gen bonding expected in the hydroxylic media, where the $n \rightarrow \pi^*$ excitation energy of the lone-pair electrons has been increased, with concomitant reduction of the contribution of its effect on the chemical shift.[9a,b] Pyridinium ion, of course, represents the extreme case of complete proton transfer. The variations in the N–C and N–H coupling constants, particularly in $^1J_{NC}$ and $^2J_{NH}$, can presumably be ascribed largely to the same source. In fact, using both chemical shifts and coupling constants, estimates of the degree of hydrogen bonding can be made, from which it can be inferred that the values of $^1J_{NC}$ in neat pyridine and in pyridinium ion are very likely of opposite sign. The argument follows from the ^{15}N chemical-shift data (Table IV), and assuming only a two-component equilibrium (free pyridine $\rightleftarrows$ hydrogen-bonded pyridine), the extent of hydrogen bonding is estimated to be about 15% in methanol, while from consideration of the values of $^2J_{NH}$, the degree of hydrogen bonding is estimated to be about 9%. That different, parameter-dependent values are obtained is to be expected because of the different degrees to which chemical shifts and coupling constants respond to electronic and environmental changes. From the average value, 12%, $^1J_{NC}$ in pyridinium ion can be predicted, depending on whether a sign change occurs in going from neat liquid to a methanolic solution. In the absence of a sign change, $^1J_{NC}$ is predicted to be 2.5 Hz, while a value of 9 Hz is obtained if such a sign change exists. The closeness of the latter value to that experimentally observed suggests that in fact a change in sign has taken place. To our knowledge this is the first experimental indication of a change in sign of any C–N coupling constant. Absolute signs of such couplings are known only for acetonitrile[6a] ($^1J_{N\equiv C} = -17.5$ Hz) and methyl isocyanide[3b] ($^1J_{NCH_3} = -10.6$ Hz, calculated from the reported ^{14}N value); in both cases the values are considerably lower than those predicted from eq 1. A study of the effects of solvent and protonation on the acetonitrile coupling would be of interest.

Acknowledgment. We are much indebted to Dr. Frank J. Weigert for helpful suggestions and to Drs. E. W. Randall and R. Price for informing us of the results of their experiments before publication.

Absolute Configuration at a Sulfenamide Chiral Axis. Crystal and Molecular Structure of *N*-(1-α-Naphthylethyl)-*N*-(benzenesulfonyl)trichloromethanesulfenamide[1]

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Abstract: The crystal structure of *N*-(1-α-naphthylethyl)-*N*-(benzenesulfonyl)trichloromethanesulfenamide has been determined by three-dimensional X-ray diffraction. The molecule crystallizes in space group $P2_1$ with lattice constants $a = 12.233$ (6) Å, $b = 8.546$ (5) Å, $c = 10.440$ (5) Å, $\beta = 110.20$ (1) °, $Z = 2$. Refinement of 1536 diffractometer data yielded a conventional discrepancy factor of 0.075. The structure found, which features a nearly planar trivalent nitrogen atom, has implications concerning torsional isomerism about heteroatom–heteroatom bonds (in this case between trivalent nitrogen and divalent sulfur) and concerning the possible existence of p-d π-bonding in S–N bonds. The incorporation of an asymmetric carbon atom of known configuration allowed the assignment of absolute configuration to the sulfenamide chiral axis.

The structure and conformational analysis of molecules with sulfur–nitrogen bonds has been a topic of recent interest. A number of X-ray crystallographic structure determinations of molecules with different kinds of sulfur nitrogen bonds have appeared.[2–4] In addition, nuclear magnetic resonance (nmr) spectroscopic studies have indicated interesting features in the structure and conformation of sulfenamides, molecules containing divalent sulfur bonded to trivalent nitrogen.[5–7]

The nmr spectra of dialkylsulfenamides[5] (RSNR′R′′) and *N*-arenesulfonylsulfenamides[6,7] (RSNR′SO$_2$Ar) exhibit chemical shift nonequivalence of diastereotopic[8] nuclei at low temperature. This nonequivalence has been adduced as evidence for asymmetry in the sulfen-

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[1] This work was supported in part by grants from the National Science Foundation (No. GP-17092 and GP-15070) and the Edmond de Rothschild Foundation. We thank the Wayne State University Computing and Data Processing Center for the use of their facilities.

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[4] For other examples, see O. Kennard and D. G. Watson, "Molecular Structures and Dimensions," Vol. 1, Crystallographic Data Centre, Cambridge, U. K., and the International Union of Crystallography, N. V. A. Oosthoek's Uitgevers Mij, Utrecht, pp 49–50, 292–299.

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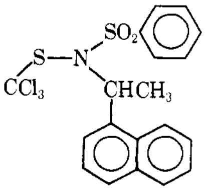
amide moiety. Two possible conformations were considered on the basis of the nmr evidence; in both hypothetical conformations the RSN plane approximately bisects the R′NR″ angle.[5]

When the temperature is increased, coalescence of the signals of diastereotopic nuclei is observed as their time averaged environments become equivalent or enantiomeric on the nmr time scale. This process, which has been termed a topomerization,[9] is associated with the reversible interconversion of a chiral sulfenamide molecule with its mirror image (degenerate racemization) or, in the case of a molecule with an additional chiral unit, reversible interconversion with its epimer at the sulfenamide chiral unit.[10] Two steps in this conformational interchange have been envisioned: (a) inversion at the nitrogen pyramid and (b) rotation about the sulfur–nitrogen bond. Experiments employing nmr spectroscopy have demonstrated that rotation rather than inversion is the slow (rate-determining) step in the overall process resulting in exchange, and that the asymmetry of the sulfenamide moiety is due to an axis of chirality along the S–N bond rather than the central chirality of an asymmetric nitrogen atom.

A single crystal X-ray diffraction study of a representative sulfenamide, *N*-(1-α-naphthylethyl)-*N*-(benzenesulfonyl)trichloromethanesulfenamide (**1**), was undertaken in order to provide further evidence concerning structural and conformational details and to test the concepts developed on the basis of nmr evidence. The molecule chosen contains an asymmetric carbon atom of known absolute configuration in order to assign unambiguously the absolute configuration to the chiral sulfenamide unit; the naphthylethyl moiety provides a configuration standard to which the chirality of the sulfenamide chiral axis may be related without the need for anomalous dispersion techniques. A knowledge of the configuration at the sulfenamide chiral axis is of interest in the interpretation of the optical rotatory dispersion spectrum of this compound which exhibits an exceptionally intense short wavelength Cotton effect (the peak to trough difference in molecular rotation is 234,000°, *i.e.*, *a* = 2340°).[11]



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Experimental Section

A single crystal of **1**, in the approximate shape of an equilateral triangular prism, of volume 0.01 mm³, was used for all diffraction work. A series of precession photographs, using Mo Kα radiation, exhibited the systematic extinction 0*k*0, $k = 2n + 1$, and Laue symmetry 2/*m*, which, for an asymmetric molecule, is consistent only with the monoclinic space group, C_2^2-$P2_1$.

Using the Mo Kα_1 peak (λ = 0.709261 Å), 20 reflections were accurately centered on a Picker four-angle card-controlled X-ray diffractometer. Based on the setting angles of these reflections, the preliminary lattice constants were refined by the method of least squares.[12] The resultant lattice constants are a = 12.233 (6), b = 8.546 (5), c = 10.440 (5) Å, β = 110.20 (1)°. The linear absorption coefficient is calculated to be μ = 0.658 mm⁻¹. Based on two molecules in a unit cell of volume 1024 Å³, the calculated density is ρ = 1.495 g cm⁻³, as compared to an experimental density of ρ = 1.44 (2) g cm⁻³, determined by the flotation technique.

The moving crystal–moving counter (θ–2θ) scan technique,[13] with a take-off angle of 1.7°, was used to collect intensity data from the octants h, $\pm k$, $\pm l$, within a limiting 2θ angle (Mo Kα) of 48°. A zirconium β filter of 1 mil thickness was used and the pulse height analyzer was set to accept approximately 90% of the generated beam.

Data were collected with the counter aperture 29.9 cm from the crystal with a scan rate of 1°/min and background counts of 15 sec at each end of the scan. The scan was asymmetric about the Mo Kα peak, going from (2θ − 0.95°) to (2θ + 1.05°). In order to test crystal and instrument stability, five standard reflections, chosen from various places in the diffraction sphere, were repeated at approximately 100 reflection intervals. After 1630 reflections had been observed, the intensities of the standards began to drop by more than 10%. The crystal was then accurately recentered with 19 reflections and data collection resumed with a scan rate of 2°/min and 7.5 sec background counts; the largest drop in the standard was then observed to be 3%. All reflections with peak intensities greater than 10,000 counts/sec were retaken with a copper filter. A total of 1795 reflections for $k \geq 0$, and 1014 reflections for $k < 0$ were collected. Standard deviations of F^2 were calculated according to formula 1 where I is the net intensity, P is the integrated intensity, $B1$ and $B2$ are the background counts, SR is the scan rate, TB is the background counting time, S is the scale factor, and $PCTI$ is an "ignorance factor."[14] A value of 0.03 was used for $PCTI$ and $\sigma(2\theta)$ was set to 0.0025. Of these reflections, 388 had net intensities less than 2.5 times their standard deviations and were rejected.

$$\sigma(F^2) = \left\{\left(\frac{I\sigma(S)}{S}\right)^2 + S^2(P + \sigma^2(B)) + (I \cdot PCTI)^2\right\}^{1/2} \quad (1)$$

$$\sigma^2(B) = \frac{B^2}{B1 + B2} + \left(\frac{30(B1 + B2)}{SR \cdot TB}\right)^2 (2\sigma^2(2\theta))$$

$$B = |2\theta_2 - 2\theta_1|\left(\frac{30}{SR \cdot TB}\right)(B1 + B2)$$

Solution and Refinement

Assuming a Cl–C bond distance of 1.76 Å and a S–C bond distance of 1.81 Å there should be six vectors of magnitude 2.83 Å corresponding to Cl ↔ Cl and Cl ↔ S(2) vectors within the $SCCl_3$ tetrahedron. A search of the calculated Patterson map for these vectors as well as the S(1) ↔ S(2) CCl_3 vectors allowed the positioning of both sulfur atoms as well as Cl(1) and Cl(2). These parameters were used to calculate structure factors and a conventional discrepancy factor $[R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|]$ of 0.39 resulted. An electron density map phased on these positions yielded the positions of Cl(3) and six of the naphthylene carbons. The remaining nonhydrogen atoms were found from a third electron density map. Inclusion of anomalous dispersion did not allow an assignment of absolute configuration to **1**.

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(12) Local versions of the following programs were used in the solution and refinement of this structure: PICK-2, J. A. Ibers' least squares program for lattice constants and orientation angles based on W. C. Hamilton's MODE 1; DACOR, D. L. Smith's program for the correction of diffractometer data and estimation of standard deviation; FORDAP, A. Zalkin's Fourier program; ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full matrix least squares program and function and error program; ORTEP, C. K. Johnson's program for drawing thermal ellipsoids of crystal structures.

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(14) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

Table I. Final Coordinates and Thermal Parameters[a]

Atom	x	y	z	B	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(1)	0.5126 (3)	0.3330	0.2207 (5)		6.50 (22)	5.86 (21)	10.96 (28)	−0.93 (20)	5.26 (19)	−2.01 (23)
Cl(2)	0.6865 (3)	0.5570 (7)	0.3377 (4)		5.66 (22)	7.24 (24)	6.73 (20)	0.40 (20)	2.03 (18)	−3.51 (20)
Cl(3)	0.5467 (5)	0.5842 (9)	0.0536 (4)		11.01 (33)	11.18 (30)	7.40 (24)	6.66 (32)	3.03 (23)	4.60 (24)
S(1)	0.9455 (2)	0.4267 (7)	0.3015 (3)		3.79 (11)	3.49 (12)	3.24 (12)	−0.71 (12)	1.67 (92)	−0.15 (10)
S(2)	0.7165 (3)	0.3436 (7)	0.1232 (3)		4.25 (16)	3.84 (15)	2.84 (12)	0.18 (12)	1.16 (92)	−0.26 (10)
O(1)	0.9952 (7)	0.4290 (13)	0.4482 (7)	4.8 (2)						
O(2)	0.9029 (7)	0.5686 (12)	0.2314 (8)	4.7 (2)						
N	0.8289 (7)	0.3028 (12)	0.2602 (7)		3.30 (37)	3.20 (30)	2.69 (31)	−0.38 (35)	1.14 (32)	−0.13 (30)
C(1)	0.6196 (9)	0.4550 (15)	0.1899 (10)	3.7 (2)						
C(2)	0.8509 (9)	0.1403 (14)	0.3194 (9)	3.1 (2)						
C(3)	0.8697 (11)	0.0213 (17)	0.2188 (12)	4.7 (3)						
$C_p(1)$	1.0508 (9)	0.3410 (19)	0.2449 (10)	3.9 (2)						
$C_p(2)$	1.1509 (12)	0.2806 (19)	0.3345 (13)	5.3 (3)						
$C_p(3)$	1.2352 (16)	0.2086 (25)	0.2905 (17)	7.8 (4)						
$C_p(4)$	1.2096 (13)	0.1997 (22)	0.1463 (14)	6.4 (4)						
$C_p(5)$	1.1112 (13)	0.2633 (21)	0.0580 (14)	7.0 (4)						
$C_p(6)$	1.0234 (11)	0.3369 (20)	0.0990 (12)	5.1 (3)						
$C_n(1)$	0.8316 (9)	0.2460 (14)	0.5846 (10)	3.4 (2)						
$C_n(2)$	0.8226 (11)	0.2923 (17)	0.7047 (12)	4.7 (3)						
$C_n(3)$	0.7308 (13)	0.2410 (21)	0.7467 (14)	6.4 (3)						
$C_n(4)$	0.6470 (11)	0.1473 (18)	0.6625 (12)	4.9 (3)						
$C_n(5)$	0.5596 (11)	0.0015 (18)	0.4466 (12)	5.2 (3)						
$C_n(6)$	0.5720 (12)	0.0512 (20)	0.3310 (13)	5.7 (3)						
$C_n(7)$	0.6629 (11)	−0.0053 (17)	0.2825 (12)	4.8 (3)						
$C_n(8)$	0.7509 (9)	0.0939 (14)	0.3685 (10)	3.4 (2)						
$C_n(9)$	0.7441 (9)	0.1453 (15)	0.4929 (9)	3.3 (2)						
$C_n(10)$	0.6493 (11)	0.0962 (17)	0.5338 (11)	4.6 (3)						

[a] Standard deviations estimated by full matrix least squares are given in parentheses for the least significant digit. The defining equation for B_{ij} is $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$, where the a_i^* and a_j^* are reciprocal lattice cell lengths. The form of the anisotropic temperature factor is exp$[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Both quadrants of data were then merged with a discrepancy factor of merging of 0.018. Full matrix least squares refinement of the averaged data including anisotropic temperature factors for the S, Cl, and N atoms proceeded routinely to $R = 0.075$ and a weighted discrepancy factor $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o|^2]^{1/2}$ of 0.096. Final atomic parameters are given in Table I.[15]

Discussion

The structure of *N*-(1-α-naphthylethyl)-*N*-(benzenesulfonyl)trichloromethanesulfenamide is shown stereoscopically in Figure 1 with bond distances and angles given in Figures 2 and 3, respectively. The average values of the S–O, C–S, and C–C bond distances are consistent with those found in other studies.[2–4,16] The alternation of bond lengths in the naphthyl group corresponds to that predicted from consideration of canonical structures and that found experimentally in naphthalenes.[16]

A number of structural and stereochemical features of the molecule deserve special mention. In contrast to the pyramidal substitution at nitrogen in simple amines, the configuration about the nitrogen atom in **1** is nearly planar. A number of quantities may be used as measures of the deviation from planarity. A commonly used measure is the sum of bond angles at nitrogen. In the compound at hand the sum of bond angles is 356.5°. This value may be compared with values of 328 and 360° corresponding to sp^3 hybridization at nitrogen (pyramidal substitution) and sp^2 hybridization at nitrogen (planar substitution), respectively. The hybridization of the lone pair of electrons may be directly calculated from the bond angles[17] using eq 2 and 3 where θ_{ij} is the angle between the *i*th and *j*th ligands and $1/(1 + \lambda_i)$ is the fractional s character in the directed orbital used in bonding to the *i*th ligand. Using the experimentally obtained bond angles the lone-pair hybridization was found to be sp,$^{41.2}$ corresponding to 98% p character and 2% s character. The calculated hybridizations and per cent s character in the nitrogen orbitals used for bonding to the three ligands are N–C, $sp^{1.91}$ 34%; N–SO_2, $sp^{2.53}$ 28%; N–S, $sp^{1.87}$ 35%. The distance to the nitrogen atom from the plane formed by its three ligated atoms (S(1), S(2), and C(2)), *viz.*, 0.175 Å, also reflects the near planarity.

$$\lambda_i\lambda_j \cos \theta_{ij} = 1 \qquad (2)$$

$$\sum_i \frac{(1)}{1 + \lambda_i^2} = -1 \qquad (3)$$

The Newman projection angles (Figure 4 and 5) along the two nitrogen–sulfur bonds deviate somewhat from the 180° which would obtain were the substitution completely planar. The dihedral angle between the plane formed by the nitrogen atom, C(2), and S(2) and that formed by the nitrogen, S(1), and S(2) differs from coplanarity by 21°. We feel that the most meaningful approach to evaluating the degree of nonplanarity is to calculate the per cent s and p character in the lone pair orbital.

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(15) Calculated and observed structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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(17) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1965, pp 14–16.

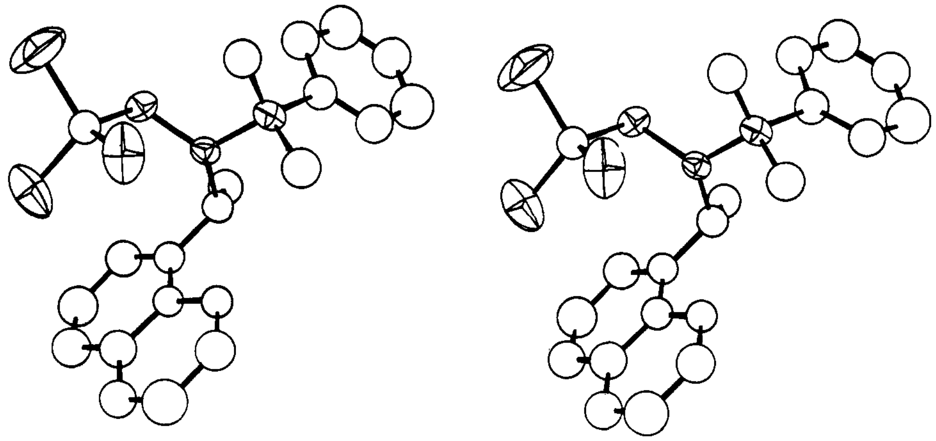

Figure 1. *N*-(1-(*α*-Naphthyl)ethyl-*N*-(benzenesulfonyl)trichloromethanesulfenamide; stereoscopic view, including thermal ellipsoids.

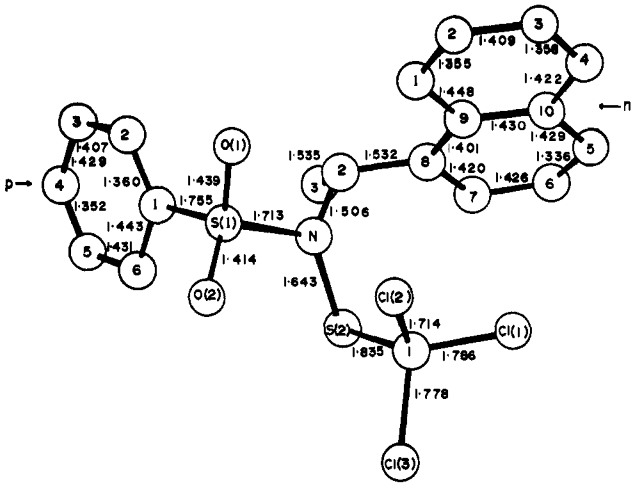

Figure 2. *N*-(1-(*α*-Naphthyl)ethyl-*N*-(benzenesulfonyl)trichloromethanesulfenamide; bond lengths. Estimated standard deviations from full variance–covariance matrix least squares refinement are C–C (0.014–0.022), C–X (0.011–0.014), X–X (0.007–0.009) Å, X = Cl, S, O, N.

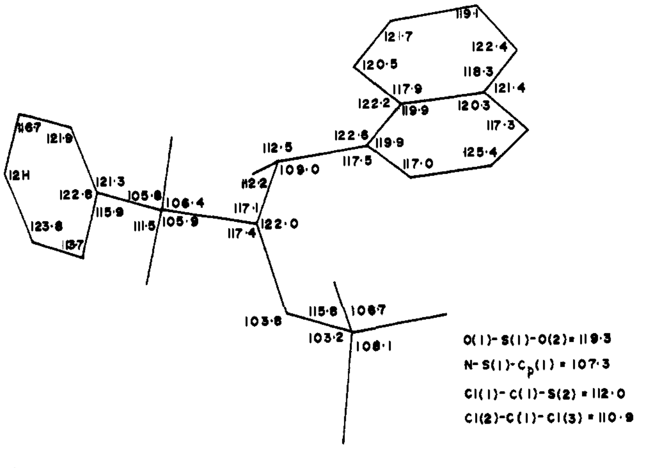

Figure 3. *N*-(1-(*α*-Naphthyl)ethyl-*N*-(benzenesulfonyl)trichloromethanesulfenamide; bond angles. Estimated standard deviations from full variance–covariance matrix least squares refinement are CCC (0.9–1.6), CCX (0.8–0.9), XCX, CXX, XXX (0.5–0.7)°, X = Cl, S, O, N.

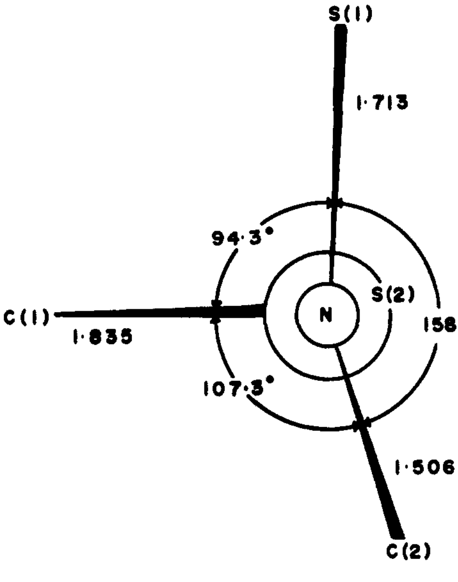

Figure 4. *N*-(1-(*α*-Naphthyl)ethyl-*N*-(benzenesulfonyl)trichloromethanesulfenamide; Newman projection down N–S(2)bond. Estimated standard deviations from full variance–covariance matrix least squares refinement for dihedral angles are 0.6–1.1°.

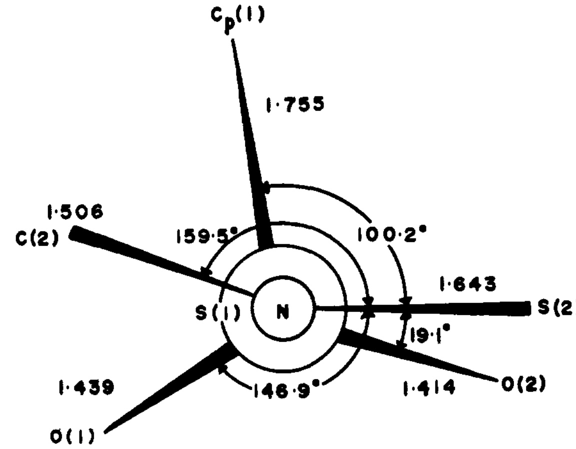

Figure 5. *N*-(1-(*α*-Naphthyl)ethyl-*N*-(benzenesulfonyl)trichloromethanesulfenamide; Newman projection down N–S(1) bond. Estimated standard deviations from full variance–covariance matrix least squares refinement for dihedral angles are 0.6–1.1°.

The deviation from planarity is even less than that found[3] for bisdimethylamine sulfone, $(CH_3)_2NSO_2N(CH_3)_2$. This sulfonamide has a sum of bond angles at nitrogen of 350.5° and the lone pair was calculated to have 93% p character and 7% s character.

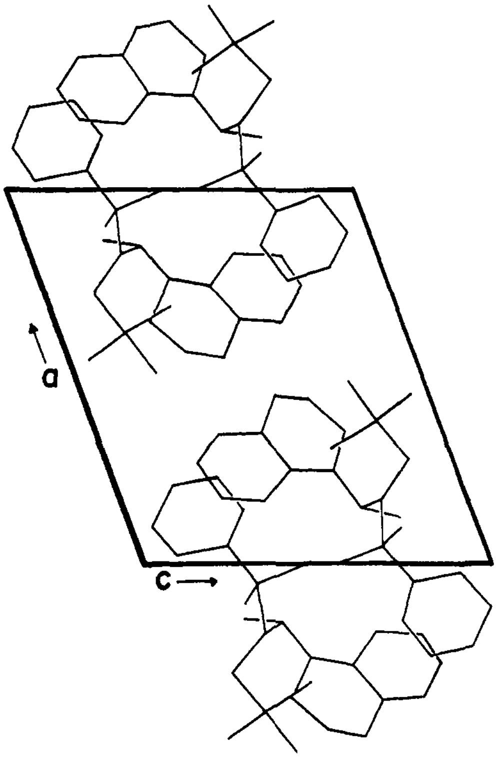

Figure 6. *N*-(1-(α-Naphthyl)ethyl-*N*-(benzenesulfonyl)trichloromethanesulfenamide; packing diagram looking down the *b* axis.

The thermal ellipsoid obtained for the nitrogen atom is almost spherical, thus implying the absence of nitrogen inversion in the crystal. This is in contrast to the thermal ellipsoids of the three chlorine atoms which all have their major axes normal to the corresponding C–Cl bonds, reflecting some torsional libration of the trichloromethyl group. Since the nitrogen atom lies near the center of the molecule it seems unlikely that crystal packing forces would deform the geometry of substitution were the barrier to nitrogen inversion substantial. The near planarity of the nitrogen in this compound provides evidence confirming our conclusion that slow nitrogen inversion cannot be responsible for chemical shift nonequivalence in this and other sulfonylsulfenamides.[5–7]

One factor which may be responsible for the increased planarity at nitrogen in this compound is overlap of the nitrogen lone pair with empty d orbitals on either or both of the sulfur atoms. An explanation also based on p–d π bonding between nitrogen and sulfur was used to account for the considerable flattening of the nitrogen pyramid in bisdimethylamine sulfone.[3] However, the importance of d orbital overlap in lowering nitrogen inversion barriers has been a topic of considerable controversy.[18–23] We note, however, that such near planarity has also been observed in an aminophosphine[24] and an aminosulfonium salt,[2] both cases where p–d π bonding is conceivable.

Bonding with sulfur d orbitals could conceivably involve either or both of the sulfur atoms bonded to nitrogen. While participation of vacant d orbitals is not generally considered significant in molecules with divalent sulfur, the electronegativity of the trichloromethyl group might be expected to facilitate bonding.[7,25] The inductive withdrawal of electron density would have the effect of contracting d orbitals as the effective core charge on sulfur is increased. This hypothesis is consistent with the observation that the bond between nitrogen and sulfenyl sulfur [N–S(2)] is considerably shorter than that to the sulfonyl sulfur atom [N–S(1)].

While increased multiple bonding probably plays a role in shortening the N–S(1) bond distance, the hybridization of the nitrogen atomic orbitals used in bonding reflects a significant difference in the amount of s character. Thus the orbital used in bonding to the sulfenyl sulfur S(2) has sp$^{1.9}$ hybridization while that used in bonding to S(1) has sp$^{2.5}$ hybridization. The greater amount of s character in the atomic orbital used in bonding to S(2) may be responsible for a considerable portion of the bond shortening. However, this, in turn, may be the result of compensation for the shift of electron density from nitrogen to S(2) *via* π bonding to a sulfur 3d orbital.

The torsion angles at the N–S(2) bond reflect the importance of repulsions between lone pairs of electrons on nitrogen and the divalent sulfur atom. The contribution of the anisotropic p atomic orbital to lone pair electron density is greatest in a plane perpendicular to that formed by the two ligands at sulfur, *i.e.*, perpendicular to the projection of the S–C bond in the Newman projection (Figure 4). The lone pair on nitrogen achieves a geometry wherein the nodal surface of the lone pair orbital is approximately tangent to this plane so as to minimize overlap repulsions between the lone pair orbitals. This geometry is in accord with suggestions based on nmr spectroscopic evidence. By contrast, the interactions between the nitrogen lone pair electrons and the S–O bonding orbitals do not seem to be determinant in defining the torsion angle of the sulfonamide bond (Figure 5). This is in contrast to the idealized conformations put forward for α-sulfonyl carbanions.

One of the C–Cl bond lengths (C–Cl(2)) was found to be anomalously short when compared with the other two, and with other sp^3 C–Cl bond lengths in the literature[16] (1.71 Å *vs.* 1.78 Å).

The incorporation of an asymmetric carbon atom of known absolute configuration in sulfenamide **1** permits an assignment of the absolute configuration at the sulfenamide chiral axis. Sulfenamide **1** was prepared from (+)-1-phenylethylamine which is known to have the absolute (*R*) configuration,[26] and the stereoformulas have been constructed so that the configuration at carbon is (*R*). We emphasize that the chirality

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of the sulfenamide grouping does not derive from an asymmetric nitrogen atom. Rather the torsional barrier about the sulfenamide S–N bond gives rise to an axis of chirality along the bond. The ligands on nitrogen and sulfenyl sulfur lie in two mutually perpendicular planes as in suitably substituted allenes. Since the sulfur is divalent, the ligancy complementation rule must be used to assign a phantom atom[27] of atomic weight zero as a sulfur ligand on the side opposite to the CCl_3 group before the Cahn–Ingold–Prelog convention[27] can be used to assign absolute configuration. This done, application of the chirality rule, in the form used for chiral axes, to the stereoformula or, more conveniently, to the Newman projection (Figure 4) indicates that the configuration at the sulfenamide bond is also (*R*). It has been shown using nmr experiments that the diastereomer in the crystal is also the more stable epimer in solution.[11] Thus, the (*R*,*R*) epimer predominates over the (*R*,*S*) epimer at equilibrium in solution.

The crystal packing (Figure 6) is normal with van der Waals forces predominating. Two intermolecular distances are shorter than the sums of the corresponding van der Waals radii[28] (Cl(1)···Cl(3),[29] 3.44 *vs.* 3.6; O(1)···C(2)″, 3.09 *vs.* 3.4 Å).[30]

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[29] Primed atoms are related to unprimed atoms by the transformation $x, y, z \rightarrow 1 - x, y - 1/2, -z$. Double primed atoms are related to unprimed atoms by $x, y, z \rightarrow 2 - x, y + 1/2, 1 - z$.

[30] A referee suggested that short intramolecular contacts O(1)··· C(2) and O(2)···S(2) might influence the degree and direction of the deviation from planar substitution at nitrogen. The two distances, 3.06 and 2.90 Å, are, in fact, shorter than sums of van der Waals radii[28] which are 3.4 and 3.25 Å, respectively. One additional contact O(2)··· Cl(2) is also comparable to the sum of van der Waals radii 3.21 Å *vs.* 3.2 Å. While the effect of these short contacts very probably has an effect on the geometry of the molecule, examination of a scale molecular model indicated no obvious relationship between these short contacts and the degree of puckering at nitrogen.

The Crystal and Molecular Structure of a Four-Membered Cyclic Oxyphosphorane with Pentavalent Phosphorus, $PO_2(C_6H_5)_2(CF_3)_4C_3H_2$

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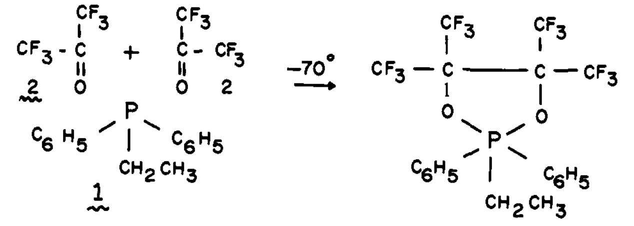
Abstract: The crystal and molecular structure of a four-membered cyclic oxyphosphorane with pentavalent phosphorus was determined by X-ray crystallography. The P atom of this intermediate in the Wittig olefin synthesis was at the center of a distorted trigonal bipyramid. The four-membered ring was in an apical–equatorial plane. Two oxygens were in apical position and three carbons were in equatorial positions. There was evidence of considerable intramolecular crowding which might contribute to the observed bending of the diapical axis (O–P–O bond angle of 165.8°) to the distortion of the ideal 120 and 90° bond angles, and to the distortion of bond angles in several tetragonal carbon atoms in the molecule.

The reaction of ethyldiphenylphosphine (**1**) with hexafluoroacetone (**2**) in hexane solution at −70° gave a five-membered cyclic oxyphosphorane[2] with pentavalent phosphorus, **3**.



3, $\delta\, ^{31}P = +6.1$ ppm
(in Benzene) vs H_3PO_4

The oxyphosphorane, **3**, was relatively stable at 30°; however, it underwent a remarkable isomerization in benzene solution at 80°. The product of this isomerization was a crystalline four-membered cyclic oxyphosphorane[3] containing also pentavalent phosphorus **4**.

A possible mechanism for this unprecedented molecular transformation involves the rupture of the P–O bond of the five-membered ring of **3** to give **5**. This is followed (or accompanied) by the rupture of a C–C bond to give the dipolar ion **6** and hexafluoroacetone (**2**). The ion **6** is the same intermediate generated from

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