case of most molecular compounds, particular the nitro complexes, characteristic color changes

occur when the components are mixed. In general these colors are
yellow, orange, red, and in some cases (aromatic amines with nitro com-
pounds) violet, brown, or black. Any satisfactory theory of molecular
compounds must indicate at least qualitatively how such colors arise.
That the color depends on both components may be seen from the following:

Benzene + tetranitromethane	yellow
Naphthalene + tetranitromethane	yellow to orange
Anthracene + tetranitromethane	red-orange
Naphthalene + s-trinitrobenzene	pale yellow
Naphthalene + 2,4,6-trinitrotoluene	colorless
Naphthalene + 2,4,6-trinitroaniline	orange-yellow
Naphthalene + 2,4,6-trinitro-chlorobenzene	bright yellow

It will be well to repeat at this point that only aromatic and
olefinic compounds show color reactions and complex formation. This
provides the clue to a possible origin of the color. All of the olefinic
and aromatic compounds exhibit characteristic absorption in the near
ultraviolet, the absorption in complicated molecules extending into the
visible (anthracene, polyenes, etc.) with the substances showing a yellow
color or tint.

It is now suggested that when a color appears in solutions of complexes
this color is to be related to the absorption bands in the near ultra-
violet, the shift of the band into the visible being caused by some non-
uniform polarization of the aromatic or olefin molecule by the second
molecule.

The essential correctness of this explanation can be seen from the
colors of the tetranitromethane complexes with the series benzene,

naphthalene, and anthracene; in these hydrocarbons the "unperturbed" absorption moves in toward the visible and the color of the complexes is accordingly deeper in the order named.

The effect of changing the second component of the complex can be seen from examining the sequence

Benzene + carbon tetrabromide (solution)	colorless
Benzene + carbon tetrachloride (")	colorless
Benzene + chlorpicrin (CCl_3NO_2)	very pale yellow
Benzene + tetranitromethane	yellow

It is evident that an increase in the group "dipole" moments results in an increase in the color of the complex. In general the amount of the shift in the absorption maximum parallels the stability of the complex, although not in a precise way.

Again it is unfortunate that no more precise treatment of the color of complexes can be given as yet. To make such calculations a more complete knowledge of the "unperturbed" absorption and of the electronic wave functions would be necessary. The suggestions made here seem to be at least qualitatively correct.

Summary of Existing Structural Data for Complex Compounds.

As has been mentioned before, no complete structure investigation of a molecular compound has been made to date. A number of x-ray investigations of crystals have been carried out as far as the determination of the unit cell and space group. In Table V these are summarized. Of those listed, the first (naphthalene : p-dinitrobenzene) is probably the one best suited to further study because of the smallness of the unit cell and the simplicity of the components.

Another complex, as yet not investigated, between hexamethylbenzene and s-trinitrobenzene may prove still simpler. A practical obstacle in this case is the preparation of good single crystals. The substance shows a marked tendency toward twinning, but this difficulty might be overcome. Certainly a complete investigation of one of the complexes would be worth the effort involved, for then the views with regard to the structure of complexes given in the previous sections could be given a direct test.

Table V

Complex	Unit Cell	Molecules of complex in unit	Space Group
Naphthalene : p-dinitrobenzene[23] 1:1	a = 9.85 ± 0.02 Å b = 10.78 ± 0.02 c = 6.97 ± 0.02 β = 69°57'	2	C_2^2 – $P2_1$ or C_{2h}^2 – $P\frac{2_1}{m}$
Aniline : picric acid[24] 1:1	a = 13.2 Å b = 7.4 c = 15.2 β = 93°	4	C_{2h}^5 – $P\frac{2_1}{c}$
Fluorene : s-trinitrobenzene[25] 3:4	a = 7.64 Å b = 7.34 c = 28.2 β = 97°	1	C_2^3 – $P2_1$
Stilbene: s-trinitrobenzene[26] 1:2	a = 12.7 Å b = 15.4 c = 7.7 α = 102°16' β = 85°30' γ = 87°35'	2	
4-Brom-1-naphthylamine : 2,6-dinitrophenol[27] yellow form 1:1	a = 14.0 Å b = 8.0 c = 14.5 β = 102°6'	4	C_{2h}^5 – $P\frac{2_1}{c}$
red form	a = 9.5 Å b = 13.5 c = 13.8 β = 105°	4	C_{2h}^5 – $P\frac{2_1}{c}$

Anthracene : s-Trinitrobenzene[27]

    1:1

$a = 13.4$ Å
$b = 16.3$
$c = 9.9$
$\beta = 122°$

4

$C_s^4 - Ia$

Fluorene : 2,7-dinitroanthraquinone[28]

    1:1

$a = 8.2$ Å
$b = 7.4$
$c = 19.0$
$\alpha = 78°$
$\beta = 82°$
$\gamma = 82°$

2

Acenaphthene : 4,6-dinitro-1,3-xylene[29]

    1:1

$a = 18.5$ Å
$b = 14.2$
$c = 7.25$
$\beta = 103°$

4

$C_{2h}^5 - P \frac{2_1}{a}$

Acenaphthene : styphnic acid[30]

    1:1

$a = 9.0$ Å
$b = 14.8$
$c = 6.8$
$\beta = 95°$

2

$C_{2h}^1 - P \frac{2_1}{m}$;

$C_2^1 - P2$; or

$C_s^1 - Pm.$

Summary

The following table is a summary of the interatomic distances and valence angles for the phosphorus and arsenic compounds discussed in part I of this thesis.

	X-O	P=O or P=S	$\angle$ X-O-X	$\angle$ O-X-O	$\angle$ O-P=O' or $\angle$ O-P=S
As_4O_6	1.80 Å		126°	100°	
P_4O_6	1.65		127.5°	99°	
P_4O_{10}	1.62	1.39 Å	123.5°	101.5°	116.5°
$P_4O_6S_4$	1.61	1.85	123.5°	101.5°	116.5°

For hexamethylenetetramine the interatomic distances and valence angles are:

C-H	1.09 Å (assumed)		$\angle$ N-C-N	109°28'
C-N	1.47		$\angle$ C-N-C	109°28'
			$\angle$ H-C-H	109°28' (assumed)

The investigation of tetranitromethane resulted in the following interatomic distances and valence angles:

C-N	1.47 Å		$\angle$ O-N-O	127° (assumed)
N-O	1.22		$\angle$ N-C-N	109°28' (assumed).

In order to obtain a satisfactory interpretation of the electron diffraction data it was necessary to assume a rotatory oscillation of the nitro groups about their C-N bonds, and to include the usually omitted temperature factor.

The remaining pages of part I are devoted to a presentation of the results of x-ray investigations of three crystals. The unit cells and space groups are the following:

$KC(NO_2)_3$
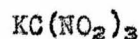
$$a_1 = 11.31 \text{ Å} \qquad\qquad Z = 8$$

$$a_3 = 8.77$$

Space group: $D_{2d}^{12} - I\bar{4}2d$

Phenylpropiolic acid

$$a_1 = 9.61 \text{ Å} \qquad\qquad Z = 4$$

$$a_2 = 15.08$$

$$a_3 = 5.12$$

Space group: $C_{2v}^{10} - P\ n\ n$

Molecular compound: naphthalene : p-dinitrobenzene

$$a_1 = 9.85 \text{ Å} \qquad\qquad Z = 2$$

$$a_2 = 10.78$$

$$a_3 = 6.97$$

$$= 69°57'$$

Space group: $C_2^2 - P2_1$ or $C_{2h}^2 - P\dfrac{2_1}{m}$

In part II of this thesis a theory of organic molecular compounds based on van der Waals stabilization of complexes is proposed, and arguments in support of the theory are presented.

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Propositions

1. Organic molecular compounds of the olefin or aromatic series can be divided into two classes depending on the function of the olefin or aromatic molecule.

2. The heats of formation of molecular compounds can be determined with greater precision and reliability than they have been to date.

3. The known structure of the tetranitromethane gas molecule is compatible with existing data on the crystal if rotation of the molecules in the crystal is assumed.

4. The electron diffraction investigation of tetranitromethane provides another type of situation for which the temperature factor must be considered.

5. Approximate predictions of bond lengths in molecules can be made from thermochemical data.

6. Simple valence bond calculations predict the following order of stability for the benzoquinones: ortho $>$ para $>$ meta.

7. A value for the molecular orbital Coulomb integral suitable for predicting ionization potentials of aromatic or unsaturated molecules is: $q = 8.6$ electron volts.

8. A probable structure for N_4S_4 is that of an eight membered ring.

9. The use of a lecture syllabus would materially improve the freshman chemistry course.

10. In the interests of a more complete training first year graduate students ought to be allowed more freedom from the inordinate time demands of research.