Notes

Crystal Structure of Bis(diphenylmethyleneamino) Monosulphide, $S(N{=}CPh_2)_2$

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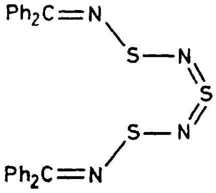
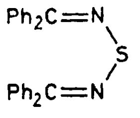
Crystals of the title compound are monoclinic with a = 21.323(6), b = 10.260(3), c = 10.271(3) Å, β = 110.50(5)°, Z = 4, and space group $P2_1/a$. The structure has been refined to R = 0.035 for 2 325 diffractometer-measured intensities for which $I > 3\sigma(I)$. The PhCNSNCPh system is largely coplanar, with the two remaining phenyl groups twisted 62.0 and 49.2° respectively out of the central CNSNC plane. Bond angles at N [121.5(2), 122.4(2)°] and S [94.7(1)°] and bond distances S–N [1.675(2), 1.676(2) Å] and C–N [1.285(3), 1.288(3) Å] indicate that the SN bonds are essentially single with no significant delocalisation of the lone-pair charge at nitrogen.

MOST cyclic sulphur–nitrogen compounds, especially those with less than six ring atoms, show angular distortion due to ring strain.[1] The extent of this distortion can be gauged by comparison with unstrained chain compounds, but since the SN bond distance and sulphur bond angle are related (see Results and Discussion section), it is necessary to compare with unstrained SN bonds for a range of bond orders. Unfortunately, although the structures of several doubly bonded SN species are known, relatively few singly bonded compounds have been studied, and only one compound (1) [2] with two adjacent formal single bonds, N–S–N.



(1)



(2)

We have therefore studied the compound (2); the bond distances and angles for the central $>C{=}N{-}S{-}N{=}C<$ portion of the molecule are consistent with essentially single SN bonds. The structure also provides further confirmation of the linearity (or closeness to linearity) of the correlation (for unstrained NSN compounds) between NSN bond angle and mean SN distance.[1]

EXPERIMENTAL

The compound $S(N{=}CPh_2)_2$ was prepared [3] from diphenylmethyleneaminolithium, $Li(N{=}CPh_2)$, and disulphur dichloride, and recrystallised from toluene. The crystal used for the data collection was approximately spherical with an average diameter of 0.15 mm.

Crystal Data.—$C_{26}H_{20}N_2S$, Monoclinic, a = 21.323(6), b = 10.260(3), c = 10.271(3) Å, β = 110.50(5)°, U = 2 104.73 Å^3, space group $P2_1/a$, Z = 4, D_c = 1.24 Mg m^{-3}, $F(000)$ = 824.0, μ = 13.63 cm^{-1} for Cu-K_α radiation, λ = 1.5418 Å.

Intensities for 3 136 independent reflections were collected in Grenoble with a CAD-4 Nonius four-circle goniometer, using graphite-monochromated Cu-K_α radiation. Measurements were made with an ω scan for θ between 3 and 60°. Scan speed was a function of peak heights and varied between 0.011 and 0.033° s^{-1}. Maximum time for measurement of one reflection was fixed at 180 s.

The crystal structure was determined with the aid of the MULTAN program.[4] In this way all atoms except C(24) and C(25) were located. The remaining two carbon atoms were found using difference-Fourier syntheses.

Least-squares refinements were made at Durham using 2 325 reflections for which $I > 3\sigma(I)$. The R value obtained prior to the inclusion of hydrogen atoms was 0.069. Hydrogens were included at positions calculated by the SHELX 76 program,[5] the C–H distance being fixed at 1.0 Å. The atomic positions and anisotropic thermal parameters were refined for non-hydrogen atoms, and isotropic thermal parameters alone for the hydrogens, to give a final R value of 0.035. Deviations from best least-squares planes and torsion angles were calculated using '*X* RAY '72 '.[6] The least-squares molecular fitting program MOLFIT [7] was used to compare the geometry of the two halves of the molecule. Final atomic positions are given in Table 1, bond distances and angles in Table 2. Structure factors, isotropic and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 23176 (18 pp.).†

RESULTS AND DISCUSSION

Although the two halves of the molecule (one on either side of the sulphur) are crystallographically in completely different environments, the similarity between them is remarkable (Figure). When one half of the molecule is rotated and compared with the other half,[7] the maximum deviation in the position of an atom in one half from the position of the corresponding atom in the other half is 0.223 Å [between C(5) and C(17)] and the mean deviation over all the atoms is only 0.110 Å. Since the central CNSNC group is approximately planar, the rotation relating the two halves of the molecule must be very near to that given by a two-fold axis.

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† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 1

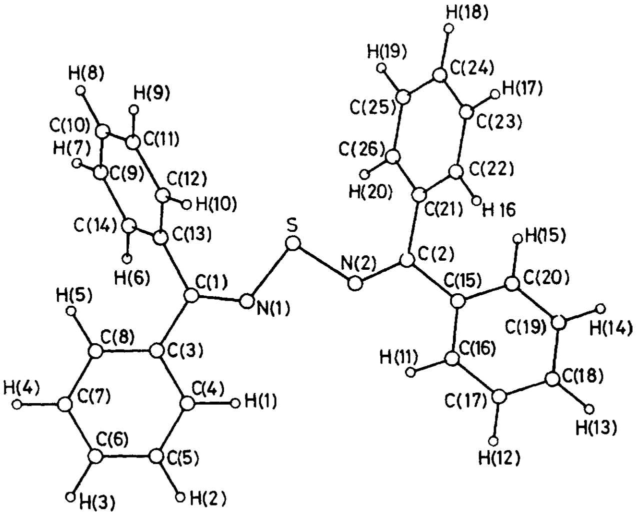
Atomic positions ($\times 10^4$; H $\times 10^3$)

Atom	x	y	z
S	1 097(0)	3 860(1)	9 414(1)
N(1)	1 526(1)	2 943(2)	785(2)
N(2)	1 034(1)	5 145(2)	369(2)
C(1)	1 810(1)	1 875(2)	641(3)
C(2)	732(1)	6 204(2)	9 817(3)
C(3)	2 211(1)	1 193(2)	1 955(2)
C(4)	2 368(1)	1 856(3)	3 213(3)
C(5)	2 719(2)	1 235(3)	4 458(3)
C(6)	2 916(2)	−39(3)	4 457(3)
C(7)	2 768(1)	−704(3)	3 221(3)
C(8)	2 412(1)	−91(3)	1 963(3)
C(9)	2 306(2)	507(3)	7 730(3)
C(10)	1 692(2)	208(3)	6 760(3)
C(11)	1 115(2)	451(3)	7 023(3)
C(12)	1 144(1)	1 014(3)	8 280(3)
C(13)	1 764(1)	1 301(2)	9 274(2)
C(14)	2 343(1)	1 044(3)	8 990(3)
C(15)	727(1)	7 262(2)	792(3)
C(16)	784(1)	6 987(3)	2 161(3)
C(17)	809(2)	7 984(3)	3 072(3)
C(18)	773(1)	9 264(3)	2 663(3)
C(19)	715(1)	9 547(3)	1 315(3)
C(20)	688(1)	8 553(2)	388(3)
C(21)	405(1)	6 437(2)	8 284(3)
C(22)	−249(1)	6 878(2)	7 745(3)
C(23)	−555(2)	7 088(3)	6 321(3)
C(24)	−209(2)	6 844(3)	5 442(3)
C(25)	437(2)	6 399(4)	5 968(3)
C(26)	748(2)	6 202(3)	7 381(3)
H(1)	222	286	321
H(2)	283	174	543
H(3)	319	−54	542
H(4)	293	−170	322
H(5)	228	−63	100
H(6)	282	126	977
H(7)	276	32	751
H(8)	166	−21	578
H(9)	64	21	625
H(10)	69	120	849
H(11)	80	598	249
H(12)	86	775	413
H(13)	79	1 004	338
H(14)	69	1 055	98
H(15)	64	878	−67
H(16)	−52	705	843
H(17)	−106	743	590
H(18)	−44	702	434
H(19)	70	618	527
H(20)	126	587	780

TABLE 2

Bond distances (Å) and angles (°)

S–N(1)	1.675(2)	C(14)–C(13)	1.388(3)
S–N(2)	1.676(2)	N(2)–C(2)	1.288(3)
N(1)–C(1)	1.285(3)	C(2)–C(21)	1.501(3)
C(1)–C(3)	1.494(3)	C(2)–C(15)	1.479(3)
C(1)–C(13)	1.493(3)	C(15)–C(16)	1.397(3)
C(3)–C(4)	1.394(3)	C(16)–C(17)	1.375(4)
C(4)–C(5)	1.390(4)	C(17)–C(18)	1.373(4)
C(5)–C(6)	1.373(4)	C(18)–C(19)	1.377(4)
C(6)–C(7)	1.377(4)	C(19)–C(20)	1.383(4)
C(7)–C(8)	1.397(4)	C(20)–C(15)	1.382(3)
C(8)–C(3)	1.385(3)	C(21)–C(22)	1.384(3)
C(13)–C(12)	1.390(3)	C(22)–C(23)	1.393(4)
C(12)–C(11)	1.396(4)	C(23)–C(24)	1.374(4)
C(11)–C(10)	1.371(4)	C(24)–C(25)	1.370(5)
C(10)–C(9)	1.374(4)	C(25)–C(26)	1.383(4)
C(9)–C(14)	1.383(4)	C(26)–C(21)	1.389(3)
N(1)–S–N(2)	94.7(1)	S–N(2)–C(2)	122.4(2)
S–N(1)–C(1)	121.5(2)	N(2)–C(2)–C(21)	125.0(2)
N(1)–C(1)–C(13)	124.5(2)	N(2)–C(2)–C(15)	116.2(2)
N(1)–C(1)–C(3)	116.0(2)	C(15)–C(2)–C(21)	118.8(2)
C(13)–C(12)–C(11)	119.4(3)	C(15)–C(16)–C(17)	120.3(3)
C(12)–C(11)–C(10)	120.3(3)	C(16)–C(17)–C(18)	121.2(3)
C(11)–C(10)–C(9)	120.6(3)	C(17)–C(18)–C(19)	119.0(3)
C(10)–C(9)–C(14)	119.6(3)	C(18)–C(19)–C(20)	120.3(3)
C(9)–C(14)–C(13)	120.6(3)	C(19)–C(20)–C(15)	121.1(3)
C(12)–C(13)–C(14)	119.4(3)	C(20)–C(15)–C(16)	118.0(3)
C(13)–C(1)–C(3)	119.5(2)	C(21)–C(22)–C(23)	120.3(3)
C(3)–C(4)–C(5)	120.4(3)	C(22)–C(23)–C(24)	120.0(3)
C(4)–C(5)–C(6)	120.2(3)	C(23)–C(24)–C(25)	119.9(3)
C(5)–C(6)–C(7)	120.1(3)	C(24)–C(25)–C(26)	120.6(3)
C(6)–C(7)–C(8)	120.3(3)	C(25)–C(26)–C(21)	120.2(3)
C(7)–C(8)–C(3)	120.1(3)	C(26)–C(21)–C(22)	118.9(3)
C(8)–C(3)–C(4)	119.0(2)	C(2)–C(21)–C(26)	120.8(2)
C(1)–C(13)–C(12)	120.4(2)	C(2)–C(21)–C(22)	120.3(2)
C(1)–C(13)–C(14)	120.2(2)	C(2)–C(15)–C(20)	120.9(2)
C(1)–C(3)–C(8)	122.0(2)	C(2)–C(15)–C(16)	121.0(2)
C(1)–C(3)–C(4)	119.0(2)		



View of one unit of the structure of bis(diphenylmethyleneamino) monosulphide

Deviations of atoms from least-squares planes are given in Table 3. The planarity of the CNSNC skeleton may be due to the constraint imposed by π bonding at NSN, but if so it is very weak; the low bond angle at sulphur [94.7(1)°] and long SN bond distances [S–N(1) 1.675(2), S–N(2) 1.676(2) Å] are consistent with predominantly localised lone pairs at sulphur [*cf.* compound (1) where NSN is 96.8° and mean d_{SN} = 1.668 Å (ref. 2)]. There is also further evidence to support this conclusion. The C=N distances [C(1)–N(1) 1.285(3), C(2)–N(2) 1.288(3) Å] and bond angles [at N(1) 121.5(2), N(2) 122.4(2)°] are close to those [1.33(4) Å and 121.5(1)°] in $Sn(N{=}CPh_2)_4$; it has been concluded [8] that in this compound there is insignificant lone-pair donation from nitrogen to tin.

Two of the phenyl groups are approximately coplanar with the central CNSNC skeleton [deviations from a best least-squares plane are less than 0.18 Å except for the four atoms C(16), C(17), C(19), and C(20) (Table 3)]; torsion angles between the central CNSNC plane and these phenyl groups are 5.6° [C(3)C(4)C(5)C(6)C(7)C(8)] and 28.4° [C(15)C(16)C(17)C(18)C(19)C(20)]. The other two phenyl rings are rotated considerably more out of the central plane, with torsion angles of 62.0° [C(9)C(10)C(11)C(12)C(13)C(14)] and 49.2° [C(21)C(22)C(23)C(24)C(25)C(26)]. The rotation of these latter two rings well out of the central plane probably avoids intramolecular

TABLE 3

Deviations (Å) of atoms from least-squares planes

Plane (*a*): N(1)N(2)SC(1)C(2)

$0.9170X + 0.3957Y - 0.0506Z - 3.9738 = 0$ *

[N(1) −0.090, N(2) −0.003, S −0.039, C(1) 0.088, C(2) 0.044]

Plane (*b*) C(3)C(4)C(5)C(6)C(7)C(8)C(1)C(15)C(16)C(17)C(18)-C(19)C(20)C(2)N(1)N(2)S

$0.9259X + 0.3752Y - 0.0436Z - 4.0064 = 0$ *

[C(3) 0.082, C(4) 0.178, C(5) 0.170, C(6) 0.064, C(7) −0.016, C(8) −0.018, C(1) 0.053, C(15) −0.078, C(16) −0.594, C(17) −0.503, C(18) 0.084, C(19) 0.587, C(20) 0.505, C(2) −0.105, N(1) 0.152, N(2) −0.123, S −0.134]

Plane (*c*): C(3)C(4)C(5)C(6)C(7)C(8)

$0.9481X + 0.3081Y - 0.0789Z - 4.0302 = 0$ *

[C(3) −0.001, C(4) 0.002, C(5) 0.002, C(6) −0.006, C(7) 0.006, C(8) 0.002, C(1) −0.041]

Plane (*d*): C(9)C(10)C(11)C(12)C(13)C(14)

$0.0964X + 0.9143Y - 0.3934Z + 2.2458 = 0$ *

[C(9) 0.007, C(10) −0.004, C(11) −0.004, C(12) 0.009, C(13) −0.007, C(14) −0.001, C(1) −0.018]

Plane (*e*): C(15)C(16)C(17)C(18)C(19)C(20)

$0.9617X + 0.0282Y + 0.2727Z - 1.6247 = 0$ *

[C(15) 0.002, C(16) −0.002, C(17) 0.002, C(18) −0.001, C(19) 0.000, C(20) −0.001, C(2) 0.069]

Plane (*f*): C(21)C(22)C(23)C(24)C(25)C(26)

$0.3110X + 0.9442Y + 0.1087Z - 6.4466 = 0$ *

[C(21) 0.001, C(22) −0.006, C(23) 0.002, C(24) 0.008, C(25) −0.014, C(26) 0.009, C(2) −0.024]

* X, Y, and Z are in Å with respect to the orthogonal axes a, b, and c^*.

repulsions between sulphur and the α-hydrogen atoms of each phenyl group. Similar relative orientations of phenyl groups are found in other $Ph_2C{=}N$ compounds, *e.g.* $M(N{=}CPh_2)_4$ where M = Si, Ge, or Sn.[8]

There are no intermolecular contacts less than the sum of the appropriate van der Waals radii.

The experimental d_{SN} and NSN [1.675(2), 1.676(2) Å and 94.7(1)°] compare well with those predicted (1.674 Å and 94.3°) using empirical correlations between d_{SN} and λ_{SN} [wavelength of i.r. absorption, which is 12.27 μm for $S(NCPh_2)_2$] and between d_{SN} and NSN.[1] The present structure thus provides further data to improve the accuracy of both of these correlations, and to improve the best straight line obtained from a statistical treatment of d_{SN} and NSN in non-cyclic molecules.[9] The improved straight line has the equation $d_{SN} = 213.14 - 0.4816\,\widehat{NSN}$.

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