

$(\text{CH}_3)_2\text{NSO}_2\text{N}(\text{CH}_3)_2$ AS A MODEL FOR α -SULFONYL CARBANIONS

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RECENT research on α -sulfonyl carbanions indicates an interesting retention of configuration. This retention is illustrated by the fact that a C atom α to the sulfone group at an optically active center undergoes deuterium-hydrogen exchange at a much faster rate than racemization.^{1,2,3} These results have been explained in terms of the Case II geometry⁴ which does not allow a plane of symmetry in the molecule.² The hybridization of the C_α^- has been interpreted in terms of a modification of sp^3 but whether it is in fact closer to sp^3 or to sp^2 is not yet known.² The comparable amounts of D-H exchange in cyclopropyl- and isopropyl-phenyl sulfones has led to the suggestion that an intermediate hybridization is present.⁵ On the other hand the S-N ... O hydrogen bond angle of 111° about N in sulfonamide⁶ is suggestive of nearly sp^3 hybridization of the C_α^- if the H atom is assumed to lie on the N ... O line. With these results in mind, we have carried out a crystallographic structure determination of $(\text{CH}_3)_2\text{NSO}_2\text{N}(\text{CH}_3)_2$,

¹ D.J. Cram, W.D. Nielson and B. Rickborn, J. Amer. Chem. Soc. **82**, 6415 (1960).

² E.J. Corey and E.T. Kaiser, J. Amer. Chem. Soc. **83**, 490 (1961).

³ D.J. Cram, D.A. Scott and W.D. Nielson, J. Amer. Chem. Soc. **83**, 3696 (1961)

⁴ H.P. Koch and W.E. Moffitt, Trans. Faraday Soc. **47**, 7 (1951).

⁵ H.E. Zimmerman and B.S. Thyagarjan, J. Amer. Chem. Soc. **82**, 2505 (1960).

⁶ K.N. Trueblood and S.W. Mayer, Acta Cryst. **9**, 628 (1956).

which is similar to the α -sulfonyl carbanions in the regions of interest relating to stereochemistry and bonding. We hoped to contribute to the unanswered questions of intramolecular steric effects, of hybridization of the C_α^- which could be sp^2 , sp^3 , or some intermediate value, and of the extent to which the lone pair orbital on the C_α^- conjugates with the d-orbitals of sulfur.

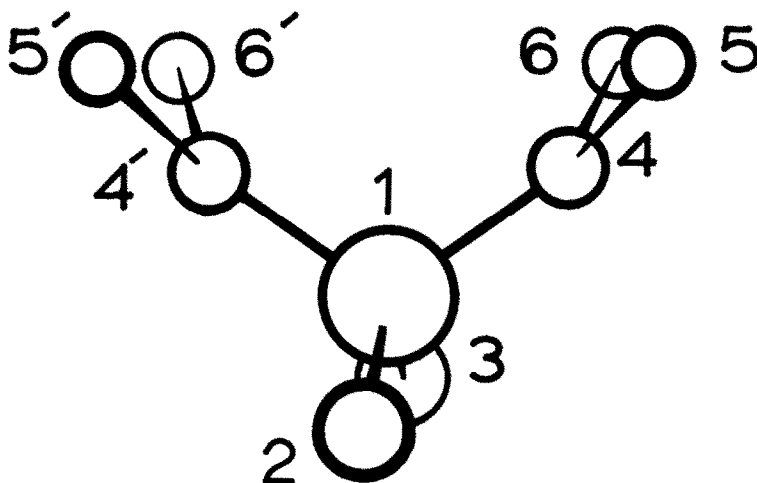


FIG. 1

The $(\text{CH}_3)_2\text{NSO}_2\text{N}(\text{CH}_3)_2$ molecule. Molecular parameters are $\text{S}_1-\text{O}_2 = 1.449$, $\text{S}_1-\text{O}_3 = 1.441$, $\text{S}_1-\text{N}_4 = 1.623$, $\text{N}_4-\text{C}_5 = 1.480$, $\text{N}_4-\text{C}_6 = 1.471$ A, $\text{C}_5\text{N}_4\text{C}_6 = 112.9^\circ$, $\text{C}_5\text{N}_4\text{S}_1 = 117.9^\circ$, $\text{C}_6\text{N}_4\text{S}_1 = 119.7^\circ$, $\text{N}_4\text{SN}_4 = 112.6$ and $\text{O}_2\text{S}_1\text{O}_3 = 119.7^\circ$. Primed atoms are related to unprimed atoms by the mirror plane of the crystal

Three dimensional data from a single crystal have yielded the structure shown in Fig. 1. There are 8 molecules in a unit cell based upon space group C_{mca} and having dimensions $a = 11.76$, $b = 5.68$ and $c = 22.03$ Å. The

value of $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ is 0.085 for the 627 observed reflections. Standard deviations are $\pm 0.005 \text{ \AA}$ for bonds to S, $\pm 0.007 \text{ \AA}$ for the CN bonds, and 0.3° to 0.4° for bond angles, but the corrections which have been made for thermal motions range from 0.009 \AA to 0.027 \AA . The normal to the CNC plane of the NMe_2 group and the normal to the NSN plane are 89.4° apart. The molecular geometry therefore belongs to the Case II category. Interestingly, the N atom is only 0.27 \AA 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 \AA would be expected if the bonding about N were tetrahedral. Although the CNC angle is 112.9° the average SNC bond angle is 119° , substantially greater than the tetrahedral angle.

In our opinion the most reliable criterion of the state of hybridization of the N atom is the conclusion, based on a standard method⁷ in which bond angles define hybrid orbitals, that the lone pair is 93 percent p. This percentage may be compared with 100 percent if the bonds are sp^2 and with 75 percent if the bonds are sp^3 , and thus leads to an average hybridization of $sp^{2.23}$ for the bonds. Ninety-six percent of this p character, i.e. 89 percent of the lone pair, is perpendicular to the N-S bond and in the NSN plane. A very substantial amount of conjugation of this lone pair with the d-orbitals of S is therefore expected in this N analogue of the carbanions, and even more conjugation is expected in the carbanions themselves because of orbital expansion upon replacement of N by C^- . This conclusion is supported by both the overlap calculations described below and the fact that the S-N bond distance is 1.623 \AA , substantially shorter than the expected single bond distance of 1.735 \AA .⁸

⁷ C.A. Coulson, V. Henri Memorial Volume, Contribution à l'Étude de la Structure Moléculaire p. 25. Desoer, Liège (1948).

⁸ Assumed radii and electronegativity corrections are 1.04 \AA for S, 0.74 \AA for N and -0.045 \AA for SN.

In C_{2v} symmetry, overlap calculations⁹ between the best linear combination¹⁰ of the d-orbitals of the S and the lone pair on the N yield an overlap of 0.31 for the actual structure, while a similar calculation with the N configuration inverted yields a value of 0.31. Moreover, a calculation assuming the lone pair is pure p, i.e. that the configuration about N is sp^2 , gives an overlap of 0.32. The extension of these results to the analogous carbanion thus seemingly contradicts a proposal³ that under conditions of symmetric solvation the normal rate of inversion of the C_α^- is reduced because of overlap of the lone pair sp^3 orbital of C_α^- with the d-orbitals of S. Indeed the overlap integrals suggest that the inversion is rapid, and hence another mechanism is required to explain the observed retention of configuration. The most obvious explanation² is in terms of some kind of hindered rotation about the S-C bond in the carbanion coupled with specific attack of the replacing ion. This explanation can apply whether the carbanion is hybridized sp^3 , sp^2 , or some intermediate value. Overlap calculations with one NMe_2 group rotated 45° and then 90° from the position in Figure 1 gives overlaps of 0.31 and 0.32 respectively for the observed non-planar configuration and overlaps of 0.30 and 0.32 if a planar configuration is assumed. Thus hindered rotation due primarily to multiple bonding seems unlikely though not impossible. Another likely source of hindered rotation is intramolecular steric effects. In the $(\text{CH}_3)_2\text{NSO}_2\text{N}(\text{CH}_3)_2$ molecule the $C_6 \dots C_6$, and $C_5 \dots C_5$, distances are 3.4 and 3.5 Å, respectively. If one of the $\text{N}(\text{CH}_3)_2$ groups is rotated by 90° about the N-S bond the closest non-bonded contacts are then $\text{N}_4 \dots C_5$, = 3.0 Å and

⁹ Slater orbitals and experimental molecular parameters were employed in the calculations.

¹⁰ This linear combination of d-orbitals was always chosen such that its overlap S with the lone pair (lp) on the N was a maximum, i.e.

$$S = (\sum_d S_{lp,d}^2)^{1/2}$$

C₅ ... C₅, = C₅ ... C₆, = 3.1 Å (while if both N(CH₃)₂ groups are rotated the C₅ ... C₅, distance is only 2.5 Å). While most of this strain could be relieved by a co-operative rotation in which the two N(CH₃)₂ groups are approximately 90° out of phase, some small steric barrier may still remain. Hence, we conclude that the retention of configuration in the carbanion is probably due to a specific attack of the replacing ion combined with a hindered rotation about the S-C bond due to multiple bonding or steric hindrance, perhaps more predominately the latter.

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