

The Synthesis and Molecular Structure of 2-Benzimidazolyl- (*N-p*-toluenesulfonyl-*S-p*-toluenesulfonylimino)-sulfenamide

ROGER J. S. BEER,^a ASBJØRN HORDVIK,^b ALAN NAYLOR^a and DAVID WRIGHT^a

^aThe Robert Robinson Laboratories, The University of Liverpool, Liverpool L69 3BX and ^bDepartment of Chemistry, Institute of Mathematical and Physical Sciences, University of Tromsø, Box 953, N-9001 Tromsø, Norway

The title compound, prepared from benzimidazole-2-thione and chloramine T, crystallizes (as the methanol solvate) in the monoclinic space group $P2_1/n$ with $Z=4$ and unit cell dimensions $a=8.8772(13)$ Å, $b=17.0340(27)$ Å, $c=16.5279(12)$ Å, and $\beta=102.70(1)^\circ$. The structure was solved by direct methods (MULTAN) and refined by least squares methods to an R of 0.032. The refinement comprises 4313 observed reflections.

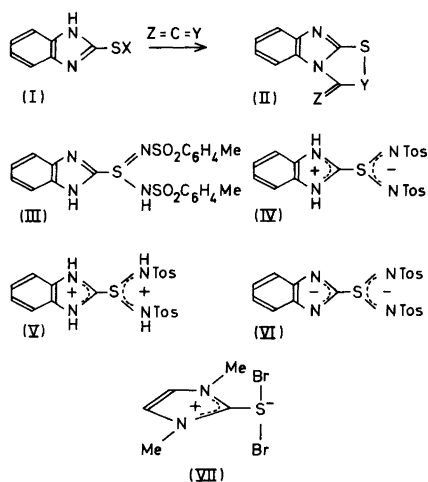
Both N atoms of the benzimidazolyl group are protonated and the molecule may be described as a zwitterion with a tetrahedral central sulfur atom, a positive unit charge delocalized in the N–C–N part of the molecule and a negative unit charge delocalized in the S–N–S–N–S part. The N–C bonds in the former part are 1.323(2) and 1.340(3) Å, respectively, and the N–S bonds in the latter part are, 1.639(2), 1.609(2), 1.609(2), and 1.605(2) Å; the N–S–N angle is $112.2(1)^\circ$ and the S–N–S angles are $117.0(1)$ and $122.0(1)^\circ$, respectively. The connecting bond between the central sulfur atom and the N-protonated benzimidazolyl group is 1.795(2) Å.

There are two hydrogen bonding systems in the crystal structure, one where the solvate methanol molecule is bridging the N-protonated benzimidazolyl group and a sulfonyl group, and one by which the molecules are held together in pairs over centres of symmetry through N–H \cdots N hydrogen bonding. The N–H \cdots O and the O–H \cdots O distances of the former system are 2.748(3) and 2.953(3) Å, respectively, and the N–H \cdots N distance of the latter is 2.779(2) Å.

In studies of reactions of the type I \rightarrow II,¹ the possibility of using sulfenamides (e.g. IX=NH.SO₂.C₆H₄.Me) was considered, and accordingly the reaction of benzimidazole-2-thione with chlor-

amine T was investigated. Addition of chloramine T to a methanolic solution of the thione gave the bisbenzimidazolyl disulfide, but the reverse mode of addition yielded a colourless crystalline product. Analytical data indicated that two toluenesulfonamide residues had been incorporated and, initially, the product was formulated as structure III, subsequently revised to structure IV on the basis of the NMR data, which showed that the tosyl groups were equivalent. This evidence and the signals for the benzimidazole aromatic protons suggested a symmetrical structure. A literature survey revealed that structures similar to III, derived from simpler thiourea derivatives, have been reported, particularly by Russian scientists.^{2,3}

The NMR spectra of compound IV in acid solution (TFA), or in alkali (D₂O, NaOD), show that symmetry is retained in these media, a surprising



result which implies that a dication V and a dianion VI are formed. Since 1,3-dimethylimidazoline-2-thione forms an adduct (VII) with bromine containing a linear Br-S-Br grouping at right angles to the plane of the 5-membered ring,⁴ it seemed important to determine the exact geometry of compound IV, for which there are several intriguing possibilities. The methanol solvate of IV, which formed suitable crystals, was therefore studied in detail by X-ray diffraction.

STRUCTURE ANALYSIS

The methanol solvate of the title compound forms colourless prismatic crystals. A crystal of dimensions $0.3 \times 0.3 \times 0.4$ mm was used for all the X-ray measurements referred to below.

Crystal data.

$C_{21}H_{20}N_4O_4S_3 \cdot CH_3OH$ F.W. = 520.63

Space group $P2_1/n$

$a = 8.8772(13)$ Å, $b = 17.0340(27)$ Å,

$c = 16.5279(12)$ Å, $\beta = 102.70(1)^\circ$

$V = 2439.7$ Å³

$D_c = 1.417$ g/cm³, $D_m(\text{floatation}) = 1.42$ g/cm³

$Z = 4$

$\mu = 3.40$ cm⁻¹ (MoK α)

The X-ray measurements were carried out on a computer-controlled Enfrat-Nonius CAD4 diffractometer using graphite monochromatized MoK α radiation ($\lambda = 0.71069$ Å). The unit cell dimensions were determined from 25 2θ values measured in the range $18 - 26^\circ$ at 20°C . A least squares procedure gave the values quoted above.

Intensity data were collected at 20°C by means of the ω - 2θ scan technique and a scan width ($^\circ$) $\Delta\omega = 0.60 + 0.35 \tan \theta$. The intensities of 5877 independent reflections in the θ -range $1 - 28^\circ$ were measured; 0 10 2 and 3 3 3 were used as standard reflections.

Lp corrections were applied but absorption corrections were considered unnecessary. Reflections for which $I > 2\sigma(I)$ is based on counting statistics, were accepted as observed. By this criterion 1564 reflections were considered unobserved and excluded from subsequent calculations; from now the data set comprises 4313 observed reflections.

The structure was solved by direct methods (MULTAN)⁵ and refined by means of CRYLSQ of X-ray-76⁶ to $R = R_w = 0.032$. The hydrogen positions were found from difference maps. All the calculations were carried out on the UNIVAC 1110 of the University of Bergen.

Final coordinates and anisotropic temperature parameters for the sulfur, oxygen, nitrogen and carbon atoms are listed in Table 1. Coordinates and isotropic temperature parameters for the hydrogen atoms are listed in Table 2. The final structure factor list is available on request.

Scattering factors given by Cromer and Mann were used for sulfur, oxygen, nitrogen and carbon.⁷ For hydrogen, the scattering factor curve given by Stewart *et al.*⁸ was used.

DISCUSSION

The molecular structure of the title compound as it occurs in crystals of the methanol solvate is shown in Fig. 1. Bond lengths and angles are given in Table 3. The standard deviations given in Table 3 are based on the standard deviations in positional parameters from the least squares refinement as given in Table 1. According to Hamilton and Abrahams, a more realistic estimate of the standard deviations would probably be obtained by multiplying those given by a factor of two.⁹

Structure IV which was formulated on the basis of the results from NMR measurements has been confirmed by the results from the present study, *cf.* Fig. 1 and Table 3. The structural environment of S(1) in IV is roughly tetrahedral and thus different from that of sulfur in compound VII where the Br-S-Br sequence is almost linear.⁴ The Br-S bonding in the latter sequence may be described in terms of three-centre four-electron σ -bonds (see *e.g.* Ref. 10) while the N-S(1) bonding in IV may be described as follows: Sigma bonds formed through combination of sp^3 orbitals on S(1) with sp^2 orbitals on the N atoms, and additional π bonding formed through combination of empty d_x orbitals on S(1) with partially filled p_x orbitals on the N atoms (backdonation). These bonding patterns are in accordance with the found bond lengths. Thus, the Br-S bonds in VII (2.50 Å) are longer than the sum of the covalent radii for bromine and sulfur (2.16 Å), and the N-S(1) bonds in IV (1.609(2) Å) are shorter than the sum of the covalent radii for nitrogen and sulfur (1.75 Å).^{11,12} This means that although both the mentioned sulfur atoms are three-coordinated, S in VII is formally two-valent while S(1) in IV is formally four-valent.

The structural environment of S(1) in the present structure resembles that of S in (NSCl)₃ where the S and N atoms, in alternating order, form a chair-

Table 1. Fractional atomic coordinates, and temperature parameters U_{ij} (\AA^2) for sulfur, oxygen, nitrogen and carbon. The expression used is $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$. Standard deviations in parentheses.

Atom	x	y	z	U	Atom	x	y	z	U	Atom	x	y	z	U	
S(1)	.04460(6)	.96547(3)	.63956(3)	.0374(3)	U ₂₂	.0263(3)	.0337(3)	.0026(2)	U ₁₃	.0123(2)	.0010(2)			U ₂₃	.0010(2)
S(2)	.08122(6)	.96547(3)	.80853(3)	.0353(3)	U ₂₃	.0420(3)	.0332(3)	.0025(2)	U ₁₂	.0062(2)	-.0073(2)				-.0073(2)
O(1)	-.23818(6)	.90209(3)	.54895(3)	.0402(3)	U ₃₃	.0346(3)	.0324(3)	.0041(2)		.0053(2)	.0033(2)				.0033(2)
O(3)	.18821(19)	1.02801(10)	.80374(11)	.0427(9)		.0611(11)	.0684(11)	-.0140(8)		.0160(8)	-.0228(9)				-.0228(9)
O(2)	.12911(19)	.90494(10)	.86984(9)	.0555(10)		.0665(11)	.0345(8)	.0231(9)		.0032(7)	.0008(8)				.0008(8)
O(3)	.15597(19)	.83188(9)	.53701(9)	.0355(10)		.0355(10)	.0461(9)	.0052(7)		.0052(7)	-.0045(7)				-.0045(7)
O(4)	-.35107(19)	.93254(10)	.48063(9)	.0548(10)		.0588(10)	.0392(9)	.0071(9)		-.0025(7)	.0081(8)				.0081(8)
O(5)	.12979(25)	.75600(10)	.77848(10)	.1140(17)		.0496(10)	.0492(10)	.0135(11)		.0345(11)	.0150(8)				.0150(8)
N(1)	.18938(19)	.82066(9)	.63641(10)	.0367(9)		.0300(9)	.0306(9)	.0043(7)		.0100(7)	.0036(7)				.0036(7)
N(2)	.19228(20)	.89451(9)	.52806(10)	.0415(10)		.0311(9)	.0338(9)	.0047(8)		.0147(8)	.0056(7)				.0056(7)
N(3)	.02802(20)	.91953(9)	.72215(10)	.0451(10)		.0314(9)	.0292(8)	-.0006(8)		.0114(8)	-.0011(7)				-.0011(7)
N(4)	-.11816(20)	.97565(9)	.57484(10)	.0409(10)		.0297(9)	.0357(9)	.0052(8)		.0108(8)	.0076(7)				.0076(7)
C(1)	.43381(29)	.68858(13)	.54209(15)	.0504(14)		.0425(13)	.0556(14)	.0127(11)		.0103(12)	-.0081(11)				-.0081(11)
C(2)	.43510(29)	.73611(15)	.47256(15)	.0511(15)		.0555(15)	.0550(15)	.0090(12)		.0226(12)	-.0104(12)				-.0104(12)
C(3)	.35828(27)	.80685(14)	.45991(13)	.0470(13)		.0494(13)	.0343(10)	.0007(8)		.0183(10)	-.0023(10)				-.0023(10)
C(4)	.27673(23)	.82799(11)	.51951(12)	.0345(11)		.0304(10)	.0343(10)	.0009(8)		.0102(9)	.0005(8)				.0005(8)
C(5)	.27556(23)	.78071(12)	.58840(12)	.0328(11)		.0319(10)	.0343(10)	.0009(8)		.0090(8)	-.0003(8)				-.0003(8)
C(6)	.35240(26)	.70928(13)	.60069(14)	.0458(13)		.0331(11)	.0440(12)	.0084(10)		.0051(10)	.0007(10)				.0007(10)
C(7)	.14257(22)	.88766(11)	.59866(12)	.0330(10)		.0299(10)	.0313(10)	.0024(8)		.0100(8)	.0022(8)				.0022(8)
C(8)	-.08451(24)	1.00981(12)	.83146(13)	.0378(11)		.0337(11)	.0337(10)	.0008(9)		.0087(9)	-.0073(9)				-.0073(9)
C(9)	-.13145(28)	.98735(14)	.90260(14)	.0508(14)		.0466(13)	.0393(12)	.0020(11)		.0134(11)	.0002(10)				.0002(10)
C(10)	-.25303(29)	1.02667(15)	.92519(15)	.0516(14)		.0592(16)	.0462(13)	.0067(12)		.0220(11)	-.0071(12)				-.0071(12)
C(11)	.33025(27)	1.08711(14)	.87691(15)	.0409(13)		.0448(13)	.0583(14)	.0040(11)		.0166(11)	-.0158(11)				-.0158(11)
C(12)	.28387(28)	1.10764(14)	.80418(15)	.0490(14)		.0485(13)	.0544(14)	.0051(11)		.0118(11)	-.0053(11)				-.0053(11)
C(13)	-.16046(27)	1.06984(13)	.78187(13)	.0494(13)		.0435(13)	.0427(12)	.0044(11)		.0140(10)	-.0003(10)				-.0003(10)
C(14)	.46126(34)	1.13043(19)	.90187(20)	.0608(18)		.0800(21)	.0991(23)	.0079(16)		.0401(17)	.0227(18)				.0227(18)
C(15)	-.32547(24)	.88647(12)	.63380(13)	.0321(11)		.0388(12)	.0387(11)	.0017(9)		.0051(9)	.0006(9)				.0006(9)
C(16)	-.43041(25)	.94110(13)	.65102(14)	.0356(12)		.0446(13)	.0541(14)	.0025(10)		.0068(11)	-.0006(11)				-.0006(11)
C(17)	-.48607(28)	.93168(16)	.72253(16)	.0347(12)		.0638(16)	.0638(16)	.0029(12)		.0146(11)	-.0132(13)				-.0132(13)
C(18)	-.43966(28)	.86902(16)	.77585(16)	.0363(12)		.0704(17)	.0506(14)	-.0029(12)		.0126(11)	-.0049(13)				-.0049(13)
C(19)	-.33900(31)	.81492(17)	.75541(17)	.0498(15)		.0613(17)	.0578(16)	.0003(13)		.0173(13)	.0179(13)				.0179(13)
C(20)	-.28082(30)	.82312(15)	.68501(16)	.0492(15)		.0464(15)	.0546(15)	.0074(12)		.0174(12)	.0125(11)				.0125(11)
C(21)	-.49491(50)	.86086(34)	.85620(24)	.0725(23)		.1105(34)	.0686(22)	-.0228(24)		.0395(19)	-.0057(22)				-.0057(22)
C(22)	.20521(69)	.69147(26)	.82385(26)	.1238(37)		.0652(22)	.0684(23)	.0112(24)		.0128(24)	.0246(18)				.0246(18)

Table 2. Fractional atomic coordinates, and temperature parameters U (\AA^2) for hydrogen. The expression used is $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$. Standard deviations in parentheses.

Atom	x	y	z	U	Atom	x	y	z	U
H(1)	.488(3)	.642(2)	.545(2)	.075(10)	H(101)	.167(4)	.803(2)	.693(2)	.116(13)
H(2)	.495(4)	.723(2)	.438(2)	.082(13)	H(210)	.174(4)	.940(2)	.493(2)	.072(11)
H(3)	.362(3)	.842(2)	.412(2)	.055(8)	H(141)	-.464(7)	1.122(3)	.947(3)	.186(23)
H(6)	.350(4)	.679(2)	.649(2)	.122(10)	H(142)	-.448(6)	1.179(3)	.905(3)	.154(21)
H(9)	-.077(4)	.938(2)	.938(2)	.073(10)	H(143)	-.553(6)	1.101(3)	.881(3)	.147(18)
H(10)	-.271(4)	1.016(2)	.976(2)	.093(13)	H(211)	-.524(6)	.905(3)	.873(3)	.137(20)
H(12)	-.338(5)	1.149(2)	.772(3)	.070(17)	H(212)	-.414(6)	.849(3)	.902(3)	.154(20)
H(13)	-.129(3)	1.089(2)	.732(2)	.063(10)	H(213)	-.558(7)	.819(3)	.856(3)	.181(27)
H(16)	-.458(3)	.985(2)	.610(2)	.062(9)	H(221)	.262(7)	.711(4)	.873(4)	.194(28)
H(17)	-.554(3)	.974(1)	.736(2)	.065(7)	H(222)	.154(8)	.654(4)	.873(4)	.239(35)
H(19)	-.307(4)	.770(2)	.790(2)	.074(11)	H(223)	.287(9)	.684(4)	.802(4)	.203(40)
H(20)	-.218(3)	.787(2)	.569(2)	.074(10)	H(501)	.132(6)	.801(3)	.803(3)	.137(22)

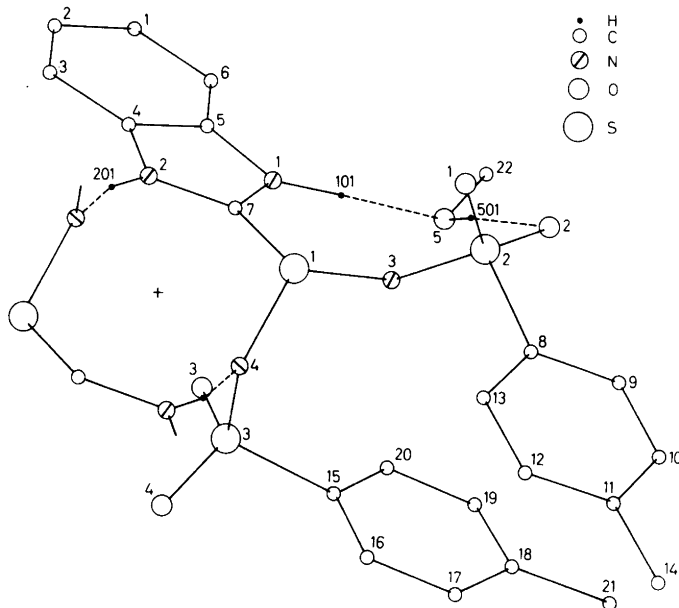


Fig. 1. The molecular structure of the title compound in *b*-axis projection showing hydrogen bonds and numbering of atoms. Methyl and phenyl hydrogens have been left out for clarity.

Table 3. Bond lengths $l(ij)$, $l(jk)$, and bond angles $\angle(ijk)$. Standard deviations in parentheses.

Atoms			Bonds		Angles	Atoms			Bonds		Angles
<i>i</i>	<i>j</i>	<i>k</i>	$l(ij)$ Å	$l(jk)$ Å	$\angle(ijk)^\circ$	<i>i</i>	<i>j</i>	<i>k</i>	$l(ij)$ Å	$l(jk)$ Å	$\angle(ijk)^\circ$
C(7)	S(1)	N(3)	1.795 (2)	1.609 (2)	95.9 (1)	C(5)	C(4)	N(2)			106.7 (2)
C(7)	S(1)	N(4)		1.609 (2)	105.5 (1)	C(4)	C(5)	C(6)	1.388 (3)		122.2 (2)
N(3)	S(1)	N(4)			112.2 (1)	C(4)	C(5)	N(1)			106.6 (2)
C(8)	S(2)	N(3)	1.768 (2)	1.605 (2)	107.6 (1)	C(6)	C(5)	N(1)			131.1 (2)
C(8)	S(2)	O(1)		1.441 (2)	106.6 (1)	C(1)	C(6)	C(5)			116.0 (2)
C(8)	S(2)	O(2)		1.443 (2)	106.6 (1)	N(1)	C(7)	N(2)			110.9 (2)
N(3)	S(2)	O(1)			112.3 (1)	N(1)	C(7)	S(1)			125.9 (2)
N(3)	S(2)	O(2)			105.1 (1)	N(2)	C(7)	S(1)			122.8 (2)
O(1)	S(2)	O(2)			118.1 (1)	C(9)	C(8)	C(13)	1.385 (3)	1.389 (3)	120.5 (2)
C(15)	S(3)	N(4)	1.765 (2)	1.639 (2)	106.3 (1)	C(9)	C(8)	S(2)			118.9 (2)
C(15)	S(3)	O(3)		1.437 (2)	108.0 (1)	C(13)	C(8)	S(2)			120.5 (2)
C(15)	S(3)	O(4)		1.432 (2)	109.1 (1)	C(8)	C(9)	C(10)	1.389 (4)		119.4 (2)
N(4)	S(3)	O(3)			110.6 (1)	C(9)	C(10)	C(11)	1.388 (3)		121.2 (2)
N(4)	S(3)	O(4)			103.4 (1)	C(10)	C(11)	C(12)	1.398 (4)		118.6 (2)
O(3)	S(3)	O(4)			118.8 (1)	C(10)	C(11)	C(14)	1.509 (4)		121.2 (2)
H(101)	N(1)	C(5)	1.04 (4)	1.395 (3)	127 (2)	C(12)	C(11)	C(14)			120.2 (2)
H(101)	N(1)	C(7)		1.323 (2)	125 (2)	C(11)	C(12)	C(13)	1.389 (4)		120.7 (2)
C(5)	N(1)	C(7)			107.9 (2)	C(12)	C(13)	C(8)			119.6 (2)
H(201)	N(2)	C(4)	.96 (3)	1.383 (3)	129 (2)	C(16)	C(15)	C(20)	1.390 (3)	1.375 (3)	121.0 (2)
H(201)	N(2)	C(7)		1.340 (3)	123 (2)	C(16)	C(15)	S(3)			119.5 (2)
C(4)	N(2)	C(7)			107.9 (2)	C(20)	C(15)	S(3)			119.3 (2)
S(1)	N(3)	S(2)			117.0 (1)	C(15)	C(16)	C(17)	1.387 (4)		118.5 (2)
S(1)	N(4)	S(3)			122.0 (1)	C(16)	C(17)	C(18)	1.388 (4)		121.2 (2)
H(501)	O(5)	C(22)	.86 (5)	1.414 (5)	119 (3)	C(17)	C(18)	C(19)	1.376 (4)		118.5 (3)
C(2)	C(1)	C(6)	1.408 (4)	1.376 (4)	121.8 (2)	C(17)	C(18)	C(21)	1.520 (5)		121.2 (3)
C(1)	C(2)	C(3)		1.378 (3)	122.3 (2)	C(19)	C(18)	C(21)			120.3 (3)
C(2)	C(3)	C(4)		1.392 (3)	115.8 (2)	C(18)	C(19)	C(20)	1.380 (4)		121.5 (3)
C(3)	C(4)	C(5)		1.397 (3)	121.7 (2)	C(15)	C(20)	C(19)			119.2 (2)
C(3)	C(4)	N(2)			131.5 (2)						

formed six-membered ring with three Cl atoms bonded to S in axial positions.¹³ The N–S bonds in the (NSCl)₃ molecule are found to be equal within the experimental error with an average length of 1.605(7) Å; the average value for the N–S–N angle is 113.4(5)°. Corresponding values for IV are N–S(1)=1.609(2) Å and N–S(1)–N=112.2(1)°, respectively. Furthermore, from Table 3. the N(3)–S(2) and the N(4)–S(3) bonds are 1.605(3) and 1.639(2) Å, respectively, with the angles S(3)–N(4)–S(1)=122.0(1)° and S(2)–N(3)–S(1)=117.0(1)°; the average value of the S–N–S angles in (NSCl)₃ is 123.9(4)°. Thus, from the dimensions of the S–N–S–N–S sequence in IV one may conclude that the formal negative charge of one electron is delocalized in this part of the molecule. The S(1)–C(7) bond of 1.795(2) Å has very little, if any, π -bond character.

There is a difference of 5.0° between the two S–N–S angles of the present structure, and the difference between the N(3)–S(1)–C(7) angle and the N(4)–S(1)–C(7) angle is 9.6°. It seems likely that both these differences are caused by hydrogen bonding in the crystal, cf. Fig. 1. There is one hydrogen bonding system in which the methanol molecule participates, and there is one system whereby the molecules are held together in pairs over centers of symmetry through N–H \cdots N hydrogen bonding. The atomic distances which correspond to hydrogen bonding are N(1) \cdots O(5)=2.748(3) Å, O(5) \cdots O(2)=2.953(3) Å, and N(2) \cdots N(4)=2.779(2) Å with the hydrogen atoms located close to the respective connecting lines.

The rings of the benzimidazolinylium substituent are not quite coplanar. The equations for the least squares plane of rings A(C(1),...,C(6)) and B(N(1),...,C(7)) are

$$6.34699x + 8.00910y + 5.74492z = 11.37595$$

and

$$6.56905x + 7.65158y + 5.38323z = 10.95042$$

respectively, and the angle between the two planes is 2.1(1)°.

The maximum deviation of ring A atoms from plane A is 0.008 Å, and the maximum deviation of ring B atoms from plane B is 0.001 Å. Corresponding standard deviations of the atoms (those defining the plane) from the planes are 0.006 and 0.001 Å, respectively. S(1) lies 0.175 Å out of the plane of ring B, and the distances from N(3), S(2), O(2),

H(501), and O(5) to this plane are, 0.157, 1.323, 1.504, 0.368, and –0.123 Å, respectively.

With one expected exception the bond lengths in the benzimidazolinylium part of the present molecule agree with those found for benzimidazol. Since N(1) and N(2) in IV both are protonated, one might expect the N(1)–C(7) and N(2)–C(7) bonds to be of equal length. A difference of 0.017 Å between these N–C bond lengths has been observed, but the difference is hardly significant. Values of 0.035 and 0.046 Å have on the other hand been reported for the corresponding bond length difference in benzimidazol where only one of the N atoms is protonated.^{14,15}

The dimensions of the *p*-toluenesulfonyl groups in IV agree closely with reported dimensions for this group.^{16,17}

Apart from the hydrogen bonding schemes mentioned above there are no close contacts in the crystal structure shorter than corresponding van der Waals distance.

EXPERIMENTAL

2-Benzimidazolyl-(N-p-toluenesulfonyl-S-p-toluenesulfonylimino)sulfenamide. Benzimidazoline-2-thione (3g), dissolved in methanol (100 ml), was added at room temperature over 45 min to a stirred solution of chloramine T (12 g) in methanol (100 ml), and stirring was then continued for a further 90 min. The product which separated was recrystallized from methanol and gave colourless needles (3.4 g), m.p. 144–5°; δ (DMSO-*d*₆) 2.30 (6H,s), 3.17 (3H,s; MeOH), 7.10–7.13 (4H,d) and 7.50–7.53 (4H,d), 7.40–7.47 (2H, m) and 7.69–7.75 (2H, m), 6.6–7.0 (2H, broad NH band removed by D₂O shake); δ (D₂O, OH[–]) 2.20 (6H, s), 3.44 (3H, s), 7.04–7.08 (4H, d) and 7.58–7.61 (4H, d), 7.25–7.30 (2H, m) and 7.76–7.81 (2H, m); δ (TFA) 2.45 (6H, s), 3.66 and 4.07 (3H, MeOH and MeOH₂⁺), 7.20–7.25 (4H, d) and 7.60–7.65 (4H, d), 7.77–7.81 (2H, m) and 7.94–7.98 (2H, m) (Found: C, 50.7; H, 4.4; N, 10.5; S, 18.7. C₂₁H₂₀N₄O₄S₃·MeOH requires C, 50.8; H, 4.6; N, 10.8; S, 18.5%).

REFERENCES

- Beer, R. J. S., Holmes, N. H. and Naylor, A. *J. Chem. Soc. Perkin Trans. 1* (1979) 2909.
- a. Kremlev, M. M. and Naumenko, R. P. *Khim. Technol.* 23 (1971) 31; *Chem. Abstr.* 77 (1972) 34419 y; b. *Ibid.* 20 (1971) 156; *Chem. Abstr.* 76 (1972) 126550 s; c. *Ibid.* 21 (1971) 154; *Chem. Abstr.* 77 (1972) 164183 c.

3. Kremlev, M. M. and Naumenko, R. P. *Vopr. Khim. Khim. Tekhnol.* 35 (1974) 118; *Chem. Abstr.* 82 (1975) 155686 v.
4. Arduengo, A. J. and Burgess, A. M. *J. Am. Chem. Soc.* 99 (1977) 2378.
5. Main, P., Wolfson, M. M. and Germain, G. *MULTAN: A Computer Program for the Automatic Solution of Crystal Structures*, Department of Physics, University of York, York 1976.
6. *The X-Ray System, Version of 1976*, Technical Report TR-446, Computer Science Center, University of Maryland, College Park 1976.
7. Cromer, D. and Mann, J. *Acta Crystallogr. A* 24 (1968) 321.
8. Stewart, R. F., Davidson, E. R. and Simpson, W. T., *J. Chem. Phys.* 42 (1965) 3175.
9. Hamilton, W. C. and Abrahams, S. C. *Acta Crystallogr. A* 26 (1970) 18.
10. Hansen, L. K., Hordvik, A. and Sæthre, L. J. In *Organic Sulphur Chemistry*, Stirling, C. J. M., Ed., Butterworths, London 1975.
11. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, New York 1960.
12. Hordvik, A. *Acta Chem. Scand.* 20 (1966) 1885.
13. Wieggers, G. A. and Vos, A. *Acta Crystallogr.* 20 (1966) 192.
14. Dik-Edixhoven, C. J., Schenk, H. and van der Meer, H. *Cryst. Struct. Commun.* 2 (1973) 23.
15. Escande, A. and Galigné, J. L. *Acta Crystallogr. B* 30 (1974) 1647.
16. Tickle, I. J. and Prout, C. K. *J. Chem. Soc. C* (1971) 3401.
17. Cameron, T. S., Prout, K., Denton, B., Spagna, R. and White, E. *J. Chem. Soc. Perkin Trans. 2* (1975) 176.

Received June 26, 1980.