Crystal Structure of 4-Phenyl-1,2-dithia-3,5-diazole Dimer

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4-Phenyl-1,2-dithia-3,5-diazolium chloride on reduction with thiocyanate ion gives the black air-sensitive title compound, $(PhCN_2S_2)_2$. Crystals have been studied by means of *X*-ray diffraction at room temperature. The compound crystallizes in the space group $P2_12_12_1$ (no. 19) with a = 16.061(1), b = 32.984(5), and c = 5.774 0(4) Å, and Z = 8. The crystal structure has been solved using 2 513 reflections and refined to a final R value of 0.082. Each asymmetric unit contains two $(PhCN_2S_2)_2$ molecules. Within each dimer the bridging mean S ··· S distance is 310.9(5) pm. The two half-molecules within each dimer are nearly parallel and are slightly twisted with respect to each other. The short (mean) CN_2S_2 ring distances (d_{CN} = 133, d_{SN} = 162, and d_{SS} = 209 pm) and the $PhCN_2S_2$ coplanarity suggest that the rings are aromatic with one electron pair delocalized at the four (disulphide) sulphur atoms.

1-CHLORO-1,2,4-TRITHIADIAZOLIUM, CHLORIDE, which contains the six π-electron cation $S_3N_2Cl^+$, can be converted, by heating *in vacuo*,[1] to the compound S_3N_2Cl. Crystal structure determinations of the analogous $S_3N_2(AsF_6)$ [2] and $S_3N_2(S_2O_6)Cl$ [3] revealed the presence of S_3N_2 rings associated in pairs. Each pair appeared to be held together by a four-centre interaction involving the adjacent sulphur atoms of the two rings.[3]

Since $S_3N_2Cl^+$ and $PhCN_2S_2^+$ are isoelectronic, we have studied reductions of the latter and have carried out a structural study of the product which, like $S_3N_2^+$, is associated in the lattice in pairs with further weaker interactions between the pairs. In each $(PhCN_2S_2)_2$ unit, the five-membered rings adopt an almost eclipsed *cis* conformation in contrast to the stepped *trans* conformation of $(S_3N_2)_2^{2+}$.

EXPERIMENTAL

The title compound was prepared from 4-phenyl-1,2-dithia-3,5-diazolium chloride by (1 : 1) reaction with sodium thiocyanate in 1,2-dimethoxyethane. Prolonged refluxing for 12 h caused decomposition of the intermediate dithiadiazolium thiocyanate to give (insoluble) polythiocyanogen and $(PhCN_2S_2)_2$. After filtration, the solution was cooled to −78 °C and the purple crystals of $(PhCN_2S_2)_2$ were filtered off and recrystallized from dichloroethane.

Crystal Data.—$C_{14}H_{10}N_4S_4$, M 362.52, Orthorhombic, space group $P2_12_12_1$, $a = 16.061(1)$, $b = 32.984(5)$ Å, $c = 5.774\,0(4)$ Å, $U = 3\,042.9(5)$ Å^3, $Z = 8$, $D_c = 1.58$ g cm^{-3}, $F(000) = 1\,488$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,7$ Å, $\mu_{Mo} = 5.99$ cm^{-1}.

A rather poor shaped crystal (mean dimension 0.2 mm) was used to collect the data on a PW1100 four-circle diffractometer, using Mo-K_α radiation monochromated by graphite. A total of 8 001 reflections were measured in the ω–2θ scan mode. Equivalent reflections were averaged to obtain the asymmetric set of intensities, which were corrected by Lorentz and polarization factors. Because of the shape of the crystal, an absorption correction was not applied. Of the 4 133 independent reflections, 1 620 were considered as unobserved using the criterion $I < 2\sigma(I)$.

Scattering factors for neutral atoms were taken from ref. 4, anomalous dispersion coefficients for S from ref. 5. The structure was solved by direct methods and further Fourier synthesis, allowing the location of all non-hydrogen atoms; 132 positional parameters and 264 thermal ones, together with the scale factor, were refined by the block-diagonal method of least squares. When convergence was attained, the hydrogen atoms were located at the calculated positions and held invariant during the last cycles of refinement. The thermal motion was considered anisotropic for S, C, and N and isotropic for H. Unit weights were applied to every reflection. The final R value was 0.082 for observed reflections only (R = 0.126 for all reflections). The final atomic co-ordinates are listed in Table 1. Tables containing structure factors and thermal parameters are available as Supplementary Publication No. SUP 22785 (19 pp.).† Most of the calculations were performed with the ' *X*-RAY '70 ' system of crystallographic programs.[6]

DISCUSSION

Description of the Structure.—The unit cell contains eight molecules of $(PhCN_2S_2)_2$, two of which are in the asymmetric unit. Figure 1 represents these two dimer molecules, together with two additional five-membered rings, to show (dotted lines) the contacts described below.

The two half-molecules are bonded together in each dimer through weak S ··· S bonds. Several short contact distances have been found between the dimers, *e.g.* that involving S(12) and S(21), 340.2 pm (sum of the van der Waals radii 360.0 pm), and that between N(21) and S(41) at a distance of 309 pm. Other contact distances are those involving S(32) and N(12) of the asymmetric unit with atoms N(12) and S(32) (respectively) in adjacent molecules in the cell (Figure 1).

The two 4-phenyl-1,2-dithia-3,5-diazole units within each dimer are nearly parallel and are twisted with respect to each other. The dihedral angles formed by the least-squares planes through the two half-molecules are 6.56 and 7.04° for the dimers 1—4 and 2—3 respectively. The twist, represented in Figure 2, can be

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

quantified by the values of the torsion angles at the intermolecular S–S bonds as listed below:

Atoms	Angle (°)
N(11)–S(11)–S(42)–N(42)	8.43
N(12)–S(12)–S(41)–N(41)	6.91
N(21)–S(21)–S(31)–N(31)	3.61
N(22)–S(22)–S(32)–N(32)	2.81

As a consequence, the four S atoms in each dimer are not coplanar, with deviations of up to 72 pm from the best least-squares plane.

Looking at the individual $PhCN_2S_2$ units, the more relevant features of their geometry can be summarized as follows. All the phenyl groups, as well as the rings S(31)–N(31)–C(31)–N(32)–S(32) and S(41)–N(41)–C(41)–N(42)–S(42), are completely planar. The same can be said for the four atoms C(1)–C(2)–C(3)–C(7) in each half-molecule. In contrast, the rings S(11)–N(11)–C(11)–N(12)–S(12) and S(21)–N(21)–C(21)–N(22)–S(22) are not planar as a consequence of important deviations of N(12) and N(21) (81 and 54 pm respectively) from the plane calculated through the other four atoms which present a perfect planarity. Thus these secondary interactions between nitrogen and sulphur affect the planarity of the ring containing the relevant nitrogen atom, but do not affect significantly the ring containing the sulphur atom(s) involved.

Figure 3 is a schematic drawing of the asymmetric unit including bond lengths and angles. Contact distances and angles are listed in Table 2. The small deviations observed in the bond lengths and angles of the four half-molecules represented in Figure 3 are not significant within the limits of error. The bond lengths and angles in the phenyl groups are as expected. The interatomic distances in the five-membered rings have considerable double-bond character. The C–N bond length is similar to that found in pyridine rings (134.0 pm) [7] and in $Cl_3C-CN_2S_2^+$ (132 pm).[8] The S–N distances are also short (mean d_{SN} = 162 pm) when compared with the single-bond value in sulphamic acid (177.1 pm).[9] Similar mean values have been found in other S–N heterocycles, such as $Cl_3C-CN_2S_2^+$ (158.4 pm),[8] $S_3N_2^+$ [158.2 (ref. 2) and 158.5 pm (ref. 3)] and $O{=}CN_2S_2$ (159.5 pm).[10] The S–S bond lengths (208.9 pm) are shorter than those in $S_3N_2^+$ (214.7 pm) [2] and $(S_3N_2)_2^{2+}$ (214.5 pm),[3] but longer than the value of 200.9 pm for $Cl_3C-CN_2S_2^+$,[8] and so, on the basis of distance alone, the S–S bonds appear to possess some degree of π character.

It seems clear from the geometry of the rings, and from

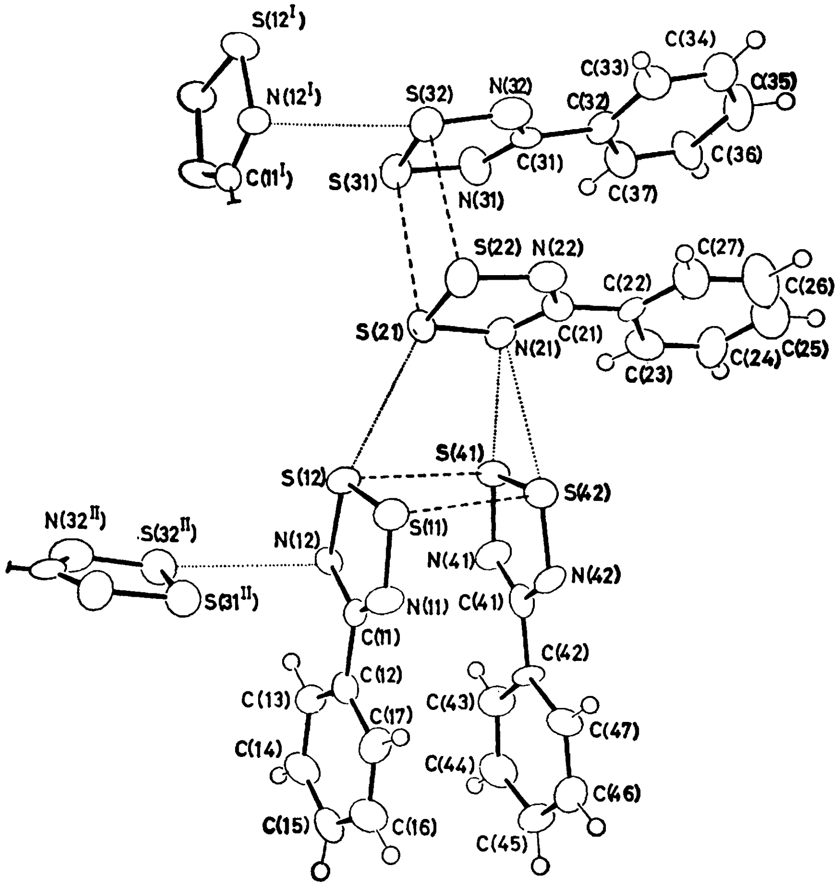


FIGURE 1 ORTEP drawing of the asymmetric unit showing the intermolecular contacts (dotted lines). The labels of the H atoms have been omitted for clarity; their numbering corresponds to that of the C to which they are bonded

the S–N and N–C bond lengths, that the S_2N_2C groups can be described as 6 π-electron Hückel rings in which each S donates two electrons, C and N one electron, and, with subtraction of one electron, give rise to the aromatic cation $PhCN_2S_2^+$.

TABLE 1

Final atomic co-ordinates (× 10^3 for H, × 10^4 for others) with standard deviations in parentheses

Atom	x/a	y/b	z/c
S(21)	1 421(2)	8 213(1)	0 903(7)
S(22)	0 981(2)	8 384(1)	4 194(6)
N(21)	1 477(6)	8 675(3)	0 005(22)
N(22)	0 951(6)	8 861(3)	3 616(20)
C(21)	1 212(7)	8 966(4)	1 433(23)
C(22)	1 228(7)	9 394(3)	0 802(25)
C(23)	1 570(8)	9 523(4)	−1 388(25)
C(24)	1 585(10)	9 923(4)	−1 969(33)
C(25)	1 265(11)	10 203(5)	−0 395(36)
C(26)	0 932(13)	10 082(5)	1 723(32)
C(27)	0 922(10)	9 685(5)	2 253(30)
S(31)	−0 462(2)	8 096(1)	−0 702(7)
S(32)	−0 842(2)	8 220(1)	2 712(7)
N(31)	−0 564(7)	8 563(3)	−1 554(21)
N(32)	−0 984(7)	8 698(4)	2 177(21)
C(31)	−0 813(7)	8 826(4)	0 038(25)
C(32)	−0 949(8)	9 268(4)	−0 500(22)
C(33)	−1 378(9)	9 509(4)	1 072(26)
C(34)	−1 523(10)	9 901(5)	0 559(35)
C(35)	−1 224(11)	10 066(5)	−1 544(39)
C(36)	−0 808(10)	9 820(4)	−3 117(25)
C(37)	−0 675(9)	9 423(4)	−2 573(28)
S(11)	3 611(2)	8 027(1)	1 730(6)
S(12)	3 176(2)	7 802(1)	−1 428(7)
N(11)	4 580(6)	8 001(3)	0 934(21)
N(12)	4 104(6)	7 732(3)	−2 524(19)
C(11)	4 717(7)	7 865(4)	−1 218(25)
C(12)	5 584(8)	7 817(4)	−2 044(22)
C(13)	5 724(8)	7 645(4)	−4 144(27)
C(14)	6 548(8)	7 605(4)	−4 958(26)
C(15)	7 192(9)	7 745(4)	−3 778(29)
C(16)	7 053(9)	7 941(5)	−1 609(33)
C(17)	6 242(9)	7 970(4)	−0 725(26)
S(41)	3 068(2)	8 689(1)	−3 265(7)
S(42)	3 349(2)	8 892(1)	0 082(7)
N(41)	4 028(6)	8 703(3)	−4 184(21)
N(42)	4 345(6)	8 950(3)	−0 437(18)
C(41)	4 582(8)	8 833(4)	−2 587(23)
C(42)	5 467(6)	8 879(4)	−3 158(24)
C(43)	5 781(8)	8 736(4)	−5 278(23)
C(44)	6 611(9)	8 752(4)	−5 747(25)
C(45)	7 151(8)	8 937(4)	−4 129(26)
C(46)	6 848(9)	9 093(5)	−2 074(29)
C(47)	6 004(8)	9 052(4)	−1 616(28)
H(23)	178	932	−236
H(24)	183	1 001	−331
H(25)	129	1 047	−077
H(26)	072	1 027	270
H(27)	069	961	369
H(33)	−155	941	242
H(34)	−183	1 007	153
H(35)	−130	1 034	−179
H(36)	−064	993	−454
H(37)	−040	926	−364
H(13)	528	754	−502
H(14)	664	748	−641
H(15)	772	770	−431
H(16)	748	805	−082
H(17)	614	809	067
H(43)	541	864	−636
H(44)	681	864	−708
H(45)	771	896	−451
H(46)	721	921	−099
H(47)	580	916	−024

So, the dimers represented in Figure 1 should be regarded as being composed of two cations $PhCN_2S_2^+$ linked by two long S · · · S bonds (303.8—318.6 pm). The positive charges on the rings are compensated by two electrons delocalized through the four S atoms. This model can be visualized in the structural formula overleaf. This approach is similar to that used [3] in describing the compound $(S_3N_2)_2^{2+}2(S_2O_6Cl^-)$. However, in this last compound, the two five-membered rings are opposite (related through a centre of symmetry), whereas in

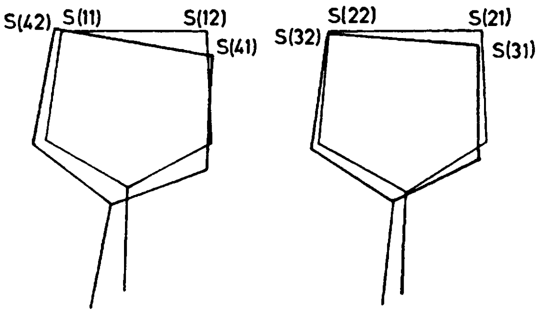


FIGURE 2 Projection of the five-membered rings showing the twist between them

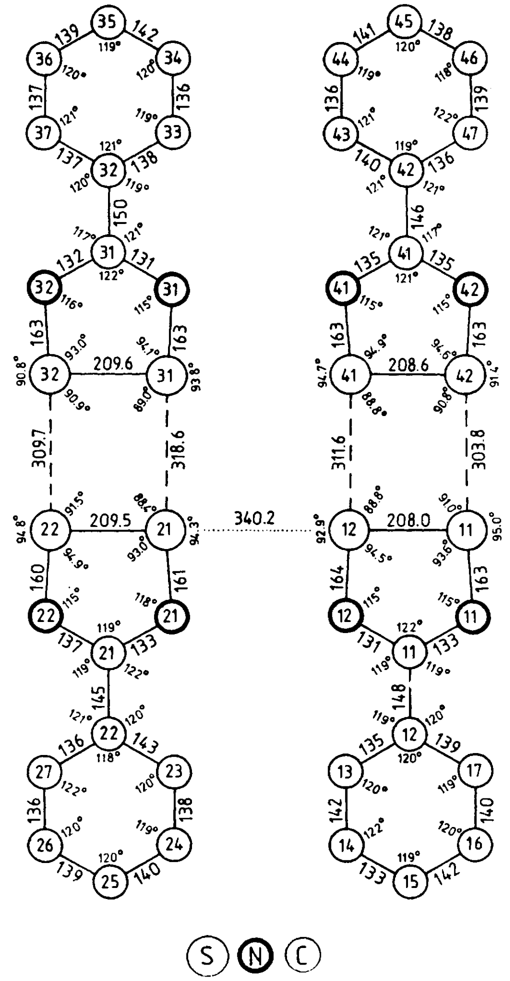


FIGURE 3 Schematic drawing of the two dimer molecules which form the asymmetric unit. Interatomic distances (pm) and angles (°) are included. The H atoms have been omitted

$(PhCN_2S_2)_2$ the two rings are almost eclipsed. The greater charge on the rings of $S_3N_2^+$, as well as the presence of bulky $S_2O_6Cl^-$ anions, is perhaps responsible for this difference in conformation.

Important differences are also observed when $(PhCN_2S_2)_2$ is compared with the corresponding cation in $[PhCN_2S_2]Cl$.[11] Not surprisingly, the cation has a shorter S–S bond length, *viz.* 199.1 against 208.9 pm in the neutral dimer.

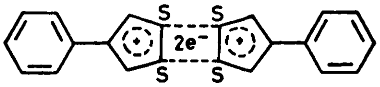
TABLE 2

Intermolecular contacts (lengths in pm, angles in degrees). The atoms are labelled as in Figure 1

Lengths			
S(12)–S(21)	340.2	S(41)–N(21)	309.0
S(32)–N(12^I)	315.0	S(42)–N(21)	317.0
S(31)–N(12^I)	338.0		
Angles			
S(12)–S(21)–S(22)	137.9	S(11)–S(12)–S(21)	78.1
S(12)–S(21)–S(31)	128.6	S(21)–S(12)–S(41)	73.3
S(12)–S(21)–N(21)	101.9	S(21)–S(12)–N(12)	164.3
S(32^{II})–N(12)–S(12)	100.1	S(42)–N(21)–S(21)	105.6
S(32^{II})–N(12)–C(11)	109.7	S(42)–N(21)–C(21)	97.8
S(31^{II})–N(12)–S(12)	95.0	S(41)–N(21)–S(21)	104.3
S(31^{II})–N(12)–C(11)	78.8	S(41)–N(21)–C(21)	97.8
S(31)–S(32)–N(12^I)	77.3	S(41)–S(42)–N(21)	72.6
S(22)–S(32)–N(12^I)	102.0	S(11)–S(42)–N(21)	85.5
N(32)–S(32)–N(12^I)	163.9	N(42)–S(42)–N(21)	166.8
S(32)–S(31)–N(12^I)	65.5	S(42)–S(41)–N(21)	68.5
S(21)–S(31)–N(12^I)	97.7	S(12)–S(41)–N(21)	80.3
N(31)–S(31)–N(12^I)	156.2	N(41)–S(41)–N(21)	162.5

Symmetry code: I $x - \frac{1}{2}, \frac{3}{2} - y, -z$; II $x + \frac{1}{2}, \frac{3}{2} - y, -z$. Standard deviations for lengths (angles) involving S, N, and C are 0.5 (0.2), 1.0 (0.4), and —pm (0.4°) respectively.

The contact distances listed in Table 2 are now discussed. The clearest interaction is at S(12)–S(21) separated by a distance of 340.2 pm, 20 pm shorter than the accepted van der Waals contact of 360 pm. This again illustrates the remarkable capacity of 1,2-dithiolium sulphur for secondary bonding. Other contacts involving S and N atoms can be explained as weak donor–acceptor interactions. The S–N distances are not much below the sum of the van der Waals radii (315 pm, if sp^2 hybridization at N is assumed). However (see angles listed in Table 2), the deviations of N(12) and N(21) from the plane of the rings [toward S(32) and S(42) respectively] and the twist of the rings forming the dimers clearly indicate some secondary interaction.



We thank Professor S. García-Blanco for the use of the PW1100 diffractometer. Thanks are also due to the staff of CPD del MEC and of JEN for the computer facilities, and to the S.R.C. for a Studentship (to R. G. H.).

[9/1537 *Received*, 26*th September*, 1979]

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