Rotation about a Sulphur(IV)–Nitrogen Double Bond

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Summary The rotation about the sulphur(IV)–nitrogen bond in *SS*-dimethyl-*N*-methylsulphonylsulphilimine ($Me_2S:N\cdot SO_2Me$) has been investigated theoretically by the extended Hückel Method; the symmetry properties of the molecule, the anomalies in its n.m.r. spectrum, and the fact that *S*-symmetrical sulphilimines cannot be resolved into antipodes are explained on the basis of the shape of the total energy curve.

N-SULPHONYLSULPHILIMINES ($R^1R^2S:N\cdot SO_2R^3$) are stable compounds with a 3-co-ordinated sulphur(IV) atom and a sulphur(IV)–nitrogen bond. *X*-Ray and i.r. spectroscopic investigations have shown that *N*-sulphonylsulphilimines contain a S^{IV}–N bond with strong d_π–p_π double bond character.[1-3] In order to examine the rotational properties of the S^{IV}–N bond in *S,S*-dimethyl-*N*-methylsulphonylsulphilimine ($Me_2S:N\cdot SO_2Me$; Figure 1) extended

Hückel (EHMO) type[4] calculations were performed on the basis of X-ray data.[1,2] The parameters used in the calculations are given in the Table.
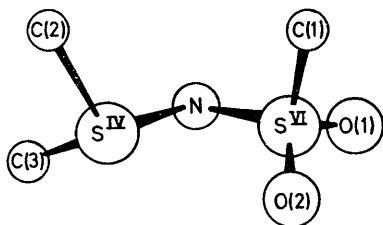

FIGURE 1. *Conformation of the molecule in the crystalline state.*

TABLE *Parameters used in EHMO calculations*

Atom	μ_s	μ_p	μ_d	H_{ss}	H_{pp}	H_{dd}
H	1·0000			13·60		
C	1·6083	1·5679		19·46	10·66	
N	1·9237	1·9170		25·54	13·14	
O	2·2458	2·2266		32·35	15·87	
S	2·1223	1·8273	1·34	24·08	17·32	7·00

The computed total energy E of the molecule as plotted against angle α of the rotation about the S^{IV}–N bond is shown in Figure 2.
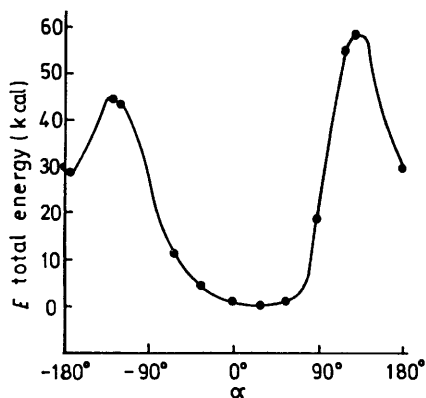

FIGURE 2. *Calculated total energies vs. angle α of rotation. $E = 0$ represents $-956\cdot83$ eV on the absolute energy scale.*

The $\alpha = 0$ arrangement represents the conformation observed in the crystalline state[1,2] (Figure 1). Computations were carried out for one isolated molecule with the bond lengths determined in the crystalline state; the slight deviation (*ca.* 8°) between the computed and empirical absolute energy minima is probably due to this.

The computed curve shows two minima; the high energy difference between them (29·1 kcal) indicates the

predominance of the rotamers in the lower energy minimum under normal conditions. The relatively high maxima (44·6 and 58·3 kcal) show the hindrance to complete rotation. The difference in the maximum values is due to the difference between the S^{IV}–C bond lengths in the S^{IV} methyl groups (1·78 and 1·80 Å) and that between the N–S^{IV}–C bond angles.[2]

The energy curve is surprisingly flat in the neighbourhood of the lower minimum. Consequently, any rotamers derived from the most stable one by a S^{IV}–N bond-rotation within a rotational interval of 80° may occur if the molecule is slightly excited (0—2 kcal). Since there is a partially free rotation about the S^{IV}–N bond, the methyl groups linked to the S^{IV} atom are not fixed in space. This explains the singlet S^{IV}–Me peak observed in the n.m.r. spectrum of SS-dimethyl-N-methylsulphonylsulphilimine[5] with two non-equivalent S^{IV}–Me groups in the crystalline ground state. The extensive thermal motion of these methyl groups[1,2] can also be interpreted on the same basis.

X-Ray data indicated the crystalline SS-dimethyl-N-methylsulphonylsulphilimine to be a racemic mixture of two enantiomers. The present results, however, show that the configurational stability of these asymmetric structures is very low and interconversion can occur easily owing to non-hindered partial rotations about the S^{IV}–N and S^{VI}–N bond.† This explains why the S-symmetric sulphilimines cannot be resolved into antipodes.[6]
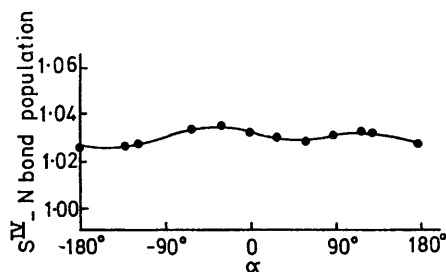

FIGURE 3. S^{IV}–N *bond populations vs. angle α of rotation.*

Computations show that the S^{IV}–N bond population is almost independent of α (Figure 3). The actual invariance of the bond population is due to the d orbitals in the sulphur atom.‡ The two maxima of the total energy curve can be correlated with the minimum $O(2) \cdots C(2)$ and $O(2) \cdots C(3)$ distances. Since the bond system is not affected appreciably by the rotation about the S^{IV}–N bond, the total energy curve seems to be controlled mainly by steric effects.

From these results it may be concluded that the rotational properties of a S^{IV}–N d_π–p_π bond are basically different from those of double bonds of p_π–p_π character.

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† Within a rotational interval of 210° a partially free rotation about the S^{IV}–N bond may occur if the molecule is slightly excited (0—4 kcal) (P. Mezey, unpublished work).

‡ On the basis of Hammett analysis the S^{II}–N bond strength in sulphenamides shows a stronger dihedral angle dependence.[7]

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