

## Structure of Bis(4-biphenyl)sulphur Diimide

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**Abstract.** C<sub>24</sub>H<sub>18</sub>N<sub>2</sub>S, monoclinic, *Cc*, *a* = 6.116 (3), *b* = 10.630 (6), *c* = 28.723 (18) Å,  $\beta$  = 91.30 (3)°, *V* = 1867 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.304, *D<sub>m</sub>* = 1.29 Mg m<sup>-3</sup> (by flotation),  $\mu(\text{Mo } K\alpha)$  = 0.197 mm<sup>-1</sup>, *M<sub>r</sub>* = 366.5. The structure has been solved by direct methods; the final *R* is 0.063 for 1108 independent reflections. Results are compared with those for the bis(*p*-tolyl) derivative.

**Introduction.** Following the structure determination of the bis(*p*-tolyl) derivative of N<sub>2</sub>S (Leandri, Busetti, Valle & Mammi, 1970) we have now determined the crystal structure of the bis(4-biphenyl) derivative, to correlate values of the bond lengths and bond angles.

Red crystals were grown by slow evaporation of ligroin solutions and that used for data collection had approximate dimensions 0.7 × 0.3 × 0.1 mm.

Cell parameters were refined by a least-squares program on 32 high-order reflection angles. Data were collected on a Philips PW 1100 four-circle single-crystal diffractometer, in the  $\theta$ -2 $\theta$  scan mode, with Mo *K* $\alpha$  radiation monochromatized by graphite; 1700 independent reflections, 1108 with *I* > 2 $\sigma$ (*I*), were collected up to 2 $\theta$  = 50°. Usual Lorentz and polarization factors were applied; absorption corrections were not necessary.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974) for non-hydrogen atoms and from Stewart, Davidson & Simpson (1965) for H atoms.

The structure was solved by direct methods with the *MULTAN* program (Germain, Main & Woolfson, 1971) and refined by full-matrix least squares, with a unitary weighting scheme, to a final residual index of 0.063.

Calculations were performed on a Cyber 76 computer, using the XRAY system of crystallographic programs (Stewart, Kundell & Baldwin, 1970).

Coordinates of H atoms, from a difference Fourier map, were refined by one cycle of full-matrix least squares with unit weights.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36344 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ( $\times 10^4$ , for H  $\times 10^3$ ) and isotropic thermal parameters (least-squares e.s.d.'s are in parentheses)

H-atom designations and *B* values are those of the attached C atom. H(8), H(17) and H(23) are in calculated positions.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
S(1)	0	3349 (8)	0	5.9 (3)
N(1)	1770 (25)	2813 (16)	319 (6)	5.5 (3)
N(2)	-2123 (25)	2529 (15)	-86 (6)	5.2 (4)
C(1)	1867 (29)	1706 (19)	588 (7)	5.2 (5)
C(2)	3873 (37)	1439 (18)	823 (8)	5.2 (5)
C(3)	4114 (33)	447 (18)	1123 (7)	5.2 (5)
C(4)	2380 (31)	-361 (17)	1215 (6)	5.2 (5)
C(5)	380 (37)	-155 (20)	965 (7)	5.4 (6)
C(6)	154 (34)	827 (18)	648 (8)	4.9 (5)
C(7)	2576 (31)	-1394 (18)	1569 (7)	5.3 (5)
C(8)	850 (34)	-1689 (20)	1840 (7)	5.5 (5)
C(9)	1016 (47)	-2660 (26)	2159 (9)	8.3 (8)
C(10)	2963 (40)	-3301 (24)	2231 (9)	7.3 (7)
C(11)	4693 (39)	-3028 (23)	1935 (9)	6.7 (7)
C(12)	4509 (33)	-2073 (18)	1627 (8)	5.2 (5)
C(13)	-3715 (28)	3025 (16)	-394 (7)	4.5 (5)
C(14)	-5015 (33)	2161 (21)	-650 (7)	5.0 (5)
C(15)	-6556 (32)	2541 (19)	-956 (8)	5.1 (5)
C(16)	-6959 (28)	3847 (17)	-1063 (7)	4.6 (5)
C(17)	-5686 (35)	4701 (22)	-772 (8)	5.2 (6)
C(18)	-4140 (33)	4311 (20)	-471 (8)	5.5 (6)
C(19)	-8594 (36)	4268 (18)	-1402 (8)	5.2 (5)
C(20)	-10629 (38)	3665 (23)	-1469 (8)	6.3 (7)
C(21)	-12161 (45)	4068 (23)	-1768 (9)	7.5 (7)
C(22)	-11765 (48)	5077 (27)	-2056 (9)	7.7 (8)
C(23)	-9797 (39)	5688 (24)	-2025 (9)	6.8 (7)
C(24)	-8184 (39)	5306 (23)	-1685 (8)	6.7 (7)
H(2)	517 (28)	216 (14)	66 (6)	
H(3)	563 (27)	32 (14)	137 (5)	
H(5)	-87 (25)	-73 (15)	105 (5)	
H(6)	-126 (25)	103 (14)	42 (6)	
H(8)	-54	-120	181	
H(9)	-35 (35)	-268 (18)	239 (7)	
H(10)	308 (31)	-418 (18)	244 (8)	
H(11)	616 (30)	-333 (18)	199 (6)	
H(12)	595 (25)	-199 (15)	150 (6)	
H(14)	-464 (25)	124 (16)	-73 (5)	
H(15)	-743 (26)	180 (16)	-124 (5)	
H(17)	-598	562	-80	
H(18)	-357 (24)	482 (16)	-33 (5)	
H(20)	-1058 (27)	308 (17)	-128 (6)	
H(21)	-1368 (29)	360 (19)	-187 (7)	
H(22)	-1311 (33)	534 (20)	-232 (7)	
H(23)	-949	640	-224	
H(24)	-694 (31)	564 (16)	-163 (6)	

**Discussion.** Atomic coordinates are given in Table 1, and bond lengths and angles in Fig. 1.

The two N—S bond lengths, which are slightly different [1.53 (1) and 1.56 (1) Å in the bis(*p*-tolyl) derivative], are closer to the double-bond value (1.540 Å) than to the single-bond value (1.764 Å) (Kálmán, Duffin & Kucsman, 1971, and references therein).

The large increase of the valence angle at N(1), with respect to the angle at N(2), agrees with the previously determined value in the bis(*p*-tolyl) derivative [130.8 (6)°], and it is not possible to explain it on the basis of steric hindrance since the same short contacts are present between H and C atoms to N(1) and N(2), see Table 2.

Phenyl-ring planes *A* [through atoms C(1) to C(6)], *B* [C(7) to C(12)], *C* [C(13) to C(18)] and *D* [C(19) to C(24)] are twisted by about the same amount:  $A \wedge B$  is 37.1 and  $C \wedge D$  39.8°.

The central part of the molecule is roughly planar; deviations from the N<sub>2</sub>S plane of C(1) and C(13) atoms are 0.05 and 0.03 Å respectively. The same plane is tilted to the *A* plane by 11.1° and to the *C* plane by 29.5°. The line through C(1), C(4), C(7) and C(10) emerges from it at 9.2° and the line through C(13), C(16), C(19) and C(22) emerges on the opposite side at 5.3°. All these atoms, except C(22), show a contraction in the valence angle.

The values of the torsion angles C(13)—N(2)—S(1)—N(1) and C(1)—N(1)—S(1)—N(2), which give the conformation around the S—N bonds, are -178 (1) and -4(2)° respectively. Some intramolecular distances are collected in Table 2. There are

Table 2. *Intramolecular distances* (Å)

S(1)—C(1)	2.67 (2)	C(4)—C(12)	2.52 (3)
S(1)—C(6)	3.26 (2)	C(5)—C(7)	2.54 (3)
S(1)—C(13)	2.539 (18)	C(7)—H(3)	2.67 (16)
S(1)—C(18)	3.02 (2)	C(7)—H(5)	2.65 (16)
S(1)—H(6)	2.85 (15)	C(8)—H(5)	2.68 (16)
S(1)—H(18)	2.83 (15)	C(12)—H(3)	2.73 (15)
N(1)—N(2)	2.64 (2)	C(15)—C(19)	2.55 (3)
N(1)—C(6)	2.52 (3)	C(15)—H(20)	2.67 (17)
N(1)—H(6)	2.67 (15)	C(16)—C(20)	2.51 (3)
N(2)—C(6)	3.09 (3)	C(16)—H(24)	2.51 (17)
N(2)—C(18)	2.50 (3)	C(17)—C(19)	2.55 (3)
N(2)—H(18)	2.67 (17)	C(17)—H(24)	2.76 (18)
C(3)—C(7)	2.53 (3)	C(19)—H(15)	2.75 (17)

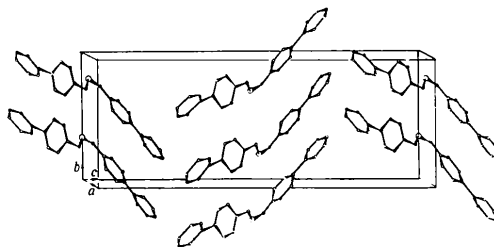


Fig. 2. Crystal-packing diagram.

no intermolecular contact distances shorter than the sum of the van der Waals radii. The crystal packing is shown in Fig. 2.

I wish to thank Professor G. Leandri of Genova University, who suggested the problem and supplied the crystals.

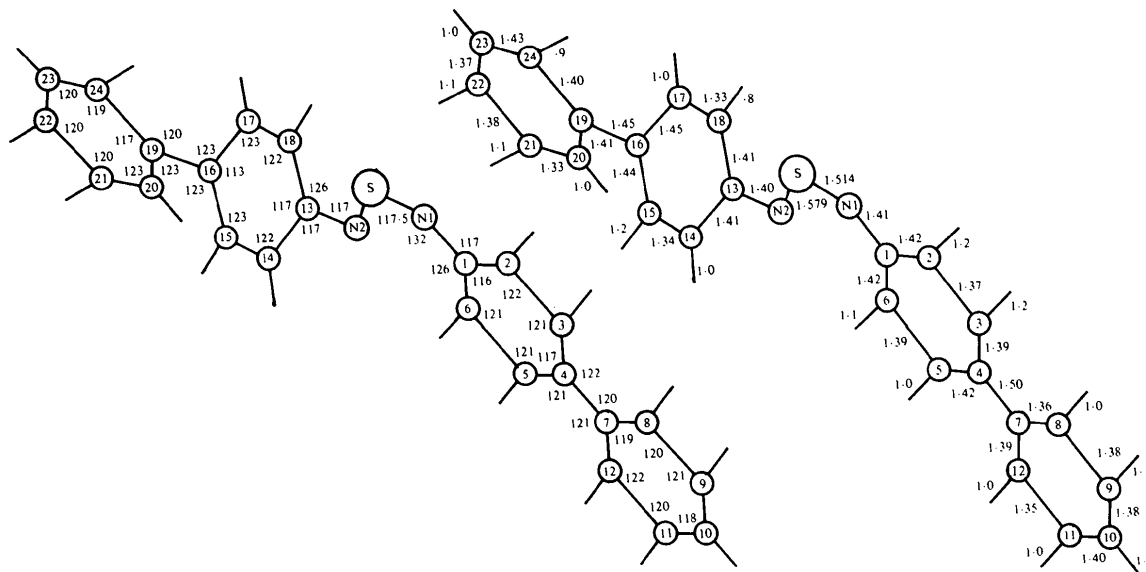


Fig. 1. Bond distances (Å), bond angles (°) and numbering of the atoms. Mean e.s.d.'s are 0.016 Å and 0.9° when the S atom is involved, 0.024–0.038 Å and 1.3–2.6° for other non-hydrogen atoms, and 0.16–0.21 Å and 7–12° for H atoms.

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## Structure of Bis(4-methylpyridine)hydrogen(I) Tetraphenylborate

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**Abstract.**  $C_{12}H_{15}N_2^+ \cdot C_{24}H_{20}B^-$ , monoclinic,  $C2/c$ ,  $a = 16.095$  (7),  $b = 10.492$  (9),  $c = 16.764$  (10) Å,  $\beta = 108.91$  (2)°,  $U = 2678.3$  Å<sup>3</sup>,  $M_r = 506.50$ ,  $D_c = 1.25$  Mg m<sup>-3</sup> for  $Z = 4$ , Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 0.037$  mm<sup>-1</sup>; final  $R$  is 0.0785 for 1004 reflections. The cation  $(\text{CH}_3\text{C}_5\text{H}_4\text{N})_2\text{H}^+$  lies across a centre of inversion with a linear, apparently centrosymmetric, N—H—N unit having N—H 1.305 (7), N...N 2.610 (15) Å.

**Introduction.** The compound was prepared by reaction of NaBPh<sub>4</sub> with a solution of CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>NH<sup>+</sup>.Cl<sup>-</sup> in CH<sub>3</sub>CN/CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N (Glidewell & Shepherd, 1975): crystals suitable for X-ray analysis were obtained directly from the preparation.

The structure was solved by direct methods using *SHELX 76* (Sheldrick, 1976) to reveal the cation lying across a centre of inversion, and the anion lying on a twofold axis, with the B atoms occupying the sites 4(e) of symmetry 2. Blocked-full-matrix least-squares refinement with complex neutral-atom scattering factors (Cromer & Mann, 1968; Cromer & Liberman, 1970) and C, B, N anisotropic gave  $R = 0.1191$  and  $R_G = 0.1189$  for 1004 unique reflections having  $F_o > 6\sigma(F_o)$ . At this stage a difference map revealed the aromatic H atoms, and the unique H atom of the cation occupying the sites 4(d) of symmetry  $\bar{1}$ . Isotropic refinement of these H-atom positions, with separate temperature parameters for the unique H, the pyridine H atoms, and the phenyl H atoms, together with inclusion of the methyl H atoms in calculated positions with  $d(\text{C—H}) = 1.08$  Å and a fourth isotropic temperature parameter,

gave a final  $R$  of 0.0785, and  $R_G$  of 0.0755.† A final difference map showed no electron density  $> 0.2$  e Å<sup>-3</sup>.

In the final cycles of refinement, 223 parameters were varied, comprising 100 positional coordinates, 118 anisotropic temperature parameters, 4 isotropic temperature parameters, and the overall scale factor. Final atomic coordinates are in Table 1 and the important geometrical parameters in Table 2. Fig. 1

† Lists of structure factors and anisotropic thermal parameters and a complete list of bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36402 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

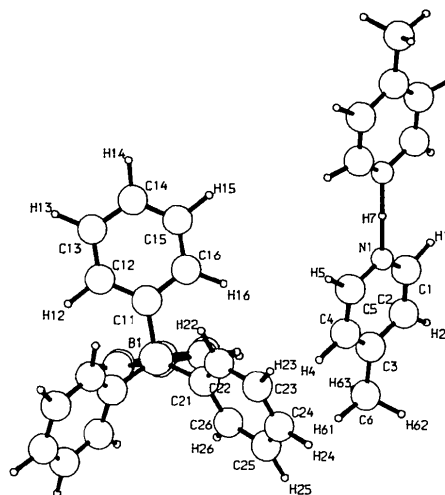


Fig. 1. The cation and the anion (two asymmetric units) showing the numbering of the atoms.

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