for the identification of the irradiated material. While in most cases these criteria may be taken as highly indicative of the identity of two materials, the irradiation of a substance such as vitamin B_{12} warrants the application of as many criteria of identity as possible. It is conceivable that complex cobalt compounds, very closely related to vitamin B_{12}, would exhibit similar behavior on chromatography. Furthermore, the possibility must not be overlooked that these compounds might also be capable of undergoing the same exchange of anions as vitamin B_{12} when different cobalamins are made from the parent compounds. Even constant specific activity might, in this case, be misleading, especially since the desired product is present in a very small amount.

Countercurrent distribution, which can so easily effect a separation of two cobalamins as closely related as vitamin B_{12} and vitamin B_{12a}, provides an excellent additional criterion for the identity of the irradiated material. Cobalt-60 labeled vitamin B_{12}, whether prepared by neutron bombardment or by microbiological synthesis, should exhibit the same ratio of radioactivity to biological activity for each tube of a countercurrent distribution. This criterion has so far been met only in the case of microbiological synthesis.[1]

In our work the results of paper chromatography were in themselves enough to question the presence of appreciable amounts of the Co-60 labeled vitamin. The countercurrent distribution merely provided additional support for that conclusion. The results of Anderson and Delabarre[4] and Smith[5] do suggest the possibility that the Co-60 labeled vitamin had actually been prepared by neutron bombardment. However, the lack of information of the behavior of their material in a countercurrent distribution must, in view of the specificity of this technique, still leave open the claim for the preparation of Co-60 labeled vitamin B_{12} by direct neutron bombardment.

The paucity of information on the retention of induced radioactivity as a function of the energy spectrum of the neutrons used for irradiation, makes difficult an exact interpretation of the reasons for the differences between our results and those reported by others.[4,5] It is hoped that further study of these variables will lead to a better understanding of the changes resulting in complex compounds under neutron irradiation.

NEW BRUNSWICK, N. J.

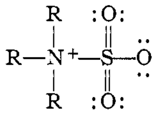
Rotations within Crystalline Trimethylamine Sulfur Trioxide

BY HEROSHI SHIMIZU AND DAN MCLACHLAN, JR.

RECEIVED APRIL 27, 1953

Although compounds of the tertiary amines with sulfur trioxide were prepared[1] in 1883 and have since been put to use in the dye industry,[2] there is still some doubt about their structure in the crystalline state.

This paper is concerned with the structure of the single compound, trimethylamine sulfur trioxide. A selection of the proper chemical structure from the four possible postulated structures of Burg[3] has been made possible by the careful work of Lecher and Hardy[4] on the basis of their own experiments, the work of other investigators,[5] the "Adjacent charge rule" of Pauling,[6,7] and spectroscopic and X-ray data of Gare and McLachlan (unpublished). Lecher and Hardy have chosen the chemical form



$$\mathrm{R{-}\overset{R}{\underset{R}{N}}{}^{+}{-}\overset{:O:}{\underset{:O:}{S}}{-}\ddot{\underset{..}{O}}{:}^{-}}$$

The present investigation needs then only to cover the possible configurations of this type of molecule in the crystal. The four possibilities were considered: 1, the R groups and O groups stationary; 2, the R groups and O groups rotating; 3, the R groups stationary and the O groups rotating; 4, the R groups rotating and the O groups stationary.

Experimental

The samples of the trimethylamine sulfur trioxide were furnished by the American Cyanamid Company through the courtesy of Dr. H. Z. Lecher. The crystals were colorless, acicular, about 5 mm. long and less than 1 sq. mm. in cross section.

Rotation pictures were taken with the crystal rotating about the longest growth axis (which proved to be the hexagonal c-axis) using molybdenum and also copper radiation. Then using copper radiation, Weissenberg X-ray pictures were taken to get the zero, first, second and third layer line pictures from which the unit cell dimensions and systematic extinctions could be determined. Using hexagonal indices, it was found that the non-extinctions were restricted to those indices which satisfy the relationship $(-h + k + 1) = 3n$ indicating a rhombohedral cell. The unit cell dimensions are: on the hexagonal lattice, $a = 9.22$ Å., $c = 6.2$ Å.; or on the rhombohedral lattice, $a = 5.71$ Å. and $\alpha = 107° 40'$. The number of molecules per unit cell is three for the hexagonal cell which is equivalent to one in the rhombohedral cell. The calculated density is 1.52 g./cm.^{3} and the molecular volume is 152 Å.^{3}. The space group is $C_{3v}^5 = R3m$.

The intensities of the zero layer line X-ray diffraction maxima were obtained from the X-ray films using multiple film technique (three films) and visual comparison.

Calculation of the Structure.—The intensities were corrected by the Lorentz and polarization factors[8] to get the "observed" structure factors, $|F_{hk0}|$. Since the phases associated with F_{hkl} values cannot be determined from X-ray data, a Fourier computation of the electronic densities, $\rho(xyz)$, could not be made immediately. To gain some knowledge of the structure, the trial method was used wherein the F_{hkl} values are calculated from various postulated structures and compared with the measured $|F_{hkl}|$ values. The phases are ob-

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(1) F. Beilstein and E. Weigand, *Ber.*, **16**, 1967 (1883).

(2) H. Z. Lecher, M. Scalera and C. T. Lester, U. S. Patent 2,403,226 (1946). See also U. S. Patents 2,402,647 (1946) and 2,396,582 (1946).

(3) A. B. Burg, THIS JOURNAL, **65**, 1629 (1943).

(4) H. Z. Lecher and W. B. Hardy, *ibid.*, **70**, 3789 (1948).

(5) For earlier controversial work see M. Delepine and R. Demars, *Bull. Sci. Pharmacol.*, **30**, 577 (1923); M. Auerbach and R. Wolffenstein, *Ber.*, **32**, 2507 (1899); and L. Mamlock and R. Wolffenstein, *Ber.*, **34**, 2499 (1901).

(6) L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 13, 17 (1937).

(7) L. Pauling, *J. Phys. Chem.*, **56**, 361 (1952).

(8) M. J. Buerger and G. E. Klein, *J. Applied Phys.*, **17**, 285 (1946).

tained as a by-product of these trials, and the $\rho(xyz)$ maps may be computed.

Since we were able to prove early in the investigation that the rotation of the groups would be about an axis parallel to the z-axis, then only the zero layer line values F_{hk0} were considered in the trials and only the $\rho(xy)$ plot was made in electron densities. The equation used in the F_{hk0} computation is

$$F_{hk0} = e^{-B\left(\frac{\sin\theta}{\lambda}\right)^2}\left[\sum_{j} f_i e^{2\pi i\,(hx_i + ky_i)} + \sum_{j'} f_{i'} J_0 \frac{(4\pi r_{i'} \sin\theta)}{\lambda}\right]$$

where j refers to the atoms in fixed positions and j′ to the atoms involved in free rotation. The values x_j and y_j are the postulated positions of atom j along the coördinates x and y; $r_{j'}$ is the perpendicular distance from the axis of rotation to atom j′ (or radius of rotation); exp $[-B(\sin\theta/\lambda)^2]$ is the temperature factor of Debye–Waller[9,10]; and J_0 $(4\pi r_{j'} \sin\theta/\lambda)$ is the zero order Bessel function which applies to free circular rotation as discussed by Zachariasen.[11] Table I gives the calculated F_{hk0} values for the four possible rotations referred to earlier for the particular projected distances (N–C) = 1.39 Å. and (S–O) = 1.50 Å. The values are normalized to F_{110} = 100 for comparison purposes. Other combinations of distances were tried but were less favorable. The Debye–Waller temperature factors have been applied to the calculated structure factors with 3 × 10^{-16} cm.^{2} as the most satisfactory value of B. It is interesting that the phases of all the structure factors turned out to be the same, *i.e.*, zero (a result which makes all structure factors positive). This result, however, is not surprising in view of the heavy concentration of atoms at the origin of the projection.

TABLE I

STRUCTURE FACTORS (NORMALIZED TO F_{110})

hk0	Observed	Calculated, $(N–C)_\perp$ = 1.39 Å., $(S–O)_\perp$ = 1.50 Å. C fixed O fixed	 C rotating O rotating	 C fixed O rotating	 C rotating O fixed
110	100	100	100	100	100
300	18.6	11.7	19.9	18.6	16.4
220	18.6	23.5	16.5	18.5	21.4
410	30.3	23.8	31.8	29.4	2.2
330	52.5	62.2	36.9	46.2	54.8
600	28.1	12.3	37.3	28.5	21.3
520	37.6	38.5	27.1	36.2	37.5
440	36.1	45.9	20.1	34.6	37.5
710	11.3	8.4	15.9	13.1	13.4
630	15.0	16.4	14.0	15.7	14.6
550	6.2	11.8	9.3	11.6	9.5
900	4.7	10.9	8.2	8.9	12.5
820	4.4	7.5	8.1	7.6	9.5
730	2.2	3.9	7.7	6.4	5.2

After discovering that the calculated structure factors were positive with all reasonably chosen atomic coördinates, it was possible to make a Fourier density summation using the observed F_{hk0} values. This is shown in Fig. 1 with arbitrary contour intervals. The high peak at the center of each group is due to superimposed nitrogen and sulfur atoms, and the six surrounding low peaks are presumed to be due to the carbon atoms. The oxygen atoms at a greater distance from the center and distributed uniformly about a circle (free rotation) contribute so little to the electron density at any particular area that its effect is hidden.

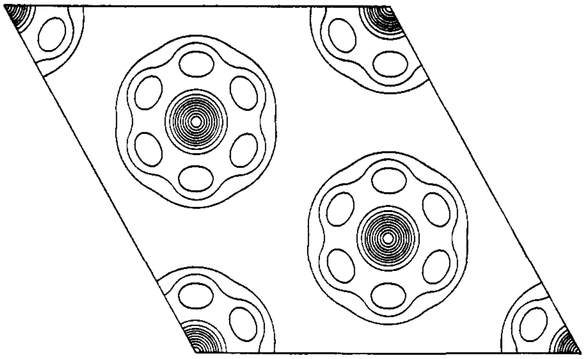

Fig. 1.—The c-axis projection of trimethylamine sulfur trioxide.

A sixfold symmetry in the zero layer of the reciprocal lattice is reflected in the sixfold symmetry of the density projection. Specific gravity considerations require that there be only one molecule per unit rhombohedral cell. For a single molecule of threefold symmetry to display sixfold symmetry, it is a further requirement that, on the average, only one-half of a carbon atom occupy each of the six positions. This condition is fulfilled by two sets of equilibrium positions being occupied by the three atoms either randomly or by highly hindered rotations.

The calculated structure factors were obtained on the basis of the one-half carbon per position. The closest fit was obtained for the conditions given in the fifth column of Table I. These values are plotted in Fig. 2 together with the observed values as a function of sin θ/λ.

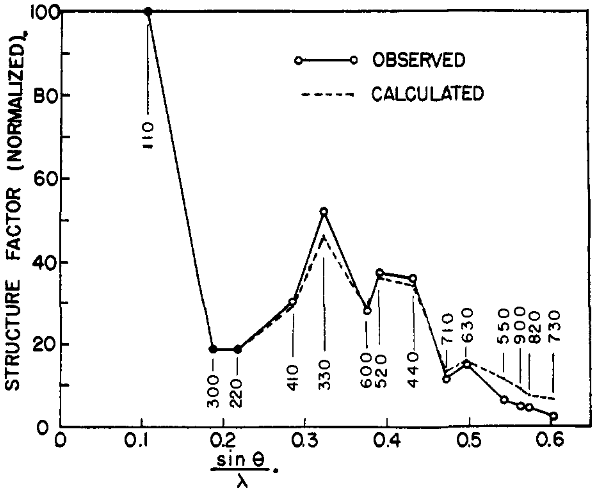

Fig. 2.—Structure factors.

The limitation of this investigation to the c-

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(9) P. Debye, *Ann. Physik*, **43**, 49 (1914).

(10) I. Waller, *Z. Physik*, **17**, 398 (1923).

(11) W. H. Zachariasen, "The Theory of X-Ray Diffraction in Crystals," John Wiley and Sons, New York, N. Y., 1945.

axis projection does not permit the determination of interatomic distances since none of the bonds is believed to be directed exactly perpendicular to the *c*-axis. However, the sulfur–oxygen projection distance is equal to the reported value of 1.50 Å. for the sulfates.

Summary.—The primary result of this investigation of the crystal structure of trimethylamine sulfur trioxide using X-ray diffraction is that, in the crystalline state, the SO_3 groups rotate about the molecular axes while the $N(CH_3)_3$ groups rotate very little, if at all. The basic unit cell was found to be a rhombohedron with a = 5.71 Å. and α = 107°40′ and containing one molecule. The space group is $C_{3v}^5 = R3m$ and the calculated density is 1.52 g./cm.^{3}.

Acknowledgments.—The authors are grateful for a grant from the University of Utah Research Fund for the support of this work and to the American Cyanamid Company for furnishing the samples.

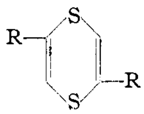
SALT LAKE CITY, UTAH

The Oxidation Products of 2,5-Diphenyl-1,4-dithiadiene

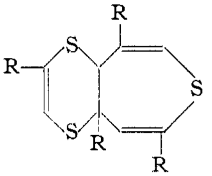
BY H. HARRY SZMANT AND JAMES DIXON

RECEIVED JUNE 1, 1953

The recent publication concerning the chemistry of the 1,4-dithiadiene system[1] and the reports of the Diels–Alder type condensation reactions in the course of the oxidation of thiophene[2] and benzothiophene[3,4] prompts us to report the results obtained in the study of the oxidation of 2,5-diphenyl-1,4-dithiadiene (I).



I



II

(R = C_6H_5)

When I was treated with an equimolar amount of hydrogen peroxide, there was obtained a compound $C_{32}H_{24}S_3$. Analogy with reactions previously studied[2,3,4] leads to the tentative assignment of structure II to this compound.

Further study is planned, but the behavior of II on vigorous oxidation is in agreement with the structure assigned. With excess hydrogen peroxide acting for a long time, 0.11 g. of II gave 0.025 of the disulfone of I, 0.093 g. of benzoic acid and 0.051 g. of barium sulfate. These amounts are 34, 174 and 169% of the expected ones, if one molecule of the disulfone were formed from each molecule of II. The deficiency in the yield of the disulfone and the excess of benzoic acid and sulfate ion indicates that the disulfone itself is not completely stable.

The disulfone was obtained directly from I, with excess hydrogen peroxide, but in only 50% yield, and accompanied by benzoic and sulfuric acids. This may indicate that even under these conditions II is an intermediate in the oxidation of I to its disulfone.

Experimental[5]

2,5-Diphenyl-1,4-dithiadiene-1,4-tetroxide.—I, 5.55 g., was heated with an excess of hydrogen peroxide in glacial acetic acid until the yellow color of the starting material faded. On cooling there was isolated 50.5% of desired disulfone of I, m.p. 232°.

Anal. Calcd. for $C_{16}H_{12}O_4S_2$: C, 57.82; H, 3.61. Found: C, 57.63; H, 3.78.

The filtrates from the oxidation reaction were concentrated and finally diluted with water in order to isolate additional material. There was obtained only benzoic acid and sulfate ion (precipitated as barium sulfate).

Oxidation of I with Equimolar Hydrogen Peroxide.—Equimolar amounts of I and hydrogen peroxide were heated in glacial acetic acid for one hour and the reaction mixture was poured on ice. The precipitate was crystallized repeatedly from isopropyl alcohol to give yellow crystals, m.p. 128° (II).

Anal. Found: C, 76.12; H, 4.64; S, 19.20; mol. wt. (Rast), 510–560. The repetition of this experiment gave the same results. Found: C, 76.28; H, 4.90. Calcd. for $C_{32}H_{24}S_3$: C, 76.16; H, 4.79; S, 19.09; mol. wt., 502.7.

Quantitative Oxidation of II with Hydrogen Peroxide.—II, 0.1094 g., was heated with an excess of hydrogen peroxide in glacial acetic acid, and nitrogen was used to sweep any carbon dioxide produced in the reaction into a solution of barium hydroxide. The reaction mixture gave on cooling 0.0247 g. (34%) of the disulfone of I, m.p. 232°. The filtrate on concentration gave no additional disulfone and was diluted with water. The aqueous solution was extracted with ether and the ether layer was dried and concentrated. The residual liquid was placed in a desiccator containing sodium hydroxide pellets, and after several days *in vacuo* the residue became solid and there was isolated 0.0928 g. of benzoic acid. The aqueous portion from the extraction was boiled to expel carbon dioxide and then was treated with barium hydroxide to give 0.0507 g. of barium sulfate.

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[1] W. E. Parham, T. M. Roder and W. R. Hasek, THIS JOURNAL, **75**, 1647 (1953).

[2] W. Davies, N. W. Gamble, F. C. James and W. E. Savige, *Chem. Ind.*, 804 (1952).

[3] W. Davies, *et al.*, *J. Chem. Soc.*, 4678 (1952).

[4] F. G. Bordwell, W. H. McKellin and D. Babcock, THIS JOURNAL, **73**, 5566 (1951).

[5] All melting points are uncorrected. Microanalyses by Mr. George Stragand, University of Pittsburgh.

Studies in Low Concentration Chemistry. IV. The Radiocolloidal Properties of Beryllium

BY GEORGE K. SCHWEITZER AND JAMES W. NEHLS

RECEIVED MAY 13, 1953

In 1950, Haymond, Garrison and Hamilton[1] noted the radiocolloidal behavior of beryllium when they found that they could separate carrier-free[2] beryllium-7 from lithium solutions by making such solutions basic and then filtering them through a glass frit. This paper constitutes a further investigation of the radiocolloidal properties of beryllium, using beryllium-7 as a tracer nuclide.

Experimental

Materials.—All inactive chemicals were of analytical reagent quality. All water was triply distilled and was pre-

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[1] H. R. Haymond, W. M. Garrison and J. G. Hamilton, *J. Chem. Phys.*, **18**, 1685 (1950).

[2] The term carrier-free is used to indicate that no inert beryllium has been intentionally added.