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The Determination of the Molecular Structure of Tetranitromethane by the Electron Diffraction Method

BY A. J. STOSICK

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 $s_0 = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$ 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_0, λ is the de Broglie wave length of the electrons, and θ is the scattering angle. The coefficients c_0 were obtained from the estimated visual intensities I_0 by multiplying the latter by $s_k^2 e^{-as_k^2}$ where s_k is the value of s_0 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.

TABLE I

Max.	Min.	I	c_0	s_0	s_{VII}/s_0
	1			1.76	(0.920)
1		8	4	2.79	(.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	.997
	6	Not accurately measurable			
6		2	15	17.20	.994
	7			19.10	1.021
7		1	6	21.70	1.018
					Mean 1.011

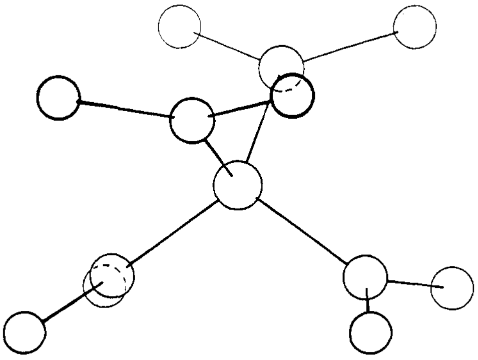

Fig. 1.

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.*, $\angle N_1CN_2 = 109°28'$. The assumed values of C–N = 1.46 Å., N–O = 1.21 Å., and the ∠O–N–O = 127° are those found by Brockway, Beach, and Pauling[3] for nitromethane.

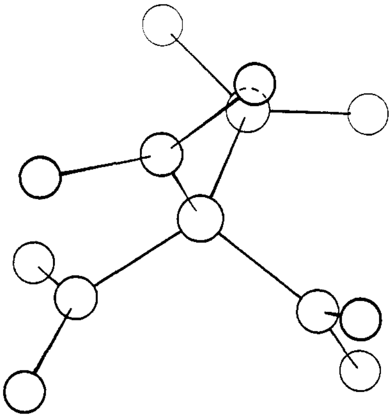

Fig. 2.

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 1 is a sketch of the molecule for $\varphi = 0°$. Figure 2 shows the equilibrium configuration of

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(1) Chattaway, *J. Chem. Soc.*, **97**, 2099 (1910).

(2) Menzies, THIS JOURNAL, **41**, 1336 (1919).

(3) Brockway, Beach, and Pauling, *ibid.*, **57**, 2693 (1935).

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 approximation that can be made. The range of oscillation was divided into three "time equal" sub-intervals: $-\varphi_0$ to $-\varphi_0/2$, $-\varphi_0/2$ to $+\varphi_0/2$, and $+\varphi_0/2$ to $+\varphi_0$. 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 $I = \Sigma\Sigma Z_i Z_j \frac{\sin sl_{ij}}{sl_{ij}}$, the coefficients for the φ dependent distances were divided equally among the three ranges of φ.

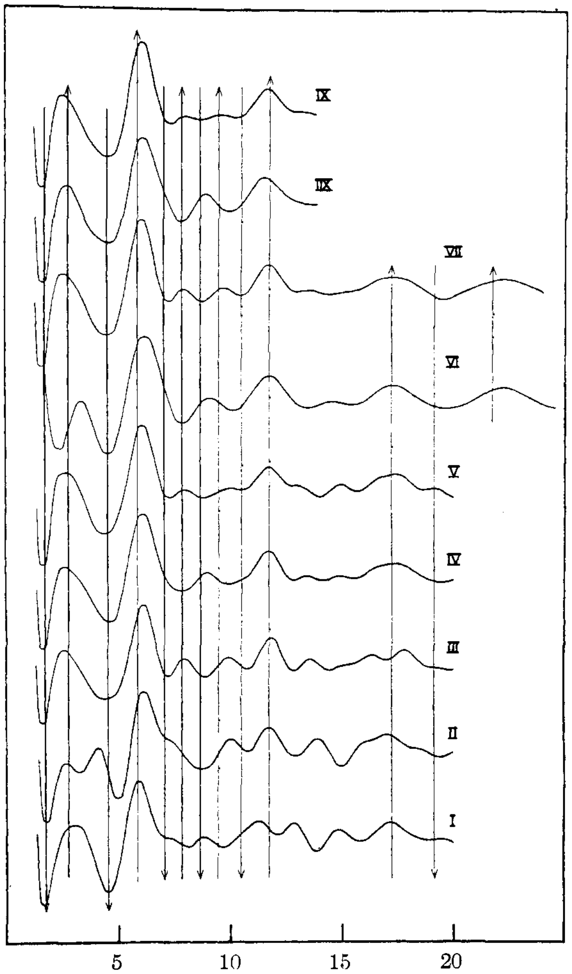

Fig. 3.

It became apparent that models I to V all showed more maxima and minima in the region beyond $s_0 = 10$ 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]

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

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_0 values since the temperature factor makes all φ dependent distances unimportant for large values of s_0. The curve resulting from this calculation (Model VI) is shown in Fig. 3, 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 tempera-

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(4) *Cf.* Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

ture 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 Fig. 3.

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.

TABLE II

Model	Type	Equilib. position	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	φ 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., ∠O–N–O = 127°, and ∠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 $s_{\text{calcd.}}/s_0$ 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 ± 0.02 Å. O–N–O = 127°
N–O = 1.22 ± 0.02 Å. 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 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 determinations 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 Sängewald[7] both indicate a zero moment to within the accuracy of the experimental measurement.

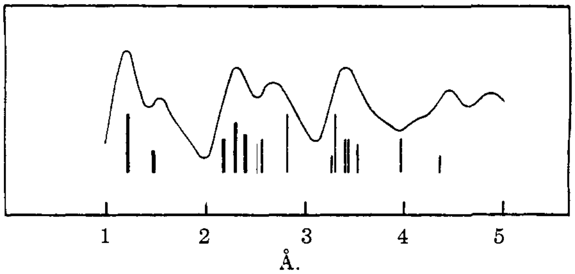

Fig. 4.

The modified radial distribution method gave very little information. The only peak which was of much value was that at 1.21 Å., which indicated the N–O distance quite accurately. The curve is shown in Fig. 4. 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 $s_0 = 0$, the importance of the φ-dependent distances falling off rapidly with increasing s_0. 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,

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(5) Mark and Noethling, *Z. Krist.*, **65**, 435 (1927).

(6) Williams, *Physik. Z.*, **29**, 271 (1928).

(7) Weissberger and Sängewald, *Ber.*, **65**, 701 (1932).

i. e., 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. There is apparently no pronounced additional shortening of the N–O bond caused by the formal change of the nitrogen atom.

Acknowledgment.—The author wishes to express his appreciation to Dr. Buchman for suggesting the problem, to Dr. Schomaker for suggesting the temperature factor treatment used, and to Professor Pauling for helpful discussions.

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.

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The Electron Diffraction Investigation of Phosphorus Sulfoxide, $P_4O_6S_4$

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Phosphorus sulfoxide, $P_4O_6S_4$, was first reported by Thorpe and Tutton[1] 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 carbon disulfide, 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 $s_0 = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$ 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_0, and the coefficients C_0 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_0 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

TABLE I

Max.	Min.	I_0	c_0	s_0	s_c/s_0
	1			2.43	(0.827)
1		10	1	3.10	(.929)
	2			3.83	(.948)
2		15	4	4.64	.974
	3			Absent	
3				Shelf; not measured	
	4			06.45	0.960
4		5	4	7.09	.994
	5			8.01	.986
5		10	14	8.87	.991
	6			10.21	.979
6		4	9	11.26	.995
	7			12.28	.998
7		5	16	13.14	.987
	8			13.87	.984
8		2	7	14.49	.977
	9			15.12	.979
9		5	20	15.81	.992
	10			16.55	.995
10		3	14	17.26	.989
	11			17.90	.987
11		4	19	18.43	.989
	12			19.24	.986
12		5	24	20.49	.991
	13			21.73	1.002
13		1	5	22.68	0.988
	14			23.57	.977
14		2	8	24.46	.984
	15			25.77	.999
				Mean	.9867

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[1] Thorpe and Tutton, *J. Chem. Soc.*, **59**, 1023 (1891).