Confirmation of a Short Intramolecular C–H · · · N Hydrogen Bond in 4,4-Bisphenylsulphonyl-2,*N*,*N*-trimethylbutylamine by *X*-Ray Crystallography

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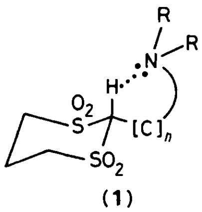
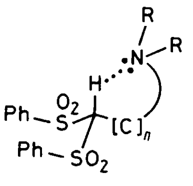
The *X*-ray crystal structure of the title compound, (**3**), reveals a close intramolecular contact between the polar methine hydrogen and amino nitrogen atoms of 2.34(3) Å, consistent with the hydrogen bonding interaction detected in solution by ^{1}H n.m.r. spectroscopy.

We recently demonstrated unequivocally by ^{1}H n.m.r. spectroscopy the presence of intramolecular C–H · · · N hydrogen bonds in both cyclic (**1**),[1a] and diphenyl (**2**),[1b] disulphones. The interaction was optimized when: (a) it formed part of a six-membered ring, (b) the acceptor was a piperidino or dimethylamino nitrogen atom, and (c) there was one methyl substituent in the side chain to reduce conformational mobility. The title compound (**3**) showed a ^{1}H n.m.r. (CD_2Cl_2; -40 °C) downfield shift for the polar methine proton of 2.18 p.p.m. relative to a model compound;[1b] we have now demonstrated the presence of the hydrogen bond in the solid state by *X*-ray crystallography.

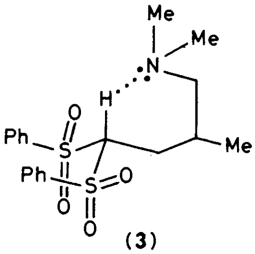
Crystals of (**3**) were grown by slow evaporation of a benzene–petroleum (b.p. 80—100 °C) solution. *Crystal data:* $C_{19}H_{25}NO_4S_2$, $M = 395.54$, triclinic, space group $P1$, $a = 10.625(3)$, $b = 12.745(2)$, $c = 8.295(2)$ Å, $\alpha =$



(1)



(2)



(3)

106.13(2), $\beta = 98.55(2)$, $\gamma = 66.39(2)°$, $U = 987.8(6)$ Å^3, $Z = 2$, $D_c = 1.330$ g cm^{-3}, μ(Mo-K_α) = 2.9 cm^{-1}. The structure was solved by direct methods and refined by full-matrix least-squares to $R = 0.052$ and $R_w = 0.039$, based on 2451 unique reflections with $F^2 > 2\sigma(F^2)$.†

The structure is shown in Figure 1. It reveals that the side chain has curled round to permit the anticipated interaction, the observed N · · · H(1) distance [2.34(3) Å] being very significantly less than the sum of the van der Waal's radii (2.75 Å) [2] for the two atoms, and to our knowledge, smaller than in any intramolecular C–H · · · N interaction yet reported.[2,3] Further, H(1) completes approximately tetrahedral geometry about the nitrogen atom, relevant angles being C(4)–N–H(1) 85.4(7), C(6)–N–H(1) 115.6(7), and C(7)–N–H(1) 123.5(7)°. The angle C(1)–H(1)–N [138(2)°] is comfortably within the range for C–H · · · X hydrogen bonding interactions.[2] Interestingly, the two (approximately parallel) phenyl rings are on the side of the molecule opposite to that predicted earlier;[1b] the C(11)–S(1)–S(2)–C(21) dihedral angle is 24.2°, with a C(11) · · · C(21) distance of 3.306(4) Å.

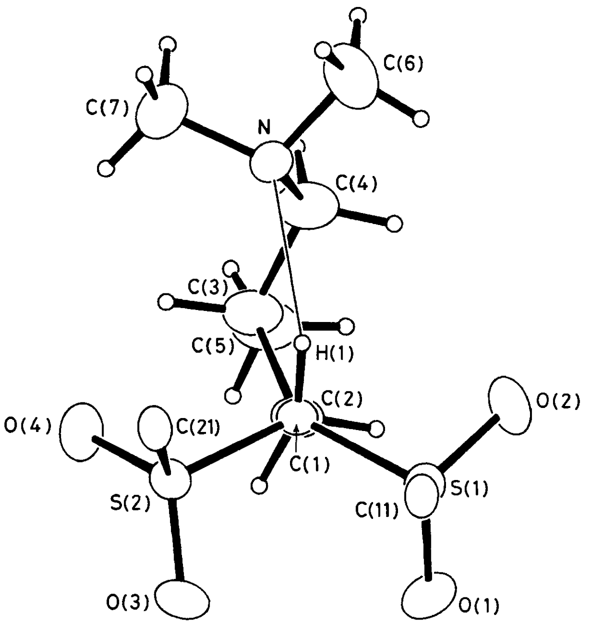


Figure 1. The C–H · · · N interaction and the conformation of the aliphatic chain as viewed parallel to the C(1)–C(2) bond. Except for C(11) and C(21), the atoms of the phenyl groups have been omitted from this drawing.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

References

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