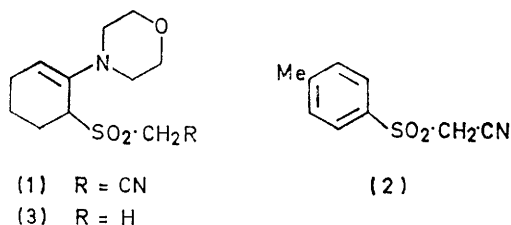


Crystal Structure, and Infrared and Proton Magnetic Resonance Spectra of 3-Cyanomethylsulphonyl-2-morpholinocyclohexene: Evidence for a C-H...N Intramolecular Hydrogen Bond

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The crystal and molecular structure of the title compound (1) has been determined from three-dimensional X-ray data by direct methods, and refined to R 0.038 for 2 263 independent reflections. Crystals are monoclinic $a = 11.635(1)$, $b = 9.315(1)$, $c = 12.103(1)$ Å, $\beta = 93.00(1)^\circ$ (at 23 °C), space group $P2_1c$, and $Z = 4$. A close C-H...N interaction, with H...N 2.47 Å, is found between a hydrogen atom of the cyanomethylsulphonyl group and the morpholino-nitrogen atom. I.r. spectroscopic evidence confirms the existence of the interaction in the solid state, thus permitting it to be classified as a weak hydrogen bond. ^1H N.m.r. and i.r. evidence indicates that the interaction may also exist in solution.

IN order to account for certain unusual features in the ^1H n.m.r. spectrum of 3-cyanomethylsulphonyl-2-morpholinocyclohexene (1), a 'weak electrostatic bond'



was postulated¹ as existing between one of the methylene hydrogen atoms of the cyanomethylsulphonyl group and the nitrogen atom of the morpholino-residue. Intermolecular hydrogen bonds involving polar C-H and a suitable electron donor are well authenticated, especially in the cases of trihalogenomethanes, hydrogen

¹ M. P. Sammes, C. M. Wylie, and J. G. Hoggett, *J. Chem. Soc. (C)*, 1971, 2151.

² R. D. Green, 'Hydrogen Bonding by C-H Groups,' Macmillan, London, 1974, and references therein.

³ A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1963, **85**, 1715.

⁴ D. J. Sutor, *J. Chem. Soc.*, 1963, 1105.

⁵ C. J. Fritchie and J. L. Wells, *Chem. Comm.*, 1968, 917.

⁶ G. C. Pimentel and A. L. McClellan, *Ann. Rev. Phys. Chem.*, 1971, **22**, 355.

cyanide, and terminal acetylenes,² but also with olefinic, aromatic, and methylene C-H, as long as the hydrogen atoms are polarised by a sufficient number of suitable electron-withdrawing substituents.^{2,3} In contrast, there appear to be no fully authenticated examples of intramolecular hydrogen bonds of this type. Many C-H...X intramolecular close approaches have been detected by X-ray crystallography, where the C...X distance is less than the sum of the classical van der Waals radii of these atoms,⁴⁻⁶ but in the absence of supporting spectroscopic evidence, these interactions cannot with certainty be classified as hydrogen bonds, and may arise merely as a result of crystal-packing forces.^{7,8} In an attempt to verify the suggestion made in ref. 1, and as part of a series of studies into molecules which may contain intramolecular C-H...O and C-H...N hydrogen bonds,^{9,10} the structure of the enamine sulphone (1) was determined. In addition, its

⁷ J. Donohue, 'Structural Chemistry and Molecular Biology,' eds. A. Rich and N. Davidson, Freeman, San Francisco, 1968, p. 443.

⁸ T. M. Gorrie and N. F. Haley, *J.C.S. Chem. Comm.*, 1972, 1081.

⁹ R. L. Harlow, S. H. Simonsen, M. P. Sammes, and C. E. Pfluger, *Acta Cryst.*, 1974, **B30**, 2264.

¹⁰ R. L. Harlow, M. P. Sammes, and S. H. Simonsen, *Acta Cryst.*, 1974, **B30**, 2903.

i.r. and ^1H n.m.r. spectra were reinvestigated and compared with those of a model compound *p*-tolylsulphonyl-acetonitrile (2).

EXPERIMENTAL

The title compound was prepared (41%) as described previously,¹ but recrystallised from benzene–light petroleum (b.p. 80–100 °C) (1:1). The model compound (2) was prepared (80%) by a known method.¹¹

Deuterium Exchange.—A solution of compound (1) (200 mg) in dry benzene (5 cm³) was stirred vigorously with D₂O (2 cm³; 99.7%) for 1 h. The benzene solution was dried (Na₂SO₄), solvent removed, and the residue recrystallised from dry CCl₄. Scrupulous precautions were taken to exclude all traces of moisture, the presence of which causes rapid re-exchange of deuterium by hydrogen.

Crystal Data.—C₁₂H₁₈N₂O₃S, *M* = 270.35. Monoclinic, space group *P*2₁/*c*, *Z* = 4. At 23 °C: *a* = 11.635(1), *b* = 9.315(1), *c* = 12.103(1) Å, β = 93.00(1)°, *U* = 1 310.0 Å³, *D*_c = 1.371 g cm⁻³. At -35 °C, *a* = 11.854(4), *b* = 9.305(2), *c* = 12.053(2) Å, β = 93.16(3)°, *U* = 1 297.1 Å³, *D*_c = 1.384 g cm⁻³. Mo-*K*_α radiation, λ = 0.7107 Å; μ(Mo-*K*_α) = 2.52 cm⁻¹.

A crystal, with dimensions of 0.20 × 0.30 × 0.30 mm perpendicular to (100), (011), and (011) respectively, was grown by sublimation. Rotation and Weissenberg photographs established the space group and approximate unit-cell dimensions. The unit-cell parameters at ambient temperature were refined by a least-squares fit of the Bragg angles of 19 reflections (80 < 2θ < 99°, Cu-*K*_{α1} = 1.540 50 Å) measured on a General Electric XRD 5 diffractometer. The crystal was then mounted on a Syntex *P*2₁ diffractometer equipped with a low-temperature apparatus which maintained the crystal at -35 °C. The Bragg angles of 24 reflections (Mo-*K*_α) were determined by the Syntex centring routine; refinement gave unit-cell dimensions at this temperature.

Intensity data for 2 977 unique reflections (4 < 2θ < 55°, graphite-monochromatized Mo-*K*_α radiation) were collected at -35 °C by the ω scan technique. Scans of 1.0° were used with scan rates ranging from 1.0 to 5.0° min⁻¹ depending on the number of counts measured in a rapid preliminary scan. Backgrounds were measured at both ends of the scan with ω displaced 1.0° from the *K*_α peak. The intensities of four standard reflections monitored after every 96 reflections showed only statistical variations. Intensities were corrected for Lorentz and polarization effects, but not for absorption.

Solution and Refinement.—The structure was solved by direct methods (MULTAN). Refinement of the structure by the full-matrix least-squares method was carried out using only those 2 263 reflections for which *I* > 2σ(*I*). A difference Fourier was used to locate the hydrogen atoms. Refinement of all positional and thermal (anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms) parameters converged at a conventional *R* of 0.038. The largest parameter shift in the final cycle of the refinement was 0.02 σ. The largest peak in the final difference map had a magnitude of 0.3 eÅ⁻³ and was located near atom S(1). Refined positional parameters are given in Table 1. Computational details are noted elsewhere.¹²

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

Bond lengths and angles are listed in Table 2, final observed and calculated structure factors and thermal parameters are in Supplementary Publication No. SUP 21655 (18 pp., 1 microfiche).*

Spectroscopic Measurements.—I.r. spectra were determined for hexachlorobuta-1,3-diene (HCB) mulls, and for

TABLE 1

Refined positional parameters for (1), with estimated standard deviations in parentheses

(a) Final atomic co-ordinates for the non-hydrogen atoms			
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
S(1)	0.359 61(4)	0.381 32(5)	0.201 38(4)
O(2)	0.345 9(1)	0.283 6(2)	0.109 0(1)
O(3)	0.458 0(1)	0.475 5(2)	0.207 9(1)
C(4)	0.375 8(2)	0.273 4(2)	0.326 0(2)
C(5)	0.288 4(2)	0.162 4(2)	0.333 4(2)
N(6)	0.220 8(2)	0.075 0(2)	0.339 4(2)
C(7)	0.228 3(2)	0.491 2(2)	0.207 8(2)
C(8)	0.184 2(2)	0.492 3(2)	0.323 3(1)
C(9)	0.085 6(2)	0.426 5(2)	0.343 4(2)
C(10)	0.010 7(2)	0.343 6(3)	0.260 6(2)
C(11)	0.067 7(2)	0.318 0(3)	0.151 8(2)
C(12)	0.135 4(2)	0.448 7(3)	0.118 7(2)
N(13)	0.259 3(1)	0.557 8(2)	0.405 5(1)
C(14)	0.285 7(2)	0.711 2(2)	0.388 9(2)
C(15)	0.379 8(2)	0.758 8(2)	0.472 3(2)
O(16)	0.349 5(1)	0.734 7(1)	0.584 0(1)
C(17)	0.326 7(2)	0.585 4(2)	0.598 8(2)
C(18)	0.229 6(2)	0.535 1(2)	0.520 4(2)

(b) Positional and thermal parameters for the hydrogen atoms *

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
H(4A)	0.448(2)	0.233(2)	0.321(2)	3.6(5)
H(4B)	0.376(2)	0.337(2)	0.387(2)	2.8(4)
H(7)	0.260(2)	0.580(2)	0.188(2)	2.2(4)
H(9)	0.059(2)	0.432(2)	0.416(2)	1.9(4)
H(10A)	-0.060(2)	0.397(2)	0.248(2)	2.9(5)
H(10B)	-0.007(2)	0.249(3)	0.296(2)	4.5(6)
H(11A)	0.009(2)	0.299(2)	0.090(2)	3.7(5)
H(11B)	0.122(2)	0.235(2)	0.156(2)	3.3(5)
H(12A)	0.084(2)	0.530(2)	0.110(2)	3.7(5)
H(12B)	0.170(2)	0.433(2)	0.051(2)	2.5(4)
H(14A)	0.215(2)	0.769(2)	0.398(2)	2.6(4)
H(14B)	0.309(2)	0.725(2)	0.315(2)	2.6(4)
H(15A)	0.391(2)	0.860(2)	0.466(2)	3.3(5)
H(15B)	0.453(2)	0.707(2)	0.460(2)	2.7(4)
H(17A)	0.307(2)	0.575(2)	0.674(2)	2.9(4)
H(17B)	0.399(2)	0.528(2)	0.583(2)	3.0(5)
H(18A)	0.156(2)	0.586(2)	0.536(2)	2.5(4)
H(18B)	0.219(2)	0.433(2)	0.533(2)	2.3(4)

* Each numbered in accord with the carbon atom to which it is bonded.

CHCl₃ and CCl₄ solutions. Spectroscopic-grade solvents were passed down an alumina (activity I) column before use. Spectra were run on a Perkin-Elmer 577 spectrophotometer, the × 5 ordinate scale-expansion facility being used for CCl₄ solutions owing to the low solubility of compounds (1) and (2). Stretching frequencies for the polar methylene group in the two compounds are given in Table 3. Polystyrene was used in calibration.

^1H N.m.r. spectra were run on a Perkin-Elmer R 1 spectrometer, and were determined for solutions in deuteriochloroform with Me₄Si as internal reference. The spectrum of compound (1) is presented in Figure 1. The polar methylene group in the tolyl sulphone (2) was identified at 4.07 (2 H, s) p.p.m.

¹¹ J. Troeger and W. Hille, *J. prakt. Chem.*, 1905, **71**, 226.

¹² R. L. Harlow, W. J. Wells, G. W. Watt, and S. H. Simonsen, *Inorg. Chem.*, 1974, **13**, 2106.

RESULTS AND DISCUSSION

Description of the Structure.—The crystal structure consists of discrete molecules with no unusually short intermolecular contacts. A stereodrawing of the molecule with the atom-labelling scheme is presented in

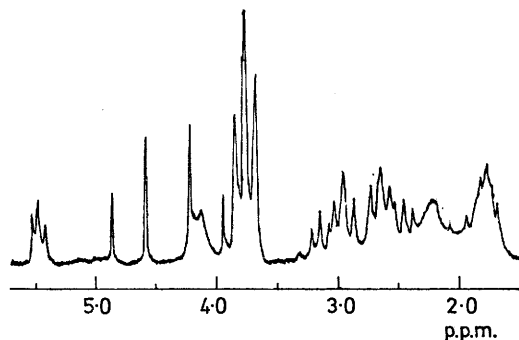


FIGURE 1 60 MHz ^1H N.m.r. spectrum (CDCl_3) of (1)

Figure 2; it is found to be in the configuration predicted previously.¹ The morpholino-group is seen to have a chair conformation, while the cyclohexene moiety exists in the half-chair conformation. Intramolecular bond distances and angles for the non-hydrogen atoms (Table 1) appear reasonable in comparison with those for previously reported structures.^{10,13-18} Bond parameters for hydrogen atoms H(4A) and H(4B) are also included in Table 2. The C-H bond distances for the remaining hydrogen atoms ranged from 0.94 to 1.02 Å; bond angles were all within 5° of the expected values.

The feature of particular relevance is the short intramolecular contact between H(4B) and N(13) (see Figure 2). The important distances (Å) and angles (°) are: H(4B) \cdots N(13) 2.47(2), and C(4) \cdots N(13) 3.145(3); C(4)-H(4B) \cdots N(13) 128(2), C(8)-N(13) \cdots

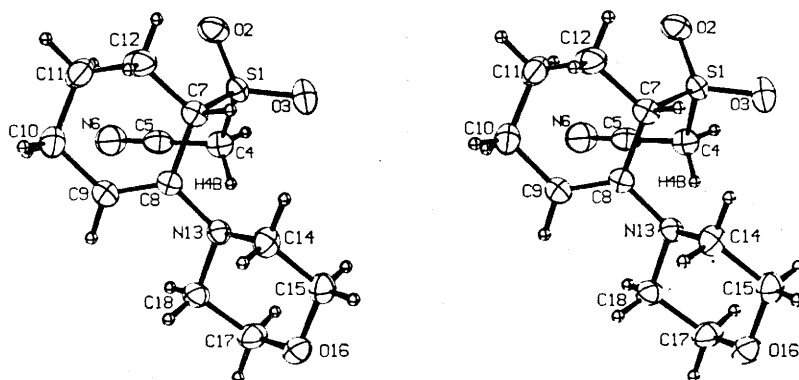


FIGURE 2 Stereodrawing of a molecule of (1)

H(4B) 84(1), C(14)-N(13) \cdots H(4B) 132(1), and C(18)-N(13) \cdots H(4B) 97(1). The N \cdots H distance is considerably shorter than 2.7 Å, the sum of the relevant

¹³ C. Pedone, E. Benedetti, A. Immirizi, and G. Allegra, *J. Amer. Chem. Soc.*, 1970, **92**, 3549.

¹⁴ T. Sundaresan and S. C. Wallwork, *Acta Cryst.*, 1972, **B28**, 3507.

¹⁵ S. Husebye, *Acta Chem. Scand.*, 1973, **27**, 756.

TABLE 2
Bond distances (Å) and angles (°) for (1), with estimated standard deviations in parentheses

(a) Distances			
S(1)-O(2)	1.440(1)	C(8)-N(13)	1.420(2)
S(1)-O(3)	1.437(1)	C(9)-C(10)	1.499(3)
S(1)-C(4)	1.808(2)	C(10)-C(11)	1.519(3)
S(1)-C(7)	1.839(2)	C(11)-C(12)	1.514(3)
C(4)-C(5)	1.453(3)	N(13)-C(14)	1.476(2)
C(4)-H(4A)	0.93(2)	N(13)-C(18)	1.461(2)
C(4)-H(4B)	0.94(2)	C(14)-C(15)	1.508(3)
C(5)-N(6)	1.134(3)	C(15)-O(16)	1.428(2)
C(7)-C(8)	1.510(3)	O(16)-C(17)	1.427(2)
C(7)-C(12)	1.531(3)	C(17)-C(18)	1.504(3)
C(8)-C(9)	1.330(3)		
(b) Angles			
O(2)-S(1)-O(3)	118.7(1)	C(7)-C(8)-C(9)	120.2(2)
O(2)-S(1)-C(4)	107.1(1)	C(7)-C(8)-N(13)	114.9(2)
O(2)-S(1)-C(7)	109.2(1)	C(9)-C(8)-N(13)	124.8(2)
O(3)-S(1)-C(4)	104.3(1)	C(8)-C(9)-C(10)	126.0(2)
O(3)-S(1)-C(7)	108.3(1)	C(9)-C(10)-C(11)	113.1(2)
C(4)-S(1)-C(7)	108.8(1)	C(10)-C(11)-C(12)	111.0(2)
S(1)-C(4)-C(5)	113.9(1)	C(11)-C(12)-C(7)	112.2(2)
S(1)-C(4)-H(4A)	103(1)	C(8)-N(13)-C(14)	116.4(1)
S(1)-C(4)-H(4B)	107(1)	C(8)-N(13)-C(18)	115.6(1)
C(5)-C(4)-H(4A)	111(1)	C(14)-N(13)-C(18)	109.3(1)
C(5)-C(4)-H(4B)	112(1)	N(13)-C(14)-C(15)	110.0(2)
H(4A)-C(4)-H(4B)	111(2)	C(14)-C(15)-O(16)	112.1(2)
C(4)-C(5)-N(6)	179.5(2)	C(15)-O(16)-C(17)	109.1(1)
S(1)-C(7)-C(8)	111.4(1)	O(16)-C(17)-C(18)	111.2(2)
S(1)-C(7)-C(12)	112.2(2)	C(17)-C(18)-N(13)	110.1(2)
C(8)-C(7)-C(12)	112.9(2)		

TABLE 3
I.r. stretching frequencies (cm^{-1}) for the active methylene group in (1) and (2)

	(1)		(2)		$\Delta\nu_{\text{as}}^a$	$\Delta\nu_s^b$
	ν_{as}	ν_s	ν_{as}	ν_s		
HCB mull	2 971	2 910	2 985	2 933	14	23
CHCl_3	2 969	2 918	2 986	2 934	17	16
CCl_4	2 970	2 917	2 986	2 934	16	17
$\text{CCl}_4 + [^2\text{H}_6]\text{Me}_2\text{SO}$			2 865	2 775	121 ^c	159 ^d
$\text{CCl}_4 + [^2\text{H}_5]\text{Pyridine}$			2 850	2 760	136 ^c	174 ^d

^a $\Delta\nu_{\text{as}} = \nu_{\text{as}}(2) - \nu_{\text{as}}(1)$. ^b $\Delta\nu_s = \nu_s(2) - \nu_s(1)$. ^c Relative to $\nu_{\text{as}}(2)$ in CCl_4 . ^d Relative to $\nu_s(2)$ in CCl_4 .

van der Waals radii. That this contact represents an interaction between $\text{H}^{\delta+}$ (the C-H bond being highly polarised by the neighbouring $-\text{SO}_2^-$ and $-\text{CN}$ groups) and $\text{N}^{\delta-}$ is supported by the geometry of the molecule.

¹⁶ G. Argay and J. Seres, *Acta Cryst.*, 1973, **B29**, 1146.

¹⁷ A. E. Smith, R. Kalish, and E. J. Smutny, *Acta Cryst.*, 1972, **B28**, 3494.

¹⁸ A. Albinati and M. Zocchi, *Acta Cryst.*, 1974, **B30**, 544.

First, although the hydrogen atom is located almost directly in line with the nitrogen lone-pair, it is not compelled 'for steric reasons' to do so.¹⁹ On the contrary, the molecule appears to adopt an unfavourable configuration in order to allow the interaction. Although the sulphonyl group normally prefers to adopt a staggered conformation with neighbouring atoms,^{9,10,20} here O(2), O(3), and C(4) eclipse respectively C(12), H(7), and C(8). The torsion angle O(2)-S(1)-C(7)-C(12) is only 2.66° (though the other two relevant angles lie between 13 and 20°), causing a close approach (2.53 Å) between H(12B) and O(2). In addition, C(5) approaches C(8) to within 3.299 Å, a distance significantly shorter than that for a normal π - π interaction (e.g. 3.35 Å in graphite²¹). Secondly, the nitrogen atom has maintained an sp^3 pyramidal conformation in order to sustain the interaction, rather than an sp^2 planar conformation which would have allowed π overlap with the neighbouring C:C double bond. In two reported structures where the nitrogen atom of the morpholino-group was bonded to $-(C:S)-$ (ref. 15) and $-(C:O)-$,¹⁷ the nitrogen atom was found to have a nearly planar conformation with mean exocyclic C-N-C angle of ca. 123°, and with very short exocyclic N-C distances (1.35 and 1.335 Å). In these two cases, considerable π overlap occurs. In 1,1,2-trimorpholinoethene,¹⁸ π overlap apparently occurs between two of the nitrogen atoms and the C:C double bond, but not with the third. Exocyclic C-N bond lengths for the three morpholino-residues are respectively 1.398, 1.415, and 1.442 Å, but more effective overlap is no doubt prevented by steric factors. Nevertheless, overlap is sufficient to cause some lengthening of the C:C bond (1.347 Å), and thus the C-N length of 1.442 Å is probably artificially long. The C:C bond length in (1) is typical for an unperturbed double bond;¹³ in addition the morpholino-group is rotated out of the plane defined by C(7)-(9) by ca. 33°. Thus the C(8)-N(13) distance (1.420 Å) may be taken to indicate essentially zero π overlap.

Solid State I.r. Spectrum.—The suggested interaction between H(4B) and N(13) is further supported by the solid-state (HCB) i.r. spectrum of (1). A comparison between this spectrum and that of the 4A,4B-D₂-derivative in the 2 900—3 000 cm⁻¹ region allowed ν_{as} and ν_s for the active methylene to be identified (see Table 3).^{*} Although these values are high when compared with the frequencies for an unperturbed methylene, they are significantly lower than those of the model compound (2) in which no interaction can occur. In

* The corresponding CD₂ modes appear at 2 235 and 2 128 cm⁻¹ (with a weak shoulder at 2 113 cm⁻¹).

† These values of $\Delta\nu$ compare well with those reported for chloroacetonitrile in CCl₄ solution in the presence of pyridine.³

‡ The bands due to non-bonded C-H appear sharply at 2 986 and 2 834 cm⁻¹; the bonded modes are very broad. In contrast, the bands in compound (1) are quite sharp, consistent with the presence of an intramolecular bond.²³

¹⁹ Ref. 7, pp. 456—459.

²⁰ S. Bradamante, P. D. Buttero, D. Landini, and S. Maiorana, *J.C.S. Perkin II*, 1974, 1676.

²¹ G. E. Bacon, *A.E.R.E. Report*, M/R 2702, 1958 (*Chem. Abs.*, 1959, 53, 8759g).

addition $\Delta\nu_s$ (23 cm⁻¹) is larger than $\Delta\nu_{as}$ (14 cm⁻¹) for the two compounds, in agreement with the findings of Allerhand and Schleyer³ for intermolecular hydrogen bonds involving polar methylene.†

I.r. and ¹H N.m.r. Spectra in Solution.—For compound (1) and the model compound (2) $\Delta\nu_{as}$ and $\Delta\nu_s$ are 16—17 cm⁻¹ both in CHCl₃ and in CCl₄ solution (see Table 3). These shifts are not due merely to the absence of an aromatic ring attached to the -SO₂- group, since 8-cyanomethylsulphonylquinoline, which also shows evidence of an intramolecular interaction, has ν_{as} and ν_s for the methylene group (CHCl₃ solution) at 2 972 and 2 927 cm⁻¹ respectively.²² They are, however, an order of magnitude smaller than the very large shifts due to intermolecular C-H...N hydrogen-bond formation found for the tolyl sulphone (2) in CCl₄ solution when respectively [²H₆]Me₂SO and [²H₅]pyridine are added (see Table 3).‡ It thus appears that the intramolecular interaction in the enamine sulphone (1), both in solution (if genuine) and in the solid state, is weak due probably to the large deviation of the C-H...N angle from linearity.¹⁹

The ¹H n.m.r. spectrum (CDCl₃ solution) of compound (1) is presented in Figure 1. The three most interesting features are: the chemical shift of H(9) (5.50 p.p.m.), the AB quartet due to the active methylene group (4.68, 4.10 p.p.m.; J_{AB} 16 Hz), and the complex pattern due to the C(14) and C(18) methylene groups (3.3—2.3 p.p.m.)

The olefinic proton. This appears ca. 1 p.p.m. lower field than in 1-morpholinocyclohexene,^{24,25} and close to the value (5.57 p.p.m.) recorded for cyclohexene.²⁴ It thus seems that even in solution there is negligible overlap between the nitrogen lone-pair and the π system of the C:C double bond.

The C(4), C(14), and C(18) protons. The unusual features in the ¹H n.m.r. spectrum due to these protons arise from a common cause: the chiral centre at C(7). Non-equivalence in the protons of an isolated methylene group, arising from a distant chiral centre, is well documented.²⁶⁻²⁸ Likewise an increase in complexity in the morpholino-splitting pattern from the familiar A₂A'₂X₂X'₂ to the A₂B₂X₂X'₂ system has also been recorded as arising from a similar cause.^{29,30} The contribution of intrinsic asymmetry to the total non-equivalence of such methylene protons is believed to be small,³¹ the greatest contribution being due to a high

²² M. P. Sammes and R. L. Harlow, following paper.

²³ G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond,' Freeman, San Francisco, 1960, pp. 172—173.

²⁴ G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkowicz, and R. Terrell, *J. Amer. Chem. Soc.*, 1963, 85, 207.

²⁵ W. D. Gurowitz and M. A. Joseph, *J. Org. Chem.*, 1967, 32, 3289.

²⁶ G. M. Whitesides, J. J. Grocki, D. Holtz, H. Steinberg, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, 87, 1058.

²⁷ J. C. Randall, J. J. McLeskey, P. Smith, and M. E. Hobbs, *J. Amer. Chem. Soc.*, 1964, 86, 3229.

²⁸ J. J. Looker, *J. Org. Chem.*, 1966, 31, 2973.

²⁹ P. Ferruti, A. Segre, and A. Fere, *J. Chem. Soc. (C)*, 1968, 2721.

³⁰ P. D. Buttero and S. Maiorana, *J.C.S. Perkin I*, 1973, 2540.

³¹ G. Binsch and G. R. Franzen, *J. Amer. Chem. Soc.*, 1969, 91, 3999.

population of a preferred conformation. This is borne out by the ^1H n.m.r. spectra of a series of 2-halogeno-3-morpholinotietan 1,1-dioxides in which the morpholino-group is attached directly to a chiral centre.³⁰ In the *trans*-series, where steric interactions are small, the morpholino-group appears as a normal $\text{A}_2\text{A}'_2\text{X}_2\text{X}'_2$ pattern. When the 2- and 3-substituents are mutually *cis*, however, a $\text{A}_2\text{B}_2\text{X}_2\text{X}'_2$ pattern is found. Compound (1) also shows a $\text{A}_2\text{B}_2\text{X}_2\text{X}'_2$ pattern for the morpholino-residue, the four triplets arising from the A_2B_2 part appearing in the 3.3—2.3 p.p.m. region (see Figure 1).

Whether the high population of one preferred conformation in (1) arises from steric factors, from the proposed $\text{C-H}\cdots\text{N}$ interaction, or from both causes is uncertain. There is evidence that 3-methylsulphonyl-2-morpholinocyclohexene (3)³² also shows non-equivalence in the morpholino N-CH_2 protons,* and this must certainly arise from steric factors since a $\text{CH}_3\cdots\text{N}$ hydrogen bond is highly unlikely.³ The low-field position of H(9) shows that the preferred conformation

* It is probable that the 'enamine mixture' [compounds (X) and (XI) of ref. 32] reported by Borowitz was in fact a single substance † (3). The mixture would be expected to give two methyl peaks in the ^1H n.m.r., rather than the one reported. The four triplets anticipated for the A_2B_2 portion of the morpholino-spectrum can be assigned to the triplet at 3.16, the group lying under the CH_3 at 2.91, the triplet at 2.60 and the group at 2.35 p.p.m. (*cf.* Figure 1). The olefinic proton would probably have been masked by solvent (CH_2Cl_2) absorption, but these suggestions need to be tested experimentally.

† Note added in proof: The 'enamine mixture' has subsequently been shown to be a single substance as suggested, and the tentative ^1H n.m.r. assignments have been confirmed.³³

does not arise from conjugation between the nitrogen lone-pair and the C:C double bond.

Two other points are worth noting. First, in the AB quartet arising from the C(4) protons, the value of 4.10 p.p.m. is normal for the $-\text{SO}_2\cdot\text{CH}_2\cdot\text{CN}$ group [*cf.* 4.07 p.p.m. in (2)]. The value of 4.68 p.p.m. implies an interaction with a nearby polar or anisotropic group. Secondly, when one drop of D_2O is added to a solution of (1) in CDCl_3 , and the mixture shaken for 3 s and allowed to separate, the C(4) proton signals are no longer visible. No evidence of exchange is shown by H(7) even after agitation for 2 h, and compound (2) does not exchange measurably under similar conditions. Such a rapid rate of exchange in the absence of added base (see also in Experimental section), implies intramolecular catalysis involving the morpholino-nitrogen atom, and further supports the suggested interaction in solution.

Conclusion.—The crystal structure and i.r. spectrum of compound (1) provide strong evidence for an intramolecular $\text{C-H}\cdots\text{N}$ interaction in the solid state, which may be classified as a weak hydrogen bond. Evidence for such an interaction in solution, while positive, is not conclusive.

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³² I. J. Borowitz, *J. Amer. Chem. Soc.*, 1964, **86**, 1146.

³³ H. K. Wah and M. P. Sammes, *J.C.S. Perkin I*, 1976, in the press.