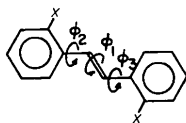
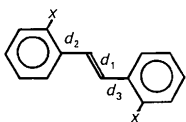


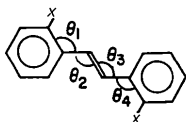
Table 3. Comparison of structural parameters for 1,2-bis(2-substituted-phenyl)ethenes



X	$\phi_1(^{\circ})$	$\phi_2(^{\circ})$	$\phi_3(^{\circ})$	Reference
Me	180	10.7 (3)	-10.7 (3)	This work
OMe	179.6 (5)	14.8 (5)	-2.3 (5)	Jungk <i>et al.</i> (1984)
OH	180	17.6 (4)	-17.6 (4)	Tirado-Rives <i>et al.</i> (1984)
H	180	5.0 (4)	-5.0 (4)	Bernstein (1975)



X	$d_1(\text{\AA})$	$d_2(\text{\AA})$	$d_3(\text{\AA})$
Me	1.284 (4)	1.469 (2)	1.469 (2)
OMe	1.320 (4)	1.461 (4)	1.454 (4)
OH	1.328 (4)	1.476 (4)	1.476 (4)
H	1.318 (3)	1.469 (4)	1.469 (4)



X	$\theta_1(^{\circ})$	$\theta_2(^{\circ})$	$\theta_3(^{\circ})$	$\theta_4(^{\circ})$
Me	120.6 (2)	128.7 (3)	128.7 (3)	120.6 (2)
OMe	120.1 (3)	128.1 (3)	127.0 (3)	120.7 (3)
OH	120.2 (3)	125.2 (3)	125.2 (3)	120.2 (3)
H	118.9 (2)	126.7 (2)	126.7 (2)	118.9 (2)

Bond distances within the aromatic ring exhibit a systematic shortening of bonds involving C(4) and C(5), which have the largest thermal parameters. This apparent shortening is probably due to librational motion, for which corrections have not been made.

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Structure of 3,5-Bis(diphenylamino)-1,2,4-thiadiazole, C₂₆H₂₀N₄S

BY HITOSHI SENDA AND JURO MARUHA

The College of Liberal Arts, Kanazawa University, Kanazawa 920, Japan

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Abstract. $M_r = 420.5$, triclinic, $P\bar{1}$, $a = 9.741$ (3), $b = 13.232$ (3), $c = 9.631$ (2) Å, $\alpha = 110.27$ (1), $\beta = 109.36$ (2), $\gamma = 71.96$ (2)°, $V = 1071.7$ Å³, $Z = 2$, $D_m = 1.30$, $D_x = 1.300$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.167$ mm⁻¹, $F(000) = 440$, $T = 298$ K, final $R = 0.075$ for 4043 observed unique reflections. One of the four phenyl groups is weakly conjugated to the central heterocyclic ring through the exocyclic N atom. The heterocyclic ring is planar with the exocyclic N atoms deviating from this plane by -0.030 and 0.033 Å. The molecules are held together mainly by van der Waals interactions.

Introduction. During the systematic studies of oxidation of substituted thioureas by the iron(III) ion, we found that 1,1-diphenylthiourea changes to a 1,2,4-thiadiazole compound. The structure of the compound has been determined to reveal the reaction mechanism. The oxidation of 1-phenylthiourea yields a heterocyclic base (Hector, 1889) and the structure has been determined from X-ray diffraction study to be a 1,2,4-thiadiazoline derivative (Butler, Glidewell & Liles, 1978). On the other hand, oxidation of 1-alkyl-3-arylthiourea gives rise to 1,2,4-thiadiazolidine compounds, and several crystallographic investigations have been published

(Christophersen, Øttersen, Seff & Treppendahl, 1975; Kinoshita, Sato & Tamura, 1976; Sato, Kinoshita, Hata & Tamura, 1977, 1980).

Table 1. *Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for non-H atoms*

	x	y	z	$B_{eq}^*(\text{Å}^2)$
S	1770.6 (5)	-269.0 (3)	-624.4 (4)	5.03
N(1)	1612 (1)	-1563 (1)	-1131 (1)	4.53
N(2)	2423 (1)	-1134.6 (9)	1539 (1)	4.19
N(3)	2064 (1)	-2907.4 (9)	230 (1)	4.62
N(4)	2654 (1)	715.8 (9)	2434 (1)	4.55
C(1)	2013 (2)	-1871 (1)	165 (1)	3.89
C(2)	2346 (2)	-206 (1)	1298 (1)	3.87
C(3)	1891 (2)	-3854 (1)	-1036 (2)	4.37
C(4)	1980 (2)	-3916 (1)	-2475 (2)	5.77
C(5)	1818 (2)	-4861 (2)	-3648 (2)	6.92
C(6)	1578 (2)	-5762 (2)	-3429 (2)	7.09
C(7)	1487 (2)	-5699 (1)	-2014 (2)	6.94
C(8)	1621 (2)	-4759 (1)	-829 (2)	5.55
C(9)	2452 (2)	-3053 (1)	1748 (2)	4.80
C(10)	3869 (2)	-3586 (1)	2344 (2)	5.99
C(11)	4245 (2)	-3701 (2)	3805 (2)	7.73
C(12)	3231 (3)	-3289 (2)	4650 (2)	8.43
C(13)	1826 (3)	-2768 (2)	4063 (2)	8.81
C(14)	1408 (2)	-2647 (2)	2588 (2)	6.42
C(15)	2744 (2)	834 (1)	3998 (2)	4.13
C(16)	1769 (2)	451 (2)	4344 (2)	6.53
C(17)	1859 (2)	586 (2)	5861 (2)	7.31
C(18)	2891 (2)	1092 (1)	7013 (2)	5.61
C(19)	3852 (2)	1469 (1)	6658 (2)	5.30
C(20)	3788 (2)	1331 (1)	5149 (2)	4.89
C(21)	2947 (2)	1582 (1)	2065 (2)	4.13
C(22)	2019 (2)	2602 (1)	2266 (2)	5.82
C(23)	2339 (2)	3445 (1)	1984 (2)	7.10
C(24)	3582 (2)	3252 (1)	1482 (2)	6.55
C(25)	4514 (2)	2239 (1)	1282 (2)	5.80
C(26)	4195 (2)	1395 (1)	1574 (2)	4.93

$$* B_{eq} = \frac{1}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab\cos\gamma + B_{13}acc\cos\beta + B_{23}bcc\cos\alpha).$$

Table 2. *Bond distances (Å) and angles (°) for non-H atoms*

S-N(1)	1.651 (1)	S-C(2)	1.727 (1)
N(1)-C(1)	1.344 (2)	C(1)-N(2)	1.363 (1)
N(2)-C(2)	1.303 (2)	C(1)-N(3)	1.379 (2)
C(2)-N(4)	1.364 (2)	N(3)-C(3)	1.421 (2)
N(3)-C(9)	1.449 (2)	N(4)-C(15)	1.434 (2)
N(4)-C(21)	1.441 (2)	C(3)-C(4)	1.390 (3)
C(3)-C(8)	1.392 (3)	C(4)-C(5)	1.375 (2)
C(5)-C(6)	1.378 (3)	C(6)-C(7)	1.367 (3)
C(7)-C(8)	1.373 (2)	C(9)-C(10)	1.373 (2)
C(9)-C(14)	1.372 (3)	C(10)-C(11)	1.382 (3)
C(11)-C(12)	1.352 (4)	C(12)-C(13)	1.357 (3)
C(13)-C(14)	1.393 (3)	C(15)-C(16)	1.377 (3)
C(15)-C(20)	1.363 (2)	C(16)-C(17)	1.384 (3)
C(17)-C(18)	1.361 (2)	C(18)-C(19)	1.365 (3)
C(19)-C(20)	1.382 (2)	C(21)-C(22)	1.362 (2)
C(21)-C(26)	1.370 (3)	C(22)-C(23)	1.378 (3)
C(23)-C(24)	1.369 (3)	C(24)-C(25)	1.357 (2)
C(25)-C(26)	1.383 (3)		
N(1)-S-C(2)	92.73 (7)	S-N(1)-C(1)	106.74 (9)
N(1)-C(1)-N(2)	119.7 (1)	C(1)-N(2)-C(2)	108.6 (1)
N(2)-C(2)-S	112.22 (9)	N(1)-C(1)-N(3)	124.8 (1)
N(2)-C(1)-N(3)	115.5 (1)	S-C(2)-N(4)	123.9 (1)
N(2)-C(2)-N(4)	123.9 (1)	C(1)-N(3)-C(3)	126.2 (1)
C(1)-N(3)-C(9)	116.0 (1)	C(3)-N(3)-C(9)	117.6 (1)
C(2)-N(4)-C(15)	122.0 (1)	C(2)-N(4)-C(21)	119.2 (1)
C(15)-N(4)-C(21)	118.9 (1)	N(3)-C(3)-C(4)	122.8 (2)
N(3)-C(3)-C(8)	118.7 (2)	N(3)-C(9)-C(10)	119.7 (2)
N(3)-C(9)-C(14)	119.9 (1)	N(4)-C(15)-C(16)	120.1 (2)
N(4)-C(15)-C(20)	120.3 (2)	N(4)-C(21)-C(22)	120.1 (2)
N(4)-C(21)-C(26)	120.0 (1)	C(4)-C(3)-C(8)	118.5 (2)
C(3)-C(4)-C(5)	119.8 (2)	C(4)-C(5)-C(6)	121.4 (2)
C(5)-C(6)-C(7)	118.6 (2)	C(6)-C(7)-C(8)	121.2 (2)
C(7)-C(8)-C(3)	120.4 (2)	C(10)-C(9)-C(14)	120.3 (2)
C(9)-C(10)-C(11)	119.6 (2)	C(10)-C(11)-C(12)	120.5 (2)
C(11)-C(12)-C(13)	120.2 (2)	C(12)-C(13)-C(14)	120.7 (2)
C(13)-C(14)-C(9)	118.7 (2)	C(16)-C(15)-C(20)	119.6 (2)
C(15)-C(16)-C(17)	119.3 (2)	C(16)-C(17)-C(18)	121.2 (2)
C(17)-C(18)-C(19)	119.1 (2)	C(18)-C(19)-C(20)	120.5 (2)
C(19)-C(20)-C(15)	120.4 (2)	C(22)-C(21)-C(26)	119.9 (2)
C(21)-C(22)-C(23)	120.1 (2)	C(22)-C(23)-C(24)	119.8 (2)
C(23)-C(24)-C(25)	120.5 (2)	C(24)-C(25)-C(26)	119.6 (2)
C(25)-C(26)-C(21)	120.2 (2)		

Discussion. The atomic coordinates for non-H atoms are listed in Table 1.* The structure of the molecule and the atom-numbering scheme are shown in Fig. 1. The bonding parameters of the molecule are indicated in Table 2. The molecular packing projected on the bc plane is given in Fig. 2.

The heterocyclic ring is planar with C(1) having the largest displacement of -0.004 Å ; however, the exocyclic N(3) and N(4) atoms deviate from this plane by -0.030 and 0.033 Å respectively. The four phenyl groups are nearly planar and steric interactions lead to a tilting of these planes. The dihedral angles of the phenyl groups A , B , C and D with the heterocyclic ring H are $A \wedge H = 20.9$, $B \wedge H = 100.3$, $C \wedge H = 47.6$ and

* Lists of structure factors, atomic coordinates for H atoms, bond distances involving H atoms, anisotropic thermal parameters, least-squares planes and dihedral and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42241 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$D \wedge H = 76.0^\circ$, respectively. Only plane *A* is nearly coplanar with plane *H*. The torsion angles C(1)–N(3)–C(3)–C(4), C(1)–N(3)–C(9)–C(10), C(2)–N(4)–C(15)–C(16) and C(2)–N(4)–C(21)–C(22) equal 15.0 , 102.2 , 38.4 and 64.3° , respectively. The S–N distance $1.651(1)$ Å is intermediate between the values for a single bond (1.73 Å) and for a double bond (1.54 Å) calculated by Pauling (1960). The S–C distance $1.727(1)$ Å agrees with those observed in 5-(1-imino-*N*-methylethylamino)-3-methyl-1,2,4-thiadiazole (I) (Iwasaki & Akiba, 1981a) and 5-[(1-aminoethylidene)amino]-3-chloromethyl-1,2,4-thiadiazole (II) (Iwasaki & Akiba, 1981b). There are a total of nine C–N bonds distributed over the compound under investigation. Five of them are in the central region and those remaining are at the junctions of the phenyl groups. The length of one of the bonds in the central region, C(2)–N(2) [$1.303(2)$ Å], is very close to the C=N double-bond distance (1.278 Å; Fischer-Hjalms & Sundbom, 1968) and the remaining four in the same region may also have double-bond character from the bond distances obtained. Out of the four C(Ph)–N bonds, the three bonds C(9)–N(3), C(15)–N(4) and C(21)–N(4) are slightly longer than the C(aromatic)–N distance (1.426 Å; *International Tables for X-ray Crystallography*, 1968), but the C(3)–N(3) bond is nearly equal to that value. These results and the coplanarity of planes *A* and *H* suggest

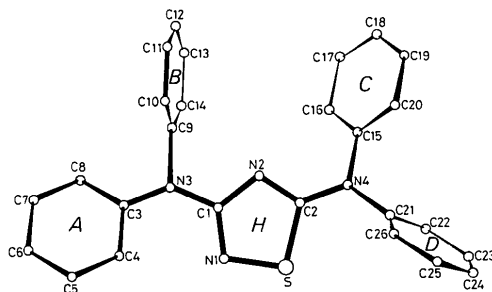


Fig. 1. Projection of the molecule on the heterocyclic plane with the atom-numbering scheme.

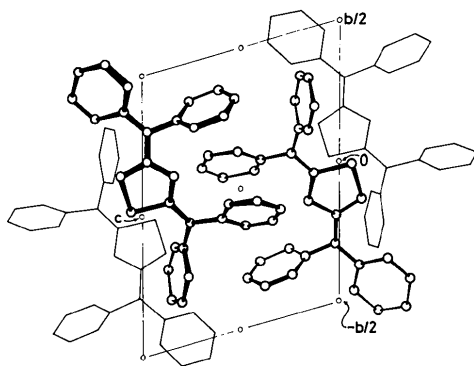
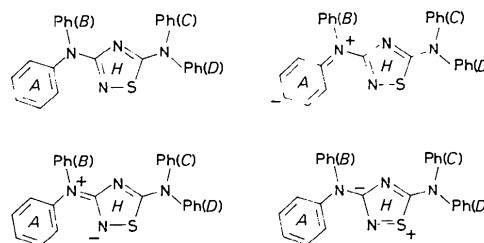


Fig. 2. Packing of the molecules projected on the *bc* plane.

π -electron delocalization. All bond angles in the heterocyclic skeleton are comparable with the corresponding bond angles in (I), (II) and 3-(*p*-bromophenylamino)-5-[1,3-bis(*p*-bromophenyl)guanidino]-1,2,4-thiadiazole (Akiba, Tsuchiya, Inamoto, Onuma, Nagashima & Nakamura, 1976). From these observations, several canonical formulae are possible and dominant forms are as follows:



All bond distances and angles of the four phenyl groups are normal.

The crystal structure consists of discrete molecules separated by normal van der Waals distances with the nearest distance of $3.426(2)$ Å for N(2)···C(19ⁱ) [$i: 1 - x, -y, 1 - z$].

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