[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

X-Ray Structure Determination of $(CH_3)_2NSO_2N(CH_3)_2$ and LCAO–MO Study of Multiple Bonding in Sulfones

BY TRUMAN JORDAN, H. WARREN SMITH, L. L. LOHR, JR., AND WILLIAM N. LIPSCOMB

RECEIVED NOVEMBER 3, 1962

The crystal and molecular structure of $(CH_3)_2NSO_2N(CH_3)_2$ has been solved, and the bonding in isoelectronic $F_2NSO_2NF_2$ has been investigated in the LCAO–MO one-electron approximation in order to provide a model for understanding the barrier to internal rotation observed in α-sulfonyl carbanions. The barrier is shown to arise from interactions involving the d-orbitals of S with the p-orbitals of bonded atoms.

Introduction.—Retention of configuration of α-sulfonyl carbanions, the subject of several recent investigations,[1-5] implies the existence of a barrier to internal rotation which has not heretofore been explained. The retention is illustrated by the much faster rate of deuterium–hydrogen exchange as compared with the rate of racemization of an optically active carbanion.[1-5] Our results for the geometry of $(CH_3)_2NSO_2N(CH_3)_2$ and valence structure of $F_2NSO_2NF_2$, similar in the region of interest in stereochemistry and bonding to α-sulfonyl carbanions, suggest that a reasonable explanation of this retention of configuration lies primarily in the competition of neighboring orbitals for the d-orbitals of S, and not in other possible sources such as modified sp^3 hybridization about the $C\alpha^-$ bond to S in the carbanions.

The particular orientation about the $C\alpha^-$ bond which does not allow a plane of symmetry is the case II geometry,[6] and this geometry is shown to occur in $(CH_3)_2NSO_2N(CH_3)_2$. We find that the bond angles about N suggest an intermediate hybridization between sp^3 and sp^2. For example, the S–N–CH_3 bond angle is 119°, as reported in our preliminary communication,[7] different from the analogous S–N . . . O hydrogen bond angle of 111° about N in sulfamide[8] in which H may not be on the N . . . O line. Intermediate hybridization is suggested[9] by the comparable amounts of exchange in cyclopropyl phenyl and isopropyl phenyl sulfones. Finally, the comparable rates of D–H exchange in phenyl 2-octyl sulfone and phenyl 1,2,2-trimethylpropyl sulfone have led to the conclusion[10] that the ion is planar, or very nearly so, and that the results can only be explained in terms of an anion having case II geometry and a barrier to internal rotation about the $C\alpha^-$–S bond.

X-Ray Diffraction Study of $(CH_3)_2NSO_2N(CH_3)_2$.—A single crystal of cross section approximately $(4\mu)^{-1}$, where μ is the linear absorption coefficient, was used to record the hKl levels for $0 \leq K \leq 5$ on the Weissenberg goniometer (CuKα radiation), and the Hkl levels for $0 \leq H \leq 3$ and hkL levels for $0 \leq L \leq 1$ on the precession goniometer (MoKα radiation). Reciprocal lattice symmetry of D_{2h}, and extinctions of hkl when $h + k$ is odd, $h0l$ when l is odd and $hk0$ when h is odd led to either Cmca or C2ca as probable space groups. Unit cell dimensions of $a = 11.76$, $b = 5.68$ and $c = 22.03$ Å. give an X-ray density of 1.37 g. cm.$^{-3}$, if 8 molecules are placed in the unit cell, in agreement with the observed density of 1.34 g. cm.$^{-3}$.

A completely satisfactory structure, including location of H atoms, was obtained on the assumption that the space group is Cmca. Clearly, however, we cannot rule out small distortions into the lower symmetry of C2ca; but in view of the agreement obtained below, these distortions must be very slight, if they occur at all, and we therefore believe that the space group Cmca is indeed correct. The initial attack on the structure was the solution of the fully resolved b-axis projection. The $h0l$ data required for this projection were present only for $l = 4n$, with three very faint exceptions, and hence only one molecule occurred in this pseudo-unit cell when projected along b. Examination of the space group led to the placement of S on a mirror plane, chosen at $x = 0$ and $z = 1/8$, with a molecular twofold axis along b. Slight deviations from this precise C_{2v} symmetry are permitted, and do occur, in the three-dimensional structure for which only molecular symmetry C_s is required in the space group Cmca if compatibility with this projection is required.

In the next stage, three-dimensional data from the films listed above were estimated visually with the use of a standard scale, corrected to F^2_{hkl}, correlated and scaled statistically. Three-dimensional Patterson functions were computed using both normal and derivative sharpening.[11] These functions quickly confirmed the x- and z-coördinates obtained from the projection, and also established the y-coordinates of all atoms except H. A minor difficulty produced either by oversharpening these functions or by the lack of satisfactory convergence because of the short b-axis was that the N . . . N and C . . . C vectors related by the mirror plane were not located in the negative region around the origin of Patterson space. Elsewhere, however, no difficulties were encountered, and the coördinates thus found did refine satisfactorily.

Three-dimensional least squares refinement starting with isotropic temperature factor constants of $B = 3$ Å.^{2} reduced $R(F^2) = \Sigma|F_0^2 - F_c^2|/\Sigma F_0^2$ from 0.62 to 0.47. Introduction of anisotropic thermal parameters reduced $R(F^2)$ to 0.28, and a one-parameter correction for secondary extinction of the eight largest reflections reduced $R(F^2)$ further to 0.21. The H atoms, omitted from the above refinements, were located from a difference synthesis in which all atoms except H were subtracted (Fig. 1). A summary of all peaks higher than 0.4 e/Å.$^{-3}$ indicates incomplete subtraction of the heavier atoms, and also shows the general level of reliability of the difference map in which the highest unexplained peak is just below the level of the least prominent H atom. Introduction of these H atoms with fixed coördinates and a B-value of 4.3 Å.^{2} reduced $R(F^2)$ to 0.17, and yielded the conventional $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ value of 0.085.

(1) D. J. Cram, W. D. Nielson and B. Rickborn, *J. Am. Chem. Soc.*, **82**, 6415 (1960).
(2) E. J. Corey and E. T. Kaiser, *ibid.*, **83**, 490 (1961).
(3) D. J. Cram, D. A. Scott and W. D. Nielson, *ibid.*, **83**, 3696 (1961).
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(5) H. L. Goering, D. L. Townes and B. Dittmer, *J. Org. Chem.*, **27**, 736 (1962).
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(9) H. E. Zimmerman and B. S. Thyagarjan, *J. Am. Chem. Soc.*, **82**, 2505 (1960).
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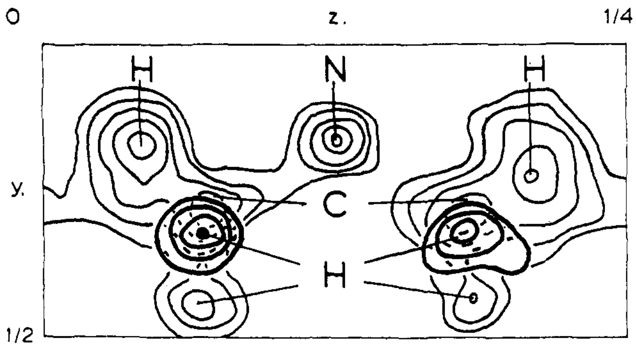

Fig. 1.—The x = 8/30 and x = 13/30 sections of the difference fourier. Contours start at 0.3 $e/Å.^3$ and are drawn at increments 0.1 $e/Å.^3$ thereafter.

The molecular structure is shown in Fig. 2, and the projection of the crystal structure is given in Fig. 3. Bond distances and angles are in Table II, position and thermal parameters are in Table III, values of the disagreement factor R are in Table IV, and a very compact list of the 627 observed F_{hkl} is given in Table V. Since the normals to the CNC plane and the NSN planes are 89.4 ± 0.3° apart, the molecule belongs to the case II category.[6] The close proximity of 3.5 Å. of an O atom of one molecule to the two methyl groups on the molecule related to it by a two-fold screw axis along y (Fig. 3) appears to provide a basis for explaining the 1.8° difference between the $S_1N_4C_6$ and $S_1N_4C_5$ angles. We therefore believe that the small but significant deviations of the molecular symmetry from C_{2v} are associated with molecular packing in the crystal, and hence we discuss the molecular parameters as averaged over C_{2v} symmetry.

TABLE I

ALL PEAKS WITH A HEIGHT GREATER THAN 0.4 $e/Å.^3$ WHICH APPEARED IN THE DIFFERENCE FOURIER

Peak height in $e/Å.^3$	x	y	z	Explanation
2.9	0.000	0.017	0.125	S_1
1.0	.000	− .133	.071	O_3
0.9	.000	− .070	.183	O_2
.8	.115	.173	.124	N_4
.7	.000	− .167	.121	0.95 Å. from S
.7	.148	.297	.069	C_5
.7	.130	.167	.042	H
.7	.147	.293	.182	C_6
.6	.128	.220	.211	H
.6	.217	.333	.067	H
.5	.117	.443	.067	H
.5	.217	.317	.181	H
.5	.130	.440	.187	H
.4	.000	− .467	.198	—
.4	.000	− .300	.183	—

Besides the molecular orbital study of the next section, there are clear indications from bond angles and distances that d-orbital participation is important in the bonding. For example, the average SNC angle is 119°, substantially greater than tetrahedral, and the CNC angle is 112.9°, slightly greater than tetrahedral. Also, the N atom is only 0.27 Å. away from the plane of the three atoms bonded to it, in a direction which increases the N . . . N separation, whereas a distance of 0.51 Å. would be expected if the bonding were tetrahedral. If bond angles do indeed define hybrid orbitals, except in small rings, then Coulson's method[12] leads to the result that the lone pair is 93% p, closer to the 100% for sp^2 than to the 75% for sp^3 bonds. Thus the hybridization is $sp^{2.23}$ for bonds involving N. Ninety-six per cent of this p-character (89% of the lone pair) is perpendicular to the N–S bond and in the NSN plane. Therefore, a substantial amount of conjugation of this lone pair with the d-orbitals of S is expected, and the observed S–N bond distance of 1.623 Å. is substantially shorter than the 1.04 Å. (S) + 0.74 Å. (N) − 0.045 Å. (electronegativity correction) = 1.735 Å. expected for a single bond. In the carbanions themselves, where $C\alpha^-$ replaces N, the relatively greater orbital size around $C\alpha^-$ can be expected to increase the multiple bonding over that in the N analog.

(12) C. A. Coulson, V. Henri Memorial Volume, Contribution à l'Étude de la Structure Moleculaire, Desoer, Liege (1948), p. 25.

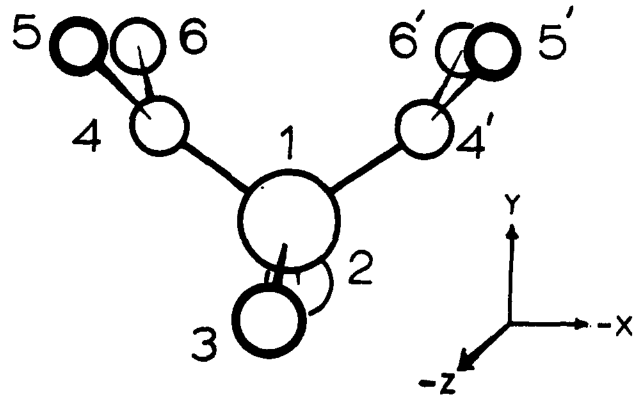

Fig. 2.—The $(CH_3)_2NSO_2N(CH_3)_2$ molecule. Primed atoms are related to unprimed atoms by the mirror plane of the crystal. An error (which has been corrected here) was made in numbering a similar figure in reference 7.

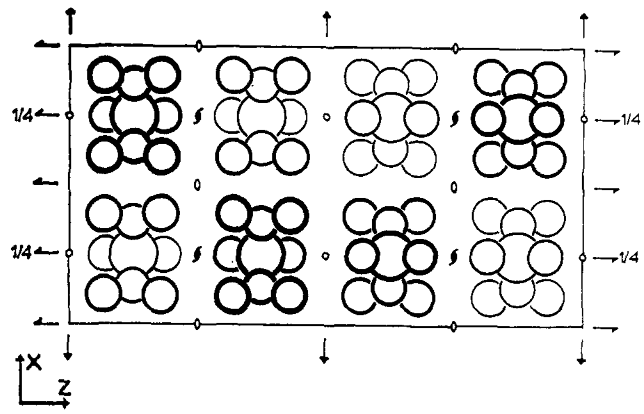

Fig. 3.—Projection of the unit cell along the y-axis. Glide and mirror planes have been excluded, but all other symmetry elements are present.

TABLE II

Bond distances in angstroms[a]		Bond angles in degrees[b]	
S_1O_2	1.449	$O_2S_1O_3$	119.7
S_1O_3	1.441	$S_1N_4C_6$	119.7
S_1N_4	1.623	$S_1N_4C_5$	117.9
N_4C_5	1.480	$C_5N_4C_6$	112.9
N_4C_6	1.471	$N_4S_1N_4$	112.6

[a] Standard deviations are 0.005 for bonds involving S and 0.007 Å. for CN bonds, but corrections which range from 0.009 to 0.029 Å. have been made for thermal motion. [b] Standard deviations are 0.4° for all angles.

We close this section on purely geometrical and hybridization effects with a remark on steric aspects. In $(CH_3)_2NSO_2N(CH_3)_2$ the $C_6 \ldots C_6'$ and $C_5 \ldots C_5'$ distances are 3.4 and 3.5 Å., respectively. If one $N(CH_3)_2$ group is rotated by 90° about the N–S bond, the closest non-bonded contacts are then N_4 . . .

TABLE III

FINAL POSITION AND THERMAL[a,b] PARAMETERS

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S_1	0.000	0.015	0.126	4.3	1.9	2.9	0.0	0.0	0.1
O_2	.000	− .101	.184	7.2	4.0	3.7	.0	.0	1.5
O_3	.000	− .120	.072	8.4	3.0	4.2	.0	.0	−1.2
N_4	.114	.172	.125	4.4	4.3	3.7	.3	.0	0.0
C_5	.144	.292	.068	5.6	4.7	5.1	− .6	1.5	0.6
C_6	.147	.306	.179	4.9	6.0	4.6	−1.3	0.3	1.2

[a] The thermal parameters are in the form:

$$\exp -(4)^{-1}[B_{11}(a^*)^2h^2 + B_{22}(b^*)^2k^2 + B_{33}(c^*)^2l^2 + 2B_{12}(a^*)(b^*)hk + 2B_{13}(a^*)(c^*)hl + 2B_{23}(b^*)(c^*)kl]$$

[b] Since no absorption corrections were made, no interpretation of the thermal parameters will be attempted.

$C_5' = 3.0$ Å. and $C_5 \ldots C_5' = C_5 \ldots C_6' = 3.1$ Å., while if both $N(CH_3)_2$ groups are rotated the $C_5 \ldots C_5'$ distance is only 2.5 Å. Most of the implied intramolecular strain can no doubt be relieved by a coöperative rotation in which the two $N(CH_3)_2$ groups are continuously maintained approximately 90° out of phase, but some steric contributions to the barrier may remain, particularly if, in other examples, bulkier groups are attached to the N or to the $C\alpha^-$ of the analogous carbanion.

LCAO-MO Study of d-Orbital Interactions.—A more detailed examination of the valence structure of $(CH_3)_2NSO_2N(CH_3)_2$ by the one-electron molecular orbital method was carried out with the simplification that the CH_3 group was replaced by the isoelectronic F atom, and the effect of changing the nuclear charge was studied. The results, described below, clearly suggest that the C_{2v}, type II, geometry as found in $(CH_3)_2NSO_2N(CH_3)_2$ is more stable than the C_s geometry in which both NF_2 groups of $F_2NSO_2NF_2$ are rotated by 90° about the SN bond. In the more stable C_{2v} geometry the lone pair of N does not compete so strongly with the orbitals on O atoms for the d-orbitals of S, whereas this competition reduces the total conjugation in the unfavorable C_s geometry which is therefore less stable.

TABLE IV

VALUES OF $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ FOR OBSERVED REFLECTIONS

Class	R	Range α sin θ	R
hkl	0.085	0.000–0.190	0.105
h even	0.087	0.190–0.260	0.066
k even	0.087	0.260–0.300	0.073
l even	0.087	0.300–0.330	0.057
h + k even	0.079	0.330–0.360	0.079
h + l even	0.072	0.360–0.375	0.082
k + l even	0.072	0.375–0.415	0.087
h + k + l even	0.087	0.415–0.460	0.110
hk0	0.123	0.460–0.490	0.102
h0l	0.076	0.490–0.550	0.142
0kl	0.088		

All nine valence orbitals of the 3s, 3p and 3d type are included for S, and four orbitals of the 2s and 2p type are included for each remaining atom of $F_2NSO_2NF_2$. All possible overlap integrals are included. The bond angles and distances, averaged where equivalent in the isolated molecule, found in the X-ray study were used. Three molecular conformations were treated: (a) the geometry found in the X-ray study averaged to C_{2v}, (b) a structure designated as C_{2v}' obtained by rotating both NF_2 groups by 180° about the S–N bond, and (c) a structure designated as C_s obtained by rotating both NF_2 groups by 90° about the S–N bond. Each conformation was studied both with and without the inclusion of the 3d-orbitals of S. As expected, we shall see that the replacement of CH_3 by F reduces the electron density in the region of interest, and hence the N–S orbital interactions are underestimated relative to those in $(CH_3)_2NSO_2N(CH_3)_2$.

The problem was formulated as a program for the IBM 7090. Real Slater orbitals were used, with p_x along x, etc., in a right-handed coordinate system (Fig. 2). The elements of the complete overlap matrix **S** are expressed as products of geometric factors computed from the atomic coordinates and the overlap integrals. The geometrical factors for interactions involving d-orbitals are obtained by coördinate transformations of the appropriate tesseral harmonics, and a method described elsewhere[13] is used for the remaining interactions. As an example, the d_{z^2} and d_{xy} orbitals are represented as matrices

$$\begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

which are transformed to a coordinate system oriented toward the atom under consideration, and then the coefficients of σ-type interactions are obtained from the 3,3 elements of the transposed arrays, while those of the π-type interactions are related to the 1,3 and 2,3 elements. The elements of the "effective Hamiltonian" matrix **H** are then related to **S** by[14]

$$H_{ij} = K(H_{ii}H_{jj})^{1/2}S_{ij}, \quad i \neq j$$

where H_{ii} is the negative of the valence state ionization potential (VSIP) of an electron in the ith atomic orbital, and K is a dimensionless constant usually set equal to −2. The VSIP listed as Coulomb integrals with Slater exponents in Table VI were taken from tables[15] and from atomic energy levels,[16] with corrections estimated for assumed charges of −0.50 on F, and +0.25 on N, −0.25 on O and +2.00 on S. The eigenvalues and eigenvectors are obtained by solution of the equation det $(\mathbf{H} - \lambda\,\mathbf{S}) = 0$, in which each matrix is 41 × 41 in size.

The results, summarized in Tables VII–XIII, require the definitions

i, k represent atomic orbitals
l, m represent atoms
j represents a molecular orbital (MO)
n_j is the occupation number of the jth MO
E_j is the energy of the jth MO, and
C_{ij} is the coefficient of the ith AO in the jth MO

The total orbital energy (Table VII) is then

$$E = \sum_j n_j E_j$$

and the orbital and overlap population matrix elements

(13) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962).
(14) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
(15) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).
(16) C. E. Moore, "Atomic Energy Levels," Natl. Bureau of Standards, Circular No. 467, Vol. I.

TABLE V

VALUES OF $10F$ OBSD. FOR $(CH_3)_2NSO_2N(CH_3)_2$

ℓ=0(h,k): (2-16,0) 1610,221,1291,1306,354,177, 198,108; (0-16,2) 324,967,1641,389,163,351, 214,80,59; (0-14,4) 199,120,154,270,154,87, 133,90; (0-10,6) 313,216,141,156,203,115.

ℓ=1(h,k): (1-15,1) 1204,1089,614,463,386,238, 93,74; (0-14,2) 488,230,353,317,59,86,62,65; (1-15,3) 146,154,387,261,45,62,135,69; (0-14,4) 78,73,58,193,a,84,57,79; (1-11,5) 90,196,95,45, 142,113; (0-12,6) 126,213,210,91,93,112,45; (1-9,7) 190,104,117,128,75; (0-2,8) 121,101.

ℓ=2(h,k): (1-11,1) 835,1767,739,320,96,153; (0-6,2) 103,76,49,47; (1-11,3) 356,86,66,185, a,51; (2-4,4) 39,54; (1-11,5) 161,268,304,141, a,47; (1-3,7) 275,127.

ℓ=3(h,k): (1-13,1) 1002,826,542,425,377,219,83; (0-10,2) 51,76,289,179,a,80; (1-13,3) 244,309, 461,288,73,86,140; (0-12,4) 93,80,200,198,a,a, 55; (1-11,5) 185,203,134,126,144,42; (0-2,6) 119,187; (1-3,7) 134,105.

ℓ=4(h,k): (0-12,0) 1967,1039,240,581,662,371, 146; (0-14,2) 343,640,806,461,247,217,162,85; (3,3) 65; (0-12,4) 309,386,439,335,193,152,121; (1-7,5) 80,14,a,60; (0-2,6) 315,261.

ℓ=5(h,k): (1-13,1) 730,304,229,343,283,143,78; (0-10,2) 493,238,101,a,186,104; (1-13,3) 114, 455,435,160,80,130,103; (0-12,4) 40,122,254, 149,a,a,63; (1-9,5) 310,191,172,183,142; (0-2,6) 115,94; (1-3,7) 152,135.

ℓ=6(h,k): (1-13,1) 316,482,68,a,251,130,73; (0-6,2) 104,89,58,40; (1-13,3) 446,217,267,268,83, a,59; (2-4,4) 77,83; (1-7,5) 76,223,215,66; (1,7) 131.

ℓ=7(h,k): (1-13,1) 539,52,68,287,249,120,70; (0-10,2) 876,323,113,183,259,60; (1-13,3) 263, 645,527,185,129,181,96; (0-10,4) 94,219,372, 109,a,82; (1-9,5) 411,195,205,233,143; (0,6) 111; (1-3,7) 84,131.

ℓ=8(h,k): (0-10,0) 518,394,266,247,215,416; (1-3,1) 112,39; (0-12,2) 670,271,350,580,290, 47,139; (1,3) 62; (0-12,4) 430,602,653,392,243, 223,42; (1-3,5) 62,18; (0-2,6) 312,304.

ℓ=9(h,k): (1-13,1) 472,111,a,272,208,68,64; (0-10,2) 979,425,a,257,283,93; (1-11,3) 136,626, 472,90,a,170; (0-10,4) 107,234,370,93,a,91; (1-9,5) 403,159,169,228,116; (0,6)113; (1-3,7) 78,115.

ℓ=10(h,k): (1-13,1)446,661,31,a,297,151,86; (2,2) 54; (1-9,3) 483,210,321,290,65; (0-4,4) 65,58,31; (1-7,5) 23,129,122,18; (1,7) 73.

ℓ=11(h,k): (1-13,1) 447,a,118,284,203,91,56; (0-8,2) 663,219,95,158,204; (1-11,3) 208,589,439, 138,133,166; (0-10,4) 163,115,264,a,23,33; (1-9,5) 353,170,168,205,98; (0,6) 85; (1-3,7) 95,111.

ℓ=12(h,k): (0-10,0) 477,511,175,a,349,337;(1,1) 61; (0-12,2) 453,406,485,451,202,92,139; (1-3,3) 33,71; (0-10,4) 397,434,436,280,222,148; (1-7,5) 61,a,a,14; (0-2,6) 236,232.

ℓ=13(h,k): (1-11,1) 456,209,206,257,191,98; (0-8,2) 359,123,80,83,128; (1-11,3) 185,399,326, 133,80,101; (2-10,4) 109,188,58,a,27; (1-7,5) 202,111,87,112; (0,6) 82.

ℓ=14(h,k): (1-13,1) 329,160,225,107,152,a,29; (3-11,3) 105,80,a,a,27; (0,4) 31; (1-7,5) 58, 99,117,61; (1-3,7) 138,99.

ℓ=15(h,k): (1-11,1) 521,410,322,298,217,127; (0-6,2) 45,a,73,50; (1-11,3) 190,259,253,143, 85,63; (4-6,4) 43,44; (1-7,5) 126,119,86,59, (2,6) 90; (1-3,7) 113,68.

ℓ=16(h,k): (0-10,0) 1273,612,223,455,456,188;(1,1) 69; (0-10,2) 191,462,505,234,112,161; (0-8,4) 186, 159,156,192,113; (1,5) 27; (0-2,6) 157,122.

ℓ=17(h,k): (1-11,1) 349,347,237,173,158,93; (0-6,2) 96,79,111,104; (1-7,3) 156,101,157,145; (0-6,4) 38,a,a,81; (1-5,5) 59,101,38; (2,6) 150; (1,7) 80.

ℓ=18(h,k): (0-4,0) 136,135,136; (1-11,1) 184, 369,214,133,a,62; (0-2,2) 80,70; (1-7,3) 108, 63,a,61; (1-5,5) 78,128,94; (1-3,7) 163,85.

ℓ=19(h,k): (1-9,1) 407,370,270,209,188; (0-6,2) 72,a,a,80; (1-7,3) 125,126,176,142; (0-6,4) 73, a,a,90; (1-3,5) 73,101; (2,6) 96; (1-3,7) 98, 66.

ℓ=20(h,k): (0-10,0) 715,416,139,326,295,126; (0-8,2) 122,285,296,124,95; (0-6,4) 107,135, 147,113; (0-2,6) 182,144.

ℓ=21(h,k): (1-9,1) 201,180,121,110,100; (1-7,3) 74,86,130,72; (0-6,4) 65,45,83,58; (1-3,5) 80, 88; (2,6) 100; (3,7) 65.

ℓ=22(h,k): (1-5,1) 95,90,48; (0,2) 54; (1-7,3) 71,61,43,40; (3,5) 141.

ℓ=23(h,k): (1-7,1) 200,154,105,111; (0,2) 96; (1-5,3) 104,160,146; (2,4) 45; (1-3,5) 136,104; (3,7) 65.

ℓ=24(h,k): (0-4,0) 211,207,123; (0-6,2) 171, 179,130,115; (0-2,4) 98,205; (2,6) 141.

ℓ=25(h,k): (1-3,1) 120,53; (0-2,2) 131,92; (1-3,3) 33,127; (1-3,5) 121,68.

ℓ=26(h,k): (1-3,1) 50,100; (1,3) 103; (3,5) 67.

ℓ=27(h,k): (1-3,1) 113,69; (0,2) 108; (1-3,3) 85,178; (1-3,5) 137,78.

ℓ=28(h,k): (0-2,0) 99,129; (0-2,2) 146,114; (2,4) 154; (2,6) 64.

ℓ=29(h,k): (1,1) 91; (0,2) 96; (3,3) 113.

(Tables VIII and IX) are

$$OP_{ii} = \sum_j n_j C_{ij}^2, \text{ and}$$

$$OP_{ik} = 2\sum_j n_j C_{ij} C_{kj} S_{ik},\ i \neq k$$

The atomic and bond charge matrix[17] (Tables X and XI) is defined by

$$Q_{lm} = \sum_{\substack{i \text{ on } l \\ k \text{ on } m}} OP_{ik}$$

In Table XII we give a partial tabulation of the fraction F_{ij} of each atomic orbital in each molecular orbital,[18] according to the relation

$$F_{ij} = C_{ij}\sum_k S_{ik}C_{ij}$$

and in Table XIII we list those elements of the overlap matrix involving the d-orbitals of S for reference in the discussion below.

Discussion.—The differences in total orbital energies (Table VII) give the observed conformation (C_{2v}) a stability of 9.54 kcal./mole relative to the C_s conformation. Moreover this stability arises almost completely from the d-orbital interactions. On the other hand, the relatively smaller difference of 3.59 kcal./mole between the C_{2v} and C_{2v}' conformations appears to be independent of the d-orbital interactions. Owing to the semi-empirical nature of the method, these exact numbers are not of significance, but the essential nature of the barrier becomes clear in the following analysis. The sum of the energies of the two highest occupied molecular orbitals is less for the C_{2v} conformation than for the C_s conformation by 12.76 kcal./

TABLE VI

	Slater exponents (s,p)	Slater exponents d	Coulomb integrals, e.v. s	Coulomb integrals, e.v. p	Coulomb integrals, e.v. d
Fluorine	2.600	—	−37.24	−19.86	—
Oxygen	2.275	—	−35.57	−18.03	—
Nitrogen	1.950	—	−27.42	−14.92	—
Sulfur	2.050	2.050	−24.08	−17.32	−7.0

TABLE VII

TOTAL ORBITAL ENERGIES

	With sulfur d	Without sulfur d
C_{2v}	−1350.606 e.v.	−1347.470 e.v.
C_{2v}'	−1350.450 e.v.	−1347.318 e.v.
C_s	−1350.191 e.v.	−1347.311 e.v.
$C_{2v}' - C_{2v}$	0.156 e.v. = 3.59 kcal./mole	0.152 e.v. = 3.50 kcal./mole
$C_s - C_{2v}$	0.415 e.v. = 9.54 kcal./mole	0.159 e.v. = 3.66 kcal./mole

(17) R. McWeeny, *J. Chem. Phys.*, **19**, 1614 (1951).

(18) R. S. Mulliken, *ibid.*, **23**, 1833 (1955).

Table VIII

Orbital Populations[a]

		With sulfur *d*			Without sulfur *d*		
		C_{2v}	C_s	C_{2v}'	C_{2v}	C_s	C_{2v}'
N	*s*	1.009	1.001	1.002	1.018	1.004	1.008
	x	1.198	0.448	0.507	1.307	0.466	0.532
	y	0.910	0.331	1.601	0.985	0.388	1.776
	z	0.247	1.598	0.246	0.246	1.732	0.246
O^I	*s*	1.638	1.641	1.639	1.600	1.604	1.601
	x	1.808	1.828	1.825	1.959	1.961	1.962
	y	1.679	1.730	1.677	1.816	1.834	1.816
	z	1.497	1.483	1.496	1.520	1.517	1.519
O^{II}	*s*	1.638	1.641	1.639	1.600	1.604	1.601
	x	1.808	1.810	1.825	1.959	1.960	1.962
	y	1.679	1.717	1.677	1.816	1.831	1.816
	z	1.497	1.485	1.496	1.520	1.519	1.519
S	*s*	0.537	0.537	0.538	0.535	0.535	0.536
	x	0.547	0.566	0.591	0.561	0.573	0.586
	y	0.550	0.518	0.498	0.528	0.514	0.495
	z	0.359	0.370	0.360	0.347	0.349	0.347
	z^2	0.061	0.051	0.065	0	0	0
	$x^2 - y^2$	0.071	0.005	0.074	0	0	0
	xy	0.063	0.043	0.061	0	0	0
	xz	0.024	0.046	0.023	0	0	0
	yz	0.028	0.076	0.028	0	0	0
F^I	*s*	1.867	1.867	1.867	1.867	1.867	1.866
	x	1.966	1.550	1.817	1.967	1.549	1.818
	y	1.856	1.860	2.004	1.859	1.861	2.008
	z	1.566	1.961	1.555	1.556	1.965	1.554
F^{III}	*s*	1.867	1.867	1.867	1.867	1.867	1.866
	x	1.966	1.978	1.817	1.967	1.979	1.818
	y	1.856	1.443	2.004	1.859	1.439	2.008
	z	1.566	1.961	1.555	1.556	1.966	1.554

[a] In the rotated C_s conformation, O^I is the oxygen atom closer to the equivalent F^I and F^{II} closest to S, while F^{III} and F^{IV} are further away

mole; *i.e.*, about 4/3 of the total of 9.54 kcal./mole. Both of these molecular orbitals consist of about 40% of p-orbitals of N, as measured by the F_{ij}, and the signs of the coefficients indicate that these orbitals roughly approximate to "lone pair" orbitals. Also there is about 3.5% less d-character in the two C_s MO's than in the two C_{2v} MO's, and this loss occurs primarily from the $d_{x^2-y^2}$ orbital. This same conclusion is also indicated by the $d_{x^2-y^2}$ overlap populations of 0.071 and 0.005 for the C_{2v} and C_s conformations, respectively (Table VIII). In the C_{2v} conformation the p_x and p_y orbitals of N, primarily lone pair orbitals, interact with d_{xy} and $d_{x^2-y^2}$, respectively, while in the C_s conformation (nuclear coördinates changed but basis functions remain along *x,y,z* of Fig. 2) the p_z-orbital of N, now primarily a lone pair orbital, interacts with d_{xz} and d_{yz} of S.

Our essential conclusion is that in the C_s conformation the lone pair of N has to compete more with the lone pairs of O atoms for d-orbital stabilization than in the C_{2v} conformation. The overlap integrals of Table XIII further support this conclusion, since overlaps with d_{xz} and d_{yz} are greatest for oxygen p-orbitals, but overlaps with $d_{x^2-y^2}$ and d_{xy} are greater for N with a strong preference for p_x and p_y thus favoring the C_{2v} conformation. It may be noted that the competition of O- and N-orbitals for particular d-orbitals of S was not included in our earlier discussion[7] in which the source of the barrier was not found. In terms of the representation of the C_{2v} group with the *y*-axis along the molecular twofold axis, the d-orbitals and their symmetries are d_{z^2} and $d_{x^2-y^2}$ of symmetry a_1, d_{xy} of symmetry b_1, d_{xz} of symmetry a_2 and d_{yz} of symmetry b_2. Thus the case II conjugation[6] of symmetries a_1 and b_1 is greater in $F_2NSO_2NF_2$ than the case I conjugation of symmetries a_2 and b_2, because the latter involves greater competition for the sulfur d-orbitals by the lone pairs of the oxygen atoms.

One set of calculations was made to test the influence of nuclear charge of the F atom on the barrier. The F atoms are essentially replaced by C atoms having a Slater exponent of 1.625, and VSIP's of 21.0 e.v. for 2s and 11.27 for 2p orbitals.[15] The energy difference between C_{2v} and C_s conformations is 24.17 kcal./mole in the same direction as found above. The sums of orbital population of d-orbitals of S are 0.657 for the C_{2v} conformation and 0.573 for the C_s conformation, and the $d_{x^2-y^2}$ population is 0.238. Thus the total d-occupancy in $C_2NSO_2NC_2$ is greater than the values of 0.247 for C_{2v} and 0.221 for C_s in $F_2NSO_2NF_2$ by about 2.6, which is about the same ratio found for the barriers. Thus no qualitative difficulties arise when $F_2NSO_2NF_2$ is used as a model for the isoelectronic $(CH_3)NSO_2N(CH_3)_2$.

Table IX

Nitrogen–Sulfur Overlap Populations: Calculations Using Sulfur d-Orbitals

	C_{2v}				C_s				C'_{2v}			
	s_N	x_N	y_N	z_N	s_N	x_N	y_N	z_N	s_N	x_N	y_N	z_N
s_S	0.104	0.062	0.022	0.000	0.102	0.062	0.026	0.000	0.104	0.056	0.032	0.000
x_S	.166	.074	.076	.000	.160	.084	.076	.000	.150	.066	.114	.000
y_S	.066	.118	.000	.000	.078	.084	.000	.000	.086	.088	.000	.000
z_S	.000	.000	.000	.006	.000	.000	.000	.036	.000	.000	.000	.006
z^2_S	.012	−.006	.010	.000	.004	.006	.002	.000	.002	.002	.014	.000
$x^2 - y^2_S$	.008	.012	.062	.000	−.002	.000	−.004	.000	−.006	.004	.090	.000
xy_S	−.004	.056	−.004	.000	.006	.012	.002	.000	.018	.034	−.008	.000
xz_S	.000	.000	.000	.000	.000	.000	.000	.048	.000	.000	.000	−.002
yz_S	.000	.000	.000	.000	.000	.000	.000	.044	.000	.000	.000	.002

Table X

Atomic Population

	S	N	O^I	O^{II}	F^I	F^{III}
	With sulfur d					
C_{2v}	2.240	3.363	6.623	6.623	7.245	7.245
C_s	2.212	3.378	6.682	6.652	7.237	7.250
C_{2v}'	2.237	3.356	6.637	6.637	7.243	7.243
	Without sulfur d					
C_{2v}	1.971	3.555	6.896	6.896	7.248	7.248
C_s	1.971	3.540	6.917	6.914	7.243	7.251
C_{2v}'	1.963	3.562	6.898	6.898	7.246	7.246

Table XI

Bond Populations

	N–S	O^I–S	O^{II}–S	N–F^I	N–F^{III}
	With sulfur d				
C_{2v}	0.842	0.908	0.908	0.390	0.390
C_s	0.826	0.876	0.900	0.390	0.388
C_{2v}'	0.852	0.898	0.898	0.390	0.390
	Without sulfur d				
C_{2v}	0.706	0.714	0.714	0.382	0.382
C_s	0.712	0.706	0.708	0.382	0.380
C_{2v}'	0.706	0.712	0.712	0.382	0.382

TABLE XII

PARTIAL COMPOSITION OF TWO HIGHEST OCCUPIED MOLECULAR ORBITALS IN TERMS OF F_{ij} (EQ. 7)

	C_{2v}		C_s	
	(b_1)	(a_1)	(a'')	(a')
i	$j = 14$	$j = 15$	$j = 14$	$j = 15$
d_{z^2}	0.000	0.000	0.000	0.000
$d_{x^2-y^2}$	0.000	0.080	0.000	0.001
d_{xy}	0.029	0.000	0.000	0.000
d_{xz}	0.000	0.000	0.026	0.000
d_{yz}	0.000	0.000	0.000	0.048

TABLE XIII

ELEMENTS OF THE OVERLAP MATRIX INVOLVING THE SULFUR d-ORBITALS[a]

	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}
Nitrogen					
s	−0.1368	0.0909	0.2187	0	0
px	0.0945	0.0402	−0.1939	0	0
py	0.0630	−0.1962	−0.0367	0	0
pz	0	0	0	0.1671	0.1116
Oxygen					
s	0.2052	−0.0721	0	0	−0.2484
px	0	0	−0.1168	0.2012	0
py	0.2221	0.0625	0	0	0.0140
pz	−0.0340	0.0936	0	0	0.2053

[a] These values apply to all three conformations, but the designation of orbitals for the lone pair of N will vary according to the model.

We have neglected the atomic cores in this analysis. These core repulsions have effectively been included in the calculation by the choice of Coulomb integrals and by the proportionality of resonance integrals (H_{ij}) to overlap, and hence are largely cancelled by electron–nuclear attractions. The resulting bonding energy is, in fact, too large by about a factor of two because the electron–electron repulsion energies are not completely cancelled. Similar results have been described elsewhere,[19] and provide a basis for an extensive and successful application of LCAO–MO methods to conformations and bonding in organic systems. The magnitude of the core repulsions, neglected here for the above reasons, is so great that the core interaction for the C_{2v} case is 7938 e.v., about six times greater than the total orbital energy, and hence leads to no bonding at all! This question has also been discussed by Ruedenberg,[20] who also justifies the neglect of core repulsions in a somewhat different, but related, analysis of the various energy contributions to the stabilities of molecules.

Finally, partial support of these conclusions comes from recent experiments[10] which eliminate the possibility of a barrier to inversion of a pyramidal configuration about $C\alpha^-$ as a cause of retention of configuration in carbanions of this type.

Acknowledgments.—We acknowledge suggestion of this problem by Professor E. J. Corey with whom we have enjoyed many discussions. This research was supported by the National Institutes of Health, the Air Force Office of Scientific Research, and by award of a Fellowship to T. J. by the Socony Mobil Company. We also thank Mr. R. M. Stevens for use of molecular integral programs, and the Computation Centers at Harvard and M.I.T. for use of facilities.

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(20) K. Ruedenberg, *ibid.*, **34**, 1861 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.; ORGANIC CHEMISTRY LABORATORY, SWISS FEDERAL INSTITUTE OF TECHNOLOGY, ZURICH, SWITZ.; DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES, CALIF.; AND THE CHEMICAL CRYSTALLOGRAPHY LABORATORY, UNIVERSITY OF OXFORD, ENG.]

The Crystal Structure of Aureomycin (Chlortetracycline) Hydrochloride. Configuration, Bond Distances and Conformation

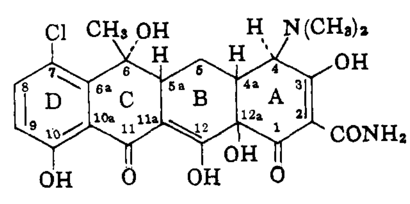
BY JERRY DONOHUE, J. D. DUNITZ, K. N. TRUEBLOOD AND MONICA S. WEBSTER

RECEIVED SEPTEMBER 13, 1962

The crystal structure of aureomycin hydrochloride has been refined with X-ray data used in a previous study and also with independent, more extensive data. The stereochemistry 1 was confirmed, and the bond distances are now in much better accord with the chemical structure. The conformation about C(4)–C(4a) is eclipsed, contrary to expectation, and is expected to remain so in this compound and in other tetracyclines. A reinterpretation of the chemistry involving this bond is indicated. In the β-tricarbonylmethane system at C(2) the hydrogen atom appears to be localized on the oxygen atom of the amide group. The hydrogen bond system is satisfactory, all eight of the possible hydrogen atoms of the cation entering into hydrogen bonds, four of which are intramolecular. The configuration at C(5) in the related compound terramycin is indicated to be OH(5) *cis* to OH(6).

Introduction

A determination of the crystal structure of aureomycin[1] hydrochloride, based on three dimensional X-ray data, has been reported by Hirokawa, Okaya, Lovell and Pepinsky.[2a,b] This work confirmed the constitution that had been derived on chemical grounds for aureomycin[3] and at the same time established the relative configurations of the five asymmetric carbon atoms in the molecule as shown in 1.



1

Some of the conclusions drawn by these authors appear, however, to conflict with 1. For example, it was stated that: "(a) ring D takes a partially quinone structure; (b) C(11) and O(11) are single bonded; (c) no double bond is localized between C(11a) and C(12)." These conclusions, which were drawn largely on the basis of the observed bond lengths, do not seem justifiable in view of the rather large standard errors of

(1) Aureomycin is the registered trade name of the American Cyanamid Co. for the compound having generic name 7-chlortetracycline. A related antibiotic is Terramycin, which is the registered trade name of Chas. Pfizer and Co. for 5-hydroxytetracycline.

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(3) C. R. Stephens, L. H. Conover, R. Pasternack, F. A. Hochstein, W. T. Moreland, P. P. Regna, F. J. Pilgrim, K. J. Brunings and R. B. Woodward, *J. Am. Chem. Soc.*, **76**, 3568 (1954).