Chemical Shift Nonequivalence in a Sulphinamide and a Sulphenamide

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JAKOBSEN AND SENNING[1] have recently observed a restriction to conformational interchange of the two *N*-methyl groups in *NN*-dimethyltrichloromethanesulphinamide, $CCl_3 \cdot SO \cdot NMe_2$ (I). Here we comment on the low temperature chemical shift nonequivalence of (I) and that of a related compound, *NN*-dibenzyltrichloromethanesulphenamide, $CCl_3 \cdot SN(CH_2Ph)_2$, (II). The two methyl groups in (I) are diastereotopic[2] and have different chemical shifts at temperatures below $-46°$.[1] At higher temperatures conformational interchange is rapid and the time-averaged environments of the two methyl groups become equivalent on the n.m.r. time scale. The authors[1] attribute this restricted interchange of the diastereotopic *N*-methyl groups to hindered rotation about the N–S bond. They regard the barrier to rotation ($\Delta F\ddagger = 11{\cdot}9$ kcal./mole) as arising from partial double bond character in the N–S bond resulting from N–S *p–d* π-bonding. However, current thinking attributes little, if any, geometrical requirement to *p–d* π-bonding in sulphur compounds which would result in a restriction to rotation of the magnitude observed in this case.[3] Whereas there may be a superficial resemblance between the structures and n.m.r. temperature dependence of (I) and many amides,[4] an explanation which attributes the barrier to restricted rotation must be regarded as unprecedented and highly speculative.

We may consider a more palatable interpretation which can account for the observed equivalence and coalescence and thus resolve the apparent discrepancy between theory[3] and experiment,[1] namely the slow pyramidal inversion of nitrogen. We note that the sulphinamide (I) possesses the same symmetry characteristics as substituted ethanes of the type $CXYZ \cdot CAB_2$, since the lone pairs of electrons on sulphur and nitrogen take the place of the X and A substituents.[2,5] In such systems, the two B substituents are diastereotopic and may exhibit chemical shift nonequivalence, *even under conditions of rapid rotation about the central bond.*[2,5–7] Thus, a restriction to either process, to rotation about the S–N bond due to *p–d* π-overlap or to nitrogen inversion may result in observable chemical shift non-equivalence, since both processes are required to exchange the environments of the two diastereotopic methyl groups.

Although the barrier to pyramidal inversion of nitrogen is expected to be small in simple amines,[8] various factors may intervene to raise the inversion barrier. For example, constriction of the C–N–C angle as in aziridines greatly increases the strain energy in the planar-transition state and a consequent increase in the inversion barrier has been noted.[9] Similarly, the presence of a hetero-atom (O, N, or S) directly bonded to the nitrogen has been observed substantially to increase the inversional barrier[10,11,12] presumably due to electronegativity effects on hybridization and lone pair–lone pair repulsions.[10a,11] In one simple case, *N*-benzyl-*NO*-dimethylhydroxylamine, an inversional barrier of 12·9 kcal./mole [comparable to that of (I)] was obtained.[10a]

To elucidate the relationship between the n.m.r. spectra and conformational processes in these systems, we have examined the temperature dependence of the n.m.r. spectrum[†] of the sulphenamide (II).[‡] Its symmetry characteristics permit a differentiation between slow rotation in a planar structure, like that in amides, and slow pyramidal inversion at nitrogen, to be made. Thus slow rotation would result in the nonequivalence of the two diastereotopic benzyl groups, *i.e.*, one *cis* and one *trans* to the trichloromethyl group and two benzyl singlets would be observed. By contrast, slow inversion would render the two methylene hydrogens within each benzyl group diastereotopic while the two benzyl groups would be enantiotopic.[2] This would be shown by the appearance of an AB quartet.[§]

At ambient temperature and above, the n.m.r. spectrum of the sulphenamide (II) features singlets at δ 7·22 (5H, phenyl) and δ 4·45 (2H, methylene). When the temperature is lowered the signal at δ 4·45 broadens and at low temperatures resolves into an AB quartet ($\Delta\nu = 8$ c./sec., $J_{AB} = 15$ c./sec., $T_C = +28° \pm 3°$). The rate constant (k) for exchange at the coalescence temperature (T_C) was calculated[13] from the chemical shift difference at low temperature ($\Delta\nu_{AB}$) and the coupling constant ($J_{\max}$), and the free energy barrier was obtained using the Eyring equation with transmition coefficient equal to unity ($\Delta F^{\ddagger} = 15·3 \pm 0·2$ kcal./mole). The appreciable value[¶] of $\Delta F^{\ddagger}$ for (II) would be difficult to understand if p–d π-bonding were the source of the nonequivalence in compounds (I) and (II), since such bonding should be less important in the sulphenate than in the sulphinate, in which the polar S–O bond confers additional partial positive charge to the sulphur. On the other hand, we would anticipate increased lone pair–lone pair repulsions in (II).

Since ample precedent, including the results for (II), may be adduced for restriction to nitrogen inversion due to the presence of an adjacent hetero-atom, this interpretation provides an explanation of the low-temperature nonequivalence and coalescence in (I) as well as in (II) which is more reasonable and consistent than one based on p–d π-bonding. In addition the substantial electronegativity of the trichloromethyl group possibly plays an important role in raising the inversion barrier as *S*-alkyl and *S*-aryl *NN*-dimethylsulphinamides exhibit chemical shift equivalence even at −60°.[14]

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[†] Spectra were measured on a Varian A-60 Spectrometer on *ca.* 15% chloroform solutions. Temperatures were calibrated using methanol spectra.

[‡] Compound (II) was prepared by the reaction of trichloromethanesulphenyl chloride with dibenzylamine in benzene solution.

[§] Restricted rotation in a nonplanar structure in which the C–S–N plane bisects the C–N–C angles would also result in an AB quartet.

[¶] This barrier to pyramidal inversion is the highest yet reported for an acyclic amine derivative.

[1] H. J. Jakobsen and A. Senning, *Chem. Comm.*, 1967, 617.

[2] K. Mislow and M. Raban, "Topics in Stereochemistry," ed. N. L. Allinger and E. L. Eliel, Wiley-Interscience, 1967, vol. I, p. 1. The term diastereotopic refers to groups which reside in diastereomeric environments and which as a consequence exhibit chemical shift nonequivalence. Enantiotopic groups, by contrast, reside in enantiomeric environments and must exhibit chemical shift equivalence in achiral solvents.

[3] G. E. Kimbal, *J. Chem. Phys.*, 1940, **8**, 188; H. P. Koch and W. E. Moffit, *Trans. Faraday Soc.*, 1951, **47**, 7; W. von E. Doering and L. K. Levy, *J. Amer. Chem. Soc.*, 1955, **77**, 509; W. von E. Doering and A. K. Hoffman, *ibid.*, p. 521.

[4] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press New York, N.Y., 1965, vol. I, p. 553 and papers cited therein.

[5] J. A. Pople, W. G. Schneider, and J. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N.Y., 1959, p. 379.

[6] M. Raban, *Tetrahedron Letters*, 1966, 3105.

[7] P. M. Nair and J. D. Roberts, *J. Amer. Chem., Soc.* 1957, **79**, 4565.

[8] G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 3396.

[9] A. J. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, 1956, **78**, 5126; 1958, **80**, 5203; A. Loewenstein, J. F. Neumer, and J. D. Roberts, *ibid.*, 1960, **82**, 3599; H. S. Gutowsky, *Ann. New York Acad. Sci.*, 1958, **70**, 786; T. J. Burdos, C. S. Zantay, and C. K. Navada, *J. Amer. Chem. Soc.*, 1965, **87**, 5796; F. A. L. Anet and J. M. Osyany, *ibid.*, 1967, **89**, 352,

[10] (a) D. L. Griffith and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 4089; (b) J. E. Anderson and J. M. Lehn. *J. Amer. Chem. Soc.*, 1967, **89**, 81.

[11] F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Amer. Chem. Soc.*, 1967, **89**, 357.

[12] E. Fahr, W. Fischer, A. Jung, L. Sauer, and A. Mannschreck, *Tetrahedron Letters*, 1967, 161.

[13] R. J. Kurland, M. B. Rubin, and W. B. Wise, *J. Chem. Phys.*, 1964, **40**, 2426.

[14] R. M. Moriarty, *Tetrahedron Letters*, 1964, 509; *J. Org. Chem.*, 1965, **30**, 600.