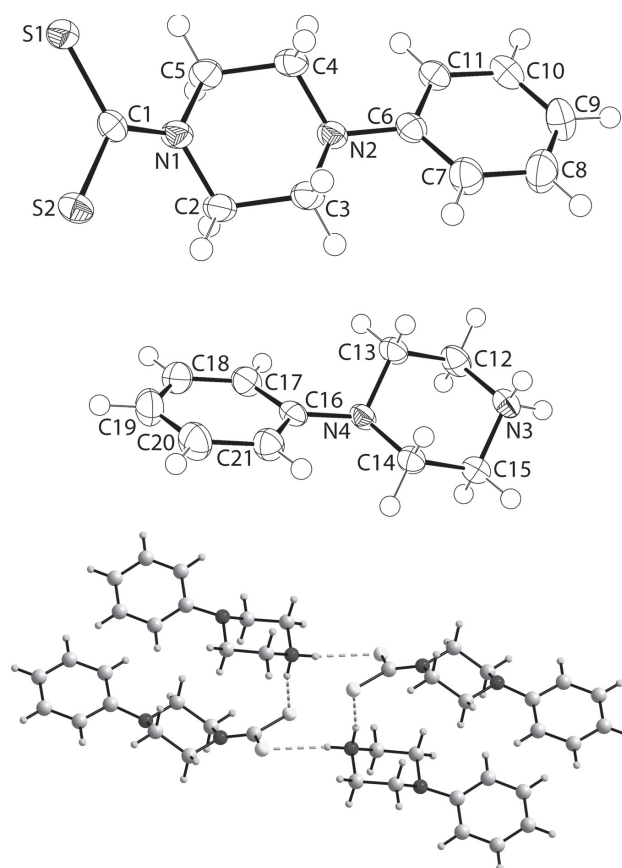


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Crystal structure of 4-phenylpiperazin-1-ium (4-phenylpiperazin-1-yl)carbothioylsulfanide, [C₁₀H₁₅N₂][C₁₁H₁₃N₂S₂]



$V = 2091.73(5) \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.0281$, $wR_{\text{ref}}(F^2) = 0.0740$, $T = 100(2) \text{ K}$.

CCDC no.: 1948406

The molecular structures of the ions are shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.12 \times 0.06 \times 0.03 \text{ mm}$
Wavelength:	Cu $K\alpha$ radiation ($1.54178 \text{ \AA}$)
μ :	2.40 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1° , $>99\%$
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	25933, 3726, 0.035
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3406
$N(\text{param})_{\text{refined}}$:	250
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

All chemicals and solvents were used as purchased without purification. The melting point was determined using a Mel-temp II digital melting point apparatus and was uncorrected. The solid-state IR spectrum was obtained on a Bruker Vertex 70v FTIR Spectrometer from 4000 to 400 cm^{-1} . The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at room temperature in CDCl_3 solution on a Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

The dithiocarbamate ligand was prepared *in situ* (methanol) from the reaction of CS_2 (Merck, 0.25 mmol) with 1-phenylpiperazine (Aldrich, 0.25 mmol) and NaOH (0.02 mL ; $50\% \text{ w/v}$); CS_2 was added dropwise into the methanol solution (10 mL). The resulting mixture solution was kept at 273 K for 1 h . The filtrate was evaporated until a beige precipitate was obtained. The precipitate was washed with *n*-hexane and recrystallised from a methanol-acetone solution to furnish colourless crystals. Yield: 0.010 g (10.0%). **M.pt:** $441\text{--}443 \text{ K}$. **IR** (cm^{-1}) 1597 (m) $\nu(\text{C--N})$, 1580 (m) $\nu(\text{C--N})$, 1491 (m)

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Abstract

[C₂₁H₂₈N₄S₂], monoclinic, $P2_1/c$ (no. 14), $a = 16.1880(2) \text{ \AA}$, $b = 6.8168(1) \text{ \AA}$, $c = 19.7605(2) \text{ \AA}$, $\beta = 106.412(1)^\circ$,

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
S1	0.46765(2)	0.26374(5)	0.60297(2)	0.01990(10)
S2	0.58043(2)	0.61634(5)	0.63185(2)	0.01875(10)
N1	0.59362(7)	0.31667(17)	0.72131(6)	0.0188(2)
N2	0.71913(7)	0.10047(16)	0.82654(6)	0.0185(2)
N3	0.38889(8)	0.63077(17)	0.50114(6)	0.0198(3)
H1N	0.4234(9)	0.567(2)	0.5392(7)	0.024*
H2N	0.4078(10)	0.598(2)	0.4635(7)	0.024*
N4	0.24784(7)	0.88689(16)	0.43912(6)	0.0184(2)
C1	0.55113(8)	0.39218(19)	0.65839(7)	0.0169(3)
C2	0.66356(9)	0.4169(2)	0.77322(7)	0.0209(3)
H2A	0.6436	0.4563	0.8142	0.025*
H2B	0.6797	0.5371	0.7519	0.025*
C3	0.74192(9)	0.2841(2)	0.79802(7)	0.0208(3)
H3C	0.7654	0.2551	0.7579	0.025*
H3D	0.7872	0.3522	0.8348	0.025*
C4	0.64930(9)	0.0005(2)	0.77370(7)	0.0203(3)
H4A	0.6333	−0.1210	0.7944	0.024*
H4B	0.6697	−0.0369	0.7327	0.024*
C5	0.57100(9)	0.1312(2)	0.74914(7)	0.0216(3)
H5A	0.5262	0.0632	0.7120	0.026*
H5B	0.5471	0.1582	0.7891	0.026*
C6	0.78829(9)	−0.0211(2)	0.86363(7)	0.0193(3)
C7	0.87425(10)	0.0325(2)	0.87526(8)	0.0269(3)
H7	0.8882	0.1485	0.8542	0.032*
C8	0.93976(10)	−0.0823(3)	0.91744(9)	0.0342(4)
H8	0.9980	−0.0431	0.9251	0.041*
C9	0.92162(10)	−0.2521(2)	0.94841(9)	0.0311(4)
H9	0.9668	−0.3285	0.9778	0.037*
C10	0.83629(10)	−0.3096(2)	0.93600(8)	0.0246(3)
H10	0.8230	−0.4270	0.9566	0.029*
C11	0.77049(9)	−0.1967(2)	0.89382(7)	0.0206(3)
H11	0.7125	−0.2388	0.8852	0.025*
C12	0.29823(9)	0.5647(2)	0.48794(8)	0.0248(3)
H12A	0.2787	0.5888	0.5304	0.030*
H12B	0.2943	0.4221	0.4781	0.030*
C13	0.24121(9)	0.6745(2)	0.42592(8)	0.0230(3)
H13A	0.2586	0.6440	0.3829	0.028*
H13B	0.1807	0.6322	0.4179	0.028*
C14	0.33664(9)	0.9518(2)	0.44995(8)	0.0220(3)
H14A	0.3405	1.0951	0.4585	0.026*
H14B	0.3548	0.9247	0.4071	0.026*
C15	0.39576(9)	0.8458(2)	0.51244(8)	0.0233(3)
H15A	0.4560	0.8880	0.5187	0.028*
H15B	0.3799	0.8799	0.5559	0.028*
C16	0.18218(9)	1.0003(2)	0.39213(7)	0.0190(3)
C17	0.09633(9)	0.9579(2)	0.38733(8)	0.0239(3)
H17	0.0833	0.8529	0.4142	0.029*
C18	0.02996(10)	1.0662(2)	0.34405(8)	0.0280(3)
H18	−0.0280	1.0340	0.3411	0.034*
C19	0.04749(10)	1.2218(2)	0.30483(8)	0.0305(4)
H19	0.0020	1.2968	0.2753	0.037*
C20	0.13211(11)	1.2654(2)	0.30958(9)	0.0302(3)
H20	0.1447	1.3716	0.2830	0.036*
C21	0.19972(10)	1.1564(2)	0.35278(8)	0.0242(3)
H21	0.2576	1.1887	0.3553	0.029*

ν(C–N), 1012 (s) ν(C–S), 756 (m) ν(C–S). ¹H NMR (CDCl₃, ppm): δ 3.16–3.29 (m, 8H, N–CH₂), 4.45–4.60 (m, 8H, N–CH₂), 6.86–6.94, 7.23–7.32 (m, 10H, Ph–H). ¹³C{¹H} NMR (CDCl₃, ppm): δ 45.7, 49.8 (N–CH₂), 116.3, 120.1, 129.2, 150.1 (Ph–C), 193.7 (CS₂).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with *U*_{iso}(H) = 1.2*U*_{eq}(C). The N-bound H-atoms were located in a difference Fourier map but were refined with a distance restraint N–H = 0.91 ± 0.01 Å, and with *U*_{iso}(H) set to 1.2*U*_{eq}(N).

Comment

The title salt of a dithiocarbamate ligand (‘S₂CNRR’) became available during the course of methodical studies evaluating the structural chemistry of the homoleptic zinc-triad dithiocarbamates [5] and their adducts with bipyridyl-type ligands aimed for the construction of coordination polymers [6]. In this context, and underscoring the importance of systematic evaluations of closely related compounds, recent work on functionalised dithiocarbamates, i.e. homoleptic morpholinodithiocarbamates, revealed a hitherto unobserved structural motif for cadmium dithiocarbamates [7], namely a linear coordination polymer with hexa-coordinated cadmium centres, {Cd[S₂CN(CH₂CH₂)₂O]₂}_n, although the binuclear zinc(II) structure of the same ligand, {Zn[S₂CN(CH₂CH₂)₂O]₂}₂, adopted the usual structural motif [5]; precedents for the linear coordination polymer motif are evident in related xanthate (‘S₂COR’) structures [8]. The presence of substituents capable of hydrogen bonding interactions in the dithiocarbamate ligands are also thought important for enhancing the biological activity of metal compounds of this potentially important class of ligands [9]. Current work in this context focuses on the exciting anti-bacterial activity exhibited by gold(I) dithiocarbamates [10, 11]. Herein, the crystal and molecular structures of the title salt, [PhN(CH₂CH₂)₂NH₂][S₂CN(CH₂CH₂)₂NPh], are described.

The constituents of the title salt are shown in the figure (70% displacement ellipsoids); the asymmetric unit comprises a 4-phenylpiperazin-1-ium cation and a (4-phenylpiperazin-1-yl)dithiocarbamate anion. The confirmation for this formulation is revealed in the pattern of hydrogen bonding exhibited by the piperazin-1-ium–N–H atoms (see below). Further, the C–N3 bond lengths [C12–N3 = 1.4861(19) Å and C15–N3 = 1.4822(18) Å] are systematically longer than the C–N4 bonds [C13–N4 = 1.4694(18) Å and C14–N4 = 1.4609(18) Å]. The piperazin-1-ium ring has a chair conformation.

In the anion, the piperazin-1-yl ring also has a chair conformation. Further support for the formation of a salt is

seen in the experimental equivalence of the C1–S1, S2 bond lengths [C1–S1 = 1.7192(14) Å and C1–S2 = 1.7249(14) Å]. As anticipated, the C1–N1 bond length [1.3419(18) Å] is considerably shorter than the C2–N1 [1.4643(17) Å] and C5–N1 [1.4660(17) Å] bond lengths, an observation consistent with a significant contribution of the $^2\text{-S}_2\text{C}=\text{N}^+(\text{CH}_2\text{CH}_2)_2\text{NPh}$ canonical form to the overall electronic structure of the S₂CN chromophore in the anion. Reflecting the equivalence of the C–S bonds, the S1–C1–N1 and S2–C1–N2 bond angles are equivalent [119.98(10) and 120.57(10)°, respectively] with S1–C1–S2 angle being very similar [119.45(8)°], observations consistent with a regular trigonal geometry about the C1 atom. This regular geometry contrasts the observations in the recently reported dithiocarbamate ester, MeSC(=S)N(Me)Ph [12], whereby the bond angles involving the thione-sulphur atom were approximately 10° wider [i.e. 123.47(11) and 123.32(13)°] than the angle involving the singly-bound sulphur atom and nitrogen [113.21(13)°].

The only prominent supramolecular contacts in the molecular packing are charge-assisted 4-phenylpiperazin-1-ium-N–H···S(dithiocarbamate) hydrogen bonds disposed about a centre of inversion [N3–H1n···S1: H1n···S1 = 2.422(14) Å, N3···S1 = 3.2380(12) Å with angle at H1n = 149.3(12)° and N3–H2n···S2ⁱ: H2n···S2ⁱ = 2.434(14) Å, N3···S2ⁱ = 3.2753(12) Å with angle at H2n = 154.1(13)° for symmetry operation (i) 1 = x, 1 = y, 1 = z]. As shown in the lower view of the figure, these interactions lead to a four-ion aggregate sustained by a 12-membered {···HNH···SCS₂}₂ synthon with a distinctive kinked conformation. The relatively large deviations from linearity of the N–H···S hydrogen bonds are readily explained by transannular interactions within the aggregate as seen in the H1n···S2 and H2n···S1ⁱ separations of 2.701(14) and 2.859(16) Å, respectively.

To analyse the molecular packing of the four-molecule aggregates in more detail, Crystal Explorer 17 [13] was utilised to calculate the Hirshfeld surface, following standard procedures [14]; herein, the Hirshfeld surfaces as well as the overall and delineated two-dimensional fingerprint plots were evaluated. The most dominant contacts contributing to the surface are H···H contacts, at 61.4%, entirely consistent with the lack of directional interactions connecting the four-molecule aggregates. The next most prominent contacts are of the type C···H/H···C [20.6%], S···H/H···S [14.2%] and N···H/H···N [3.0%].

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