Ar–(N_2S)–Ar: *X*-Ray Structure of the *p,p'*-Ditolyl Derivative

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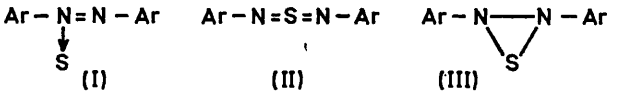
Summary A single-crystal *X*-ray diffraction study of *p*-MeC_6H_4–(N_2S)–C_6H_4Me-*p'* has shown that the –N_2S– group has the bis-imino-sulphur structure –N=S=N–.

SEVERAL symmetrical Ar-(N_2S)-Ar compounds have been prepared[1–8] and structures such as azothioarene (I), bis-arylimino-sulphur (II) and 2,3-diaryl-1,2,3-thiodiazirine (III) have been suggested.[1,2,7,9,10]

Chemical evidence, partial assignment of the i.r. spectra[2,9] dipole moment measurements,[10] and n.m.r. data[11] did not allow the structure of the -(N_2S)- group to be assigned unambiguously, geometric isomerism also being possible. The n.m.r. spectrum of the *p,p'*-ditolyl derivative[12] consists of a single peak at δ 2·30 p.p.m. (CH_3) (δ values from Me_4Si, in CCl_4) and a symmetrical resonance group centred at δ 7·18 p.p.m., which resembles an A_2B_2 system of *p*-disubstituted benzenes,[13] with an integration ratio of 4:3. No other peaks are observed. The apparent spectral equivalence



of the two tolyl groups suggests a symmetrical structure, since, by analogy with azoxy compounds,[14–16] structure (I) would show two methyl resonances.

We now show by *X*-ray analysis that the *p,p'*-ditolyl compound has the bis-imino-sulphur structure –N=S=N–, in the crystal.

Crystal data. $C_{14}H_{14}N_2S$, $M = 242·2$, triclinic, space group $P\bar{1}$, $a = 11·24$, $b = 11·09$, $c = 6·00$ Å, $\alpha = 95·8°$,

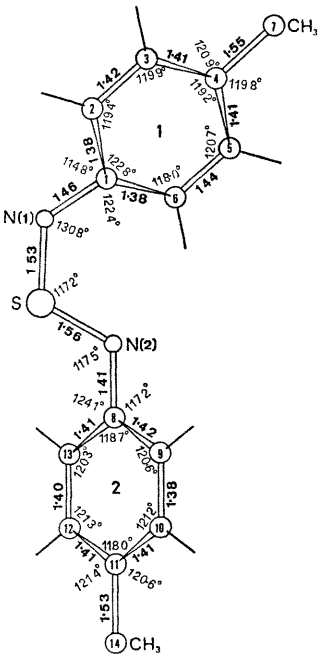
$\beta = 102{\cdot}6°$, $\gamma = 113{\cdot}8°$, $U = 648$ Å^3, $Z = 2$, $D_m = 1{\cdot}22$, $D_c = 1{\cdot}24$ g. cm^{-3}. The presence of a centre of symmetry, indicated by the zero moment test, was confirmed by the structure refinement. The crystals were obtained by slowly evaporating ligroin solutions and their density was measured by flotation.

The *hkl* reflexions were collected in a Weissenberg camera (equi-inclination technique, $l = 0, \ldots, 5$) using Cu-K_α Ni-filtered radiation, and the intensity of 1482 independent reflexions was estimated by an integrating microdensitometer. The *h*0*l* and 0*kl* reflections collected in a precession camera with Mo-K_α Zr-filtered radiation were used for the inter-layer scaling.

The structure was solved by the parallel and integrated use of direct methods[17] and of Buerger's minimum function[18] applied to two-dimensional data, and then refined with the complete set of three-dimensional data by full-matrix least-square methods with anisotropic temperature factors, to $R(hkl) = 0{\cdot}10$.

The estimated standard deviations of bond lengths and angles involving sulphur are 0·009 Å and 0·4° respectively, those involving other atoms are about 0·012 Å and 0·6°.

The structure of the molecule is shown in the Figure. The two N–S bond lengths, which are approximately equal, are much closer to the double bond (1·52 Å) than to the single bond value (1·74 Å). The N(1)–N(2) distance of 2·64 Å rules out structure (III). The molecular conformation is approximately planar, except for rotation of the two phenyl rings: the internal rotation angles around the S–N(1) and S–N(2) bonds are −1·9° and +177·8° respectively, while those around the bonds N(1)–C(1) and N(2)–C(8) are +21·9° and +39·9°, respectively. The one-*cis* one-*trans* conformation of the two S–N bonds and the small rotation of the ring 1 bring the C(6) atom and its hydrogen atom rather close to the N(2) atom (3·1 and 2·4 Å, respectively) and thus may be responsible for the large increase of the valence angles in the C(1)–N(1)–S moiety. The observed S–N and N–C bond lengths suggest that contributions from resonance structures other than –N=S=N–,[2,16] if any, are likely to be very small.



FIGURE

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[1] G. Leandri and P. Rebora, *Experientia*, 1957, **13**, 70; *Gazzetta*, 1957, **87**, 503.
[2] R. Cramer, *J. Org. Chem.*, 1961, **26**, 3476.
[3] A. V. Kirsanov and E. S. Levchenko, U.S.S.R. Pat. (26th July 1963); *Chem. Abs.*, 1964, **60**, 11,949.
[4] E. S. Levchenko and A. V. Kirsanov, *Zhur. org. Khim.*, 1965, **1**, 300; *Chem. Abs.*, 1965, **62**, 16,099.
[5] E. S. Levchenko, B. N. Ugarov, and J. E. Sheikman, *Zhur. org. Khim.*, 1966, **2**, 1388; *Chem. Abs.*, 1967, **67**, 2848.
[6] H. M. Hoerhold and K. D. Flossmann, *Z. Chem.*, 1967, **7**, 345; *Chem. Abs.*, 1967, **67**, 116,675.
[7] C. Carpanelli, G. Leandri, and G. Poluzzi, *Ricerca Sci.*, 1968, **38**, 35.
[8] T. Minami, H. Miki, H. Matsumoto, Y. Ohshiro, and T. Agawa, *Tetrahedron Letters*, 1968, **26**, 3049.
[9] A. Foffani, G. Leandri, I. Zanon, and C. Carpanelli, *Tetrahedron Letters*, 1959, **11**, 21; "Advances in Molecular Spectroscopy," Pergamon Press, Oxford, 1962, p. 91.
[10] L. Jannelli, O. Sciacovelli, and C. Carpanelli, *Ann. Chim.* (*Italy*), 1963, **53**, 1541.
[11] G. Leandri and F. Taddei, unpublished results.
[12] M. Mammi and L. Strasorier, personal communication.
[13] J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice Hall, London, 1965, p. 110.
[14] D. L. Webb and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1964, **86**, 2419.
[15] J. P. Freeman, *J. Org. Chem.*, 1963, **28**, 2508.
[16] D. H. Clemens, A. J. Bell, and J. L. O'Brien, *Tetrahedron Letters*, 1965, **20**, 1487.
[17] M. H. Woolfson, "Direct Methods in Crystallography," Clarendon Press, Oxford, 1961.
[18] M. J. Buerger, *Acta Cryst*, 1951, **4**, 531.