Crystal Structure of 1-(Mesityl-2-sulphonyl)-3-nitro-1,2,4-triazole

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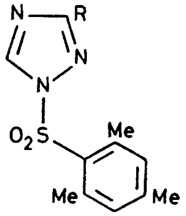
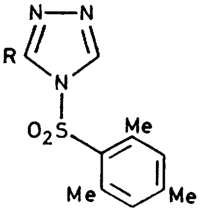
The crystal structure of 1-(mesityl-2-sulphonyl)-3-nitro-1,2,4-triazole (1a) has been determined from three-dimensional diffractometer data. The triclinic unit cell, $P\bar{1}$, has dimensions a = 8.001(1), b = 8.140(2), c = 12.892(1) Å, α = 98.22(1)°, β = 105.49(1)°, γ = 102.12(1)°, and Z = 2. The structure was solved by the heavy-atom method and refined to R 0.0736 for 2 926 reflections ($F_o > 3\sigma F_o$). The crystal structure confirms that the product of reaction of 3-nitrotriazole and mesitylenesulphonyl chloride is 1-(mesityl-2-sulphonyl)-3-nitro-1,2,4-triazole.

THE purpose of the present study was to determine whether the compound, m.p. 130—132 °C, obtained[1,2] by treating 3-nitro-1,2,4-triazole with mesitylene-2-sulphonyl chloride and triethylamine in dioxan solution, may be assigned the structure 1-(mesityl-2-sulphonyl)-3-nitro-1,2,4-triazole (1a) (MSNT). This is a matter of some importance as MSNT now appears to be the condensing agent of choice in the synthesis both of oligoribo-[2] and oligodeoxyribo-nucleotides[3] by the phosphotriester approach.[4]



(1) a; R = NO_2
b; R = H



(2) a; R = NO_2
b; R = H

Although it is clear from its ^{1}H n.m.r. spectrum, δ ($CDCl_3$) 2.33 (3 H, s), 2.67 (6 H, s), 7.02 (2 H, s), and 8.80 (1 H, s), that MSNT is a pure compound, it is not possible to exclude structure (2a) on the basis of n.m.r. or other spectroscopic evidence. 1-(Mesityl-2-sulphonyl)-1,2,4-triazole, m.p. 133—134 °C, obtained by treating 1,2,4-triazole with mesitylene-2-sulphonyl chloride and triethylamine essentially [†] under the conditions described in the literature[5] and then recrystallizing the isolated product from toluene, clearly has the originally assigned[5] structure (1b) on the evidence of its ^{1}H n.m.r. spectrum, δ ($CDCl_3$) 2.30 (3 H, s), 2.65 (6 H, s), 6.98 (2 H, s), 7.95 (1 H, s), and 8.77 (1 H, s). However, while the isolated product of the latter reaction was apparently homogeneous (by t.l.c.) before recrystallization, its n.m.r. spectrum contained additional singlet resonance signals at δ 2.60 and 8.41. The latter signal is situated approximately halfway between the two triazole proton resonance signals (at δ 7.95 and 8.77) in (1b) and may therefore reasonably be assigned to the resonance of the triazole protons in (2b). By integration of the n.m.r. spectrum, it may be estimated that mesitylene-2-sulphonyl chloride reacts with 1,2,4-triazole and triethylamine in dioxan solution to give (1b) and (2b) in the approximate relative proportions of 4 : 1.

DISCUSSION

The crystal-structure determination verified that the reaction product was 1-(mesityl-2-sulphonyl)-3-nitro-1,2,4-triazole with the atomic arrangement shown in Figure 1. Tables 1 and 2 list the interatomic bond lengths and angles.

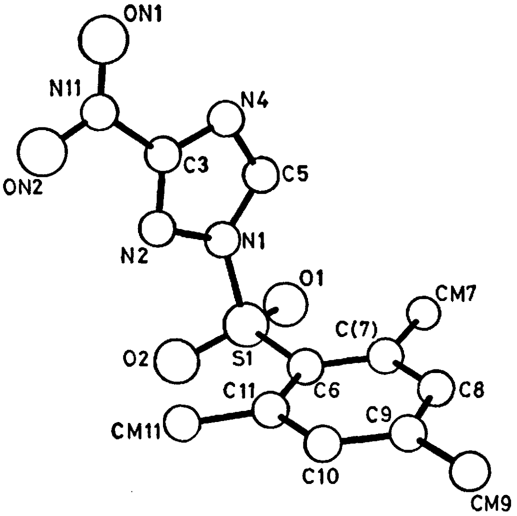


FIGURE 1 The molecular structure showing the atom labelling

The N(1)–N(2) bond length [1.360(2) Å] is similar to that found for 1,2,4-triazole[6] [1.354(3) Å] and is significantly shorter than the N–N single-bond length[7] (1.470 Å). The C–N bond lengths in the triazole ring

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[†] Except that the reaction was carried out in dioxan rather than in dichloromethane solution.

Table 1

Bond lengths for 1-(mesityl-2-sulphonyl)-3-nitro-1,2,4-triazole and benzene (Å). Estimated standard deviations are in parentheses

N(1)–S(1)	1.736(2)
O(1)–S(1)	1.417(2)
O(2)–S(1)	1.419(2)
N(1)–N(2)	1.360(2)
N(2)–C(3)	1.309(2)
C(3)–N(4)	1.341(3)
N(4)–C(5)	1.311(4)
C(5)–N(1)	1.349(3)
N(11)–ON(1)	1.219(3)
N(11)–ON(2)	1.229(3)
S(1)–C(6)	1.758(2)
C(6)–C(7)	1.406(3)
C(8)–C(9)	1.392(3)
C(9)–C(10)	1.393(3)
C(10)–C(11)	1.391(3)
C(11)–C(6)	1.417(3)
C(7)–CM(7)	1.524(3)
C(9)–CM(9)	1.516(3)
C(11)–CM(11)	1.501(3)
CB(1)–CB(2)	1.377(5)
CB(2)–CB(3)	1.396(5)

Table 2

Bond angles for 1-(mesityl-2-sulphonyl)-3-nitro-1,2,4-triazole and benzene (°). Estimated standard deviations are in parentheses

O(1)–S(1)–O(2)	120.5(1)
N(1)–S(1)–O(1)	102.5(1)
N(1)–S(1)–O(2)	104.6(1)
C(6)–S(1)–O(1)	111.8(1)
C(6)–S(1)–O(2)	112.5(1)
N(1)–S(1)–C(6)	102.5(1)
S(1)–N(1)–N(2)	121.7(1)
S(1)–N(1)–C(5)	128.3(2)
N(1)–N(2)–C(3)	100.2(2)
N(2)–C(3)–N(4)	118.1(2)
C(3)–N(4)–C(5)	101.4(2)
N(4)–C(5)–N(1)	110.4(2)
C(5)–N(1)–N(2)	110.0(2)
C(3)–N(11)–ON(1)	117.4(2)
C(3)–N(11)–ON(2)	117.2(2)
ON(1)–N(11)–ON(2)	125.4(2)
S(1)–C(6)–C(7)	119.7(1)
S(1)–C(6)–C(11)	118.7(2)
C(6)–C(7)–C(8)	118.3(2)
C(7)–C(8)–C(9)	122.0(2)
C(8)–C(9)–C(10)	118.4(2)
C(9)–C(10)–C(11)	122.4(2)
C(10)–C(11)–C(6)	117.4(2)
C(11)–C(6)–C(7)	121.6(2)
C(6)–C(11)–CM(11)	125.6(2)
C(10)–C(11)–CM(11)	117.0(2)
C(6)–C(7)–CM(7)	126.4(2)
C(8)–C(7)–CM(7)	115.3(2)
C(8)–C(9)–CM(9)	120.6(2)
C(10)–C(9)–CM(9)	120.9(2)
CB(1)–CB(2)–CB(3)	119.3(3)

range from 1.309(3) to 1.341(3) Å. The C–N pairs symmetrically related to the triazole substituents and the N(1)–N(2) bond are interesting in having comparable C–N bond lengths: C(3)–N(4) 1.341(3) and C(5)–N(1) 1.349(3) Å; C(3)–N(2) 1.309(2) and C(5)–N(4) 1.311(4) Å.

In contrast to the C–N ring bonds the C–N bond distance for the nitro-substituent shows more single-bond character [1.447(3) Å]. The N–O bond lengths 1.229(3) and 1.219(3) Å are at the extreme of the commonly observed N–O bond lengths [8] [1.14—1.21(±4) Å].

The S–C bond length [1.758(2) Å] is longer than in methanesulphonanilide [9] [1.746(2) Å], although comparable with the sulphonyl–mesitylene S–C bond in one of two independent molecules in a crystal of mesityl phenyl sulphone [1.797, 1.754(8) Å].[10] The N–S bond is long compared with the N–S bond in 1-(imidazol-4-ylsulphonyl)-4-phenylimidazole [11] [1.672(4) Å] indicating less delocalisation between the triazole and the SO_2 group, compared with the imidazole compound.[11]

The S–O bond distances of the sulphonyl group [1.419(2) Å] are similar to those found for 1-(imidazol-4-ylsulphonyl)-4-phenylimidazole [11] [1.408(4) Å] and are in the range of commonly observed values.[12] The geometry around the sulphonyl group also parallels that for the imidazole compound,[11] with the exception of the bond angles C(6)–S(1)–O(1) [118.1(1)°] and C(6)–S(1)–O(2) [112.5(1)°] which are larger [108.4(2) and 107.6(2)° for O–S–C in 1-(imidazol-4-ylsulphonyl)-4-phenylimidazole], due to the steric strain that has been previously reported to occur, between the methyl groups on mesitylene and the SO_2 group.

The mesitylene group is planar, having similar bond lengths and angles to those found for mesitylphenyl sulphone.[10] The triazole and mesitylene rings are staggered with respect to each other and the angle between the normals to the triazole and mesitylene planes is 80.4° (shown in Figure 2).

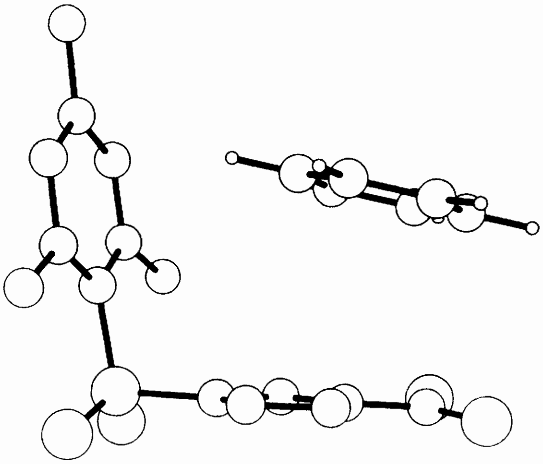

Figure 2 A view showing the stacking of the benzene solvate on the triazole ring

The length of the sulphur–nitrogen bond in this structure [S(1)–N(1) 1.736(2) Å] is close to the upper limit reported for such bonds. In *trans*-4-t-butyl-1-(*N*-ethyl-*N*-*p*-tolylsulphonylamino)-1-thioniacyclohexane fluoroborate,[13] the S–N distances are 1.644 and 1.681 Å, which have been taken to indicate *p*(N)–*d*(S) π-bonding. S–N Distances of 1.616 Å have been reported for *N*-tosyl-2,12-ethano-2-ethyl-8-methoxy-1,4-methylene-1,2,3,4,5,6,12,13-octahydrophenanthridin-3-one,[14] and 1.634, 1.652, and 1.694 Å respectively in three 2,2,-6,6-tetramethyl-4-oxopiperidine derivatives.[15] The S–N bond in 2-(*p*-tolylsulphonyl)-3-(*p*-chlorophenyl)oxaziri-

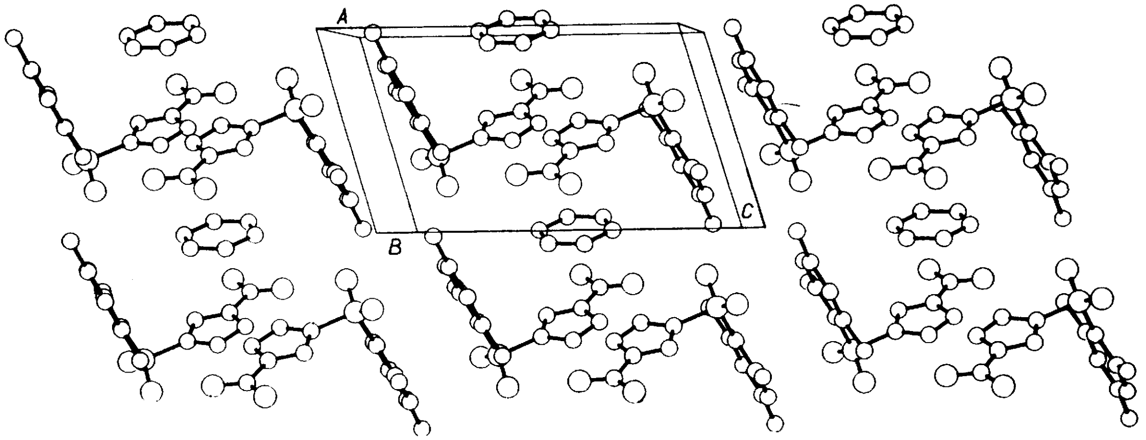

FIGURE 3 A view of the crystal packing

dine,[16] on the other hand, is 1.738 Å. Both this value, and that found in this analysis, are very close to the calculated values[13,15] of 1.73—1.74 Å for sulphur–nitrogen pure single bonds. Thus, it may be concluded that the S(1)–N(1) bond here is a true single one.

In the crystal structure there is partial stacking between the triazole ring and the benzene solvent molecule as shown in Figure 2. The solvent benzene molecule is not stacked parallel to the plane of the triazole ring, but is inclined with respect to it (Figure 2). In contrast to the commonly observed 3.4 Å parallel stack separation the distance from CB(1)′ [the symmetry-related equivalent of CB(1)] to N(4) of the triazole ring is 3.804 Å. A view of the crystal packing is presented in Figure 3.

TABLE 3

Fractional co-ordinates for 1-(mesityl-2-sulphonyl)-3-nitro-1,2,4-triazole and benzene (× 10^4). Estimated standard deviations are in parentheses

Atom name	x	y	z
S(1)	3 842(1)	2 903(1)	1 571(0)
O(1)	2 282(2)	3 433(2)	1 619(2)
O(2)	3 696(2)	1 318(2)	886(1)
N(1)	4 723(2)	2 634(2)	2 902(1)
N(2)	5 742(2)	1 509(2)	3 121(2)
C(3)	6 086(3)	1 741(3)	4 190(2)
N(4)	5 422(3)	2 897(3)	4 687(2)
C(5)	4 559(3)	3 443(3)	3 845(2)
N(11)	7 105(3)	723(3)	4 799(2)
ON(1)	7 236(3)	869(3)	5 773(2)
ON(2)	7 732(3)	−246(3)	4 282(2)
C(6)	5 522(2)	4 594(3)	1 366(2)
C(7)	5 427(3)	6 301(3)	1 735(2)
C(8)	6 817(3)	7 612(3)	1 692(2)
C(9)	8 283(3)	7 279(3)	1 397(2)
C(10)	8 331(3)	5 567(3)	1 124(2)
C(11)	6 980(3)	4 198(3)	1 150(2)
CM(7)	3 941(4)	6 886(4)	2 094(3)
CM(9)	9 800(3)	8 741(3)	1 386(3)
CM(11)	7 231(4)	2 427(3)	879(3)
CB(1)	9 635(4)	5 865(5)	4 201(3)
CB(2)	18(4)	4 479(5)	3 934(3)
CB(3)	671(4)	3 614(5)	4 749(3)

EXPERIMENTAL

Crystals were obtained by crystallization from benzene, and since these readily deteriorated in air a crystal was mounted in a capillary with solvent. Accurate cell dimensions were obtained using a Nonius CAD4 diffractometer by computer-centring 25 reflections followed by least-squares refinement of the setting angles. Intensity data collected by a ω–2θ scan ($1.5 < \theta < 70°$) and 3 127 reflections were collected of which 2 926 were considered observed [$F_o > 3\sigma(F_o)$].

Crystal Data.—$C_{14}H_{15}N_4O_4S$, $M = 335.4$. Triclinic, $a = 8.001(1)$, $b = 8.140(2)$, $c = 12.892(1)$ Å, $\alpha = 98.22(1)$, $\beta = 105.49(1)$, $\gamma = 102.12(1)°$, $U = 773.2$ Å^3, space group $P1$ or $P\bar{1}$ ($P\bar{1}$ confirmed by structure refinement), $Z = 2$, $D_c = 1.44$ g cm^{-3}, $F(000) = 175$, $\mu(\text{Cu-}K_\alpha) = 9.91$ cm^{-1}, $\lambda(\text{Cu-}K_\alpha) = 1.541\ 838$ Å.

The structure was solved by the heavy-atom method and difference-Fourier synthesis, refining by least-squares to final R and R_w values of 0.0736 and 0.0849, with all the non-hydrogen atoms assigned anisotropic temperature factors. The hydrogen atoms were treated isotropically. All hydrogen atoms were refined using positional parameters from the difference maps with the exception of the methyl protons and the benzene protons, which were generated geometrically.

The weighting scheme used was $w = 1.0/(\sigma^2F_o + |g|F_o^2)$ with g set to an initial value of 0.001 and refined to a final value of 0.029 93.

Final non-hydrogen atom co-ordinates are given in Table 3. Hydrogen atom positions, thermal parameters, and structure factor listings are available as Supplementary Publication No. SUP 23250 (15 pp.).*

Structure solution and refinement programs used were from the Enraf-Nonius SDP and SHELX76 packages. Molecular plots were made using the PLUTO program.

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index issue.

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