

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 2.747$
$R[F^2 > 2\sigma(F^2)] = 0.0428$	$\Delta\rho_{\max} = 0.215 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.1328$	$\Delta\rho_{\min} = -0.145 \text{ e } \text{\AA}^{-3}$
$S = 0.628$	Extinction correction: none
1416 reflections	Atomic scattering factors
120 parameters	from <i>International Tables</i>
H atoms refined isotropically	for <i>Crystallography</i> (1992,
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$	Vol. C, Tables 4.2.6.8 and
where $P = (F_o^2 + 2F_c^2)/3$	6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	U_{eq}
C1	0.33209 (12)	-0.1833 (4)	0.0931 (5)	0.0434 (4)
C2	0.33233 (13)	-0.0144 (4)	0.2138 (5)	0.0433 (4)
C3	0.24702 (13)	0.0826	0.1607 (4)	0.0406 (4)
C4	0.16236 (12)	0.0130 (3)	-0.0110 (4)	0.0398 (4)
C5	0.16440 (12)	-0.1561 (3)	-0.1302 (4)	0.0382 (4)
C6	0.24880 (14)	-0.2560 (3)	-0.0801 (4)	0.0418 (4)
C7	0.4200 (2)	-0.2871 (5)	0.1493 (7)	0.0704 (8)
C8	0.2467 (2)	0.2570 (4)	0.2919 (6)	0.0619 (6)
C9	0.0773 (2)	-0.2309 (4)	-0.3094 (5)	0.0560 (6)
N1	0.4893 (2)	-0.3663 (7)	0.1975 (8)	0.1145 (14)
N2	0.2465 (2)	0.3933 (4)	0.4012 (7)	0.0959 (10)
N3	0.0093 (2)	-0.2902 (5)	-0.4519 (7)	0.0875 (9)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

C1—C2	1.386 (3)	C4—C5	1.387 (3)
C1—C6	1.387 (3)	C5—C6	1.390 (3)
C1—C7	1.447 (3)	C5—C9	1.444 (3)
C2—C3	1.388 (3)	C7—N1	1.131 (4)
C3—C4	1.390 (2)	C8—N2	1.135 (3)
C3—C8	1.440 (3)	C9—N3	1.134 (3)
C2—C1—C6	121.3 (2)	C6—C5—C4	121.3 (2)
C2—C1—C7	119.8 (2)	C6—C5—C9	119.0 (2)
C6—C1—C7	118.9 (2)	C4—C5—C9	119.7 (2)
C3—C2—C1	118.9 (2)	C5—C6—C1	118.6 (2)
C2—C3—C4	121.1 (2)	N1—C7—C1	178.8 (4)
C2—C3—C8	118.9 (2)	N2—C8—C3	178.8 (3)
C4—C3—C8	120.0 (2)	N3—C9—C5	179.5 (3)
C5—C4—C3	118.8 (2)		

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
C2—H2...N1 ⁱ	0.96 (3)	2.45 (3)	3.381 (4)	164 (2)
C2—H2...N1 ⁱⁱ	0.96 (3)	2.89 (3)	3.253 (4)	103 (2)
C4—H4...N3 ⁱⁱⁱ	0.93 (3)	2.85 (3)	3.447 (4)	124 (2)
C4—H4...N3 ^{iv}	0.93 (3)	2.55 (3)	3.354 (4)	145 (2)
C6—H6...N2 ^v	0.91 (3)	2.85 (3)	3.291 (4)	111 (2)
C6—H6...N2 ^{vi}	0.91 (3)	2.52 (3)	3.372 (4)	156 (2)

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, 1 - z$; (ii) $1 - x, \frac{1}{2} + y, -z$; (iii) $-x, \frac{1}{2} + y, -z$; (iv) $-x, \frac{1}{2} + y, -1 - z$; (v) $x, y - 1, z$; (vi) $x, y - 1, z - 1$.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: SE1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,3-Diethyl-5,6,7,8-tetrahydro-2a λ^4 -thia-2,3,4a,8a-tetraazacyclo[cd]azulene-1(2H),4(3H)-dithione

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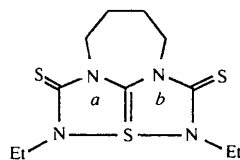
Abstract

The title compound, C₁₁H₁₈N₄S₃, contains elongated N—S bonds [1.877 (1) and 1.903 (1) \AA] which are greater by 7.9 and 9.4%, respectively, than the two-centre two-electron N—S bond [1.74 \AA ; Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19]. The lengths of corresponding bonds and the size of the corresponding bond angles in the two halves of the triheteropentalene framework are very similar, differing from one another at most by 0.027 \AA and 0.83 $^\circ$, respectively.

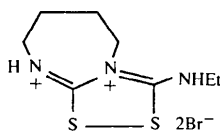
Comment

The structure determination of the title compound, (1), was carried out to establish whether the product from the reaction of the salt (2) with ethyl isothiocyanate in dichloromethane in the presence of triethylamine contains

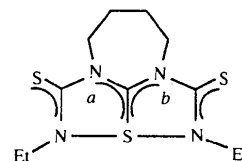
the N—S—N sequence or the S—S—S sequence, and to further investigate the effect of the bridge substituent on the *N_a* and *N_b* atoms.



(1)



(2)



(3)

The reaction product possesses structure (1) and the C(1)=S(1) bond length of 1.715 (1) Å lies between the length of a C—S single bond (1.75 Å) and that of a C=S double bond (1.63 Å) (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The C(1)—N(4) [1.342 (2) Å] and C(1)—N(3) [1.346 (2) Å] bond lengths lie between the length of a C=N double bond (1.28 Å) and that of a C—N single bond (1.48 Å) (Allen *et al.*, 1987). These data taken together indicate that N(4) and N(3) are conjugated with C(1)=S(1). The C=S bond lengths of 1.6797 (14) for C(6)=S(3) and 1.6819 (13) Å for C(7)=S(2) are smaller than the length of a C—S single bond (1.75 Å) and greater than the length of a C=S double bond (1.63 Å). The C—N bond lengths, 1.300 (2) for C(6)—N(1) and 1.291 (2) Å for C(7)—N(2), are slightly longer than a C=N double bond (1.28 Å) and much shorter than a C—N single bond (1.48 Å) (Allen *et al.*, 1987). These data imply that C(6)=S(3) and C(7)=S(2) have a conjugative interaction with the attached pairs of heteroatoms N(1) and N(2), respectively. In contrast, the lengths of the C(6)—N(4) and C(7)—N(3) bonds [both 1.428 (2) Å] are closer to the C—N single-bond length (1.48 Å) (Allen *et al.*, 1987), which indicates that there is little conjugative interaction between N(4) and C(6)=S(3) and between N(3) and C(7)=S(2).

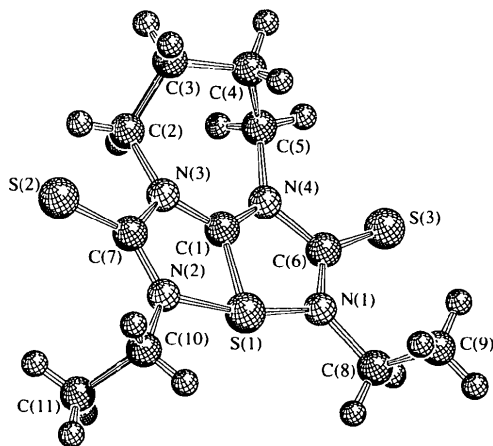


Fig. 1. Molecular structure and atomic labelling of (1).

The bonding system in (1) is thus segmented into three islands of conjugation, namely the N(1)—C(6)—S(3) unit, the N(2)—C(7)—S(2) unit and the N(3),N(4)—C(1)—S(1) unit, as depicted by (3).

Experimental

The title compound was recrystallized from a 2:1 mixture of hexane and dichloromethane as colourless crystals, m.p. 413–414 K

Crystal data

C₁₁H₁₈N₄S₃
M_r = 302.47
 Monoclinic
*P*2₁
a = 5.615 (2) Å
b = 10.0655 (10) Å
c = 13.0482 (10) Å
 β = 100.13 (2)°
V = 726.0 (3) Å³
Z = 2
D_x = 1.384 Mg m⁻³

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 15–20°
 μ = 0.499 mm⁻¹
T = 293 (2) K
 Rectangular
 0.45 × 0.37 × 0.09 mm
 Clear, colourless

Data collection

Nonius CAD-4 diffractometer
 ω -2 θ scans
 Absorption correction: analytical
 T_{\min} = 0.781, T_{\max} = 0.851
 5043 measured reflections
 5043 independent reflections

3037 observed reflections
 $[F_o > 4\sigma(F_o)]$
 θ_{\max} = 20°
h = -10 → 10
k = -1 → 18
l = -23 → 23
 3 standard reflections
 frequency: 60 min
 intensity decay: random fluctuations

Refinement

Refinement on *F*²
R(*F*) = 0.03
 $wR(F^2)$ = 0.09
S = 0.946
 5043 reflections
 165 parameters
 H atoms refined in calculated positions

$w = 1/[\sigma^2(F_o) + (0.1P)^2]$
 where $P = [\max(F_o, 0) + 2F_c^2]/3$
 $(\Delta/\sigma)_{\max}$ = 0.04
 $\Delta\rho_{\max}$ = 0.266 e Å⁻³
 $\Delta\rho_{\min}$ = -0.241 e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U _{eq}
S(1)	0.3882 (1)	0.0374	0.1650 (1)	0.046 (1)
S(2)	0.0090 (1)	0.0366 (1)	0.4312 (1)	0.063 (1)
S(3)	0.9326 (1)	-0.2501 (1)	0.1069 (1)	0.062 (1)
N(1)	0.6201 (2)	-0.0464 (2)	0.0997 (1)	0.051 (1)
N(2)	0.1745 (2)	0.0920 (2)	0.2551 (1)	0.051 (1)
N(3)	0.3619 (2)	-0.0785 (1)	0.3424 (1)	0.045 (1)
N(4)	0.6368 (2)	-0.1709 (1)	0.2408 (1)	0.044 (1)
C(1)	0.4712 (2)	-0.0816 (1)	0.2585 (1)	0.042 (1)
C(2)	0.4465 (3)	-0.1544 (2)	0.4382 (1)	0.058 (1)
C(3)	0.4003 (3)	-0.3011 (2)	0.4270 (2)	0.068 (1)
C(4)	0.4918 (3)	-0.3618 (2)	0.3336 (2)	0.066 (1)
C(5)	0.7085 (3)	-0.2897 (2)	0.3050 (1)	0.056 (1)
C(6)	0.7255 (2)	-0.1507 (2)	0.1459 (1)	0.047 (1)
C(7)	0.1803 (2)	0.0217 (2)	0.3383 (1)	0.048 (1)
C(8)	0.6482 (4)	-0.0020 (2)	-0.0040 (1)	0.065 (1)
C(9)	0.4791 (5)	-0.0771 (3)	-0.0862 (2)	0.089 (1)
C(10)	0.0155 (3)	0.2059 (2)	0.2264 (1)	0.060 (1)
C(11)	0.1037 (4)	0.3286 (2)	0.2873 (2)	0.084 (1)

Table 2. Selected geometric parameters (Å, °)

S(1)—C(1)	1.7149 (13)	N(2)—C(7)	1.291 (2)
S(1)—N(1)	1.8765 (13)	N(3)—C(11)	1.346 (2)
S(1)—N(2)	1.9032 (14)	N(3)—C(7)	1.428 (2)
S(2)—C(7)	1.6819 (13)	N(4)—C(1)	1.342 (2)
S(3)—C(6)	1.6797 (14)	N(4)—C(6)	1.428 (2)
N(1)—C(6)	1.300 (2)		
C(1)—S(1)—N(1)	83.44 (6)	N(4)—C(1)—S(1)	117.06 (9)
C(1)—S(1)—N(2)	83.33 (6)	N(3)—C(1)—S(1)	117.18 (10)
N(1)—S(1)—N(2)	166.77 (6)	N(1)—C(6)—N(4)	108.51 (12)
C(6)—N(1)—S(1)	116.61 (9)	N(1)—C(6)—S(3)	128.63 (11)
C(7)—N(2)—S(1)	115.82 (11)	N(4)—C(6)—S(3)	122.87 (11)
C(1)—N(3)—C(7)	114.20 (12)	N(2)—C(7)—N(3)	109.34 (11)
C(1)—N(4)—C(6)	114.31 (11)	N(2)—C(7)—S(2)	128.59 (12)
N(4)—C(1)—N(3)	125.75 (12)	N(3)—C(7)—S(2)	122.07 (11)

Data collection was carried out using standard Enraf-Nonius routines. Data reduction was performed using the PC version of *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) and refined using *SHELXL93* (Sheldrick, 1993). During refinement cognizance was taken of the non-centrosymmetric space group of the compound. Refinement of the Flack (1983) absolute structure parameter gave a value of -0.12950, indicating that this is the 'correct' absolute structure of the compound. Refinement of the enantiomorphic structure resulted in slightly higher figures of merit and an absolute structure parameter of 0.55 (5). H atoms were placed in geometrically calculated positions and allowed to refine, riding on the atoms to which they are attached, with a common isotropic displacement parameter. The labelled structure diagram was produced using *SCHAKAL88* (Keller, 1988).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Three BEDT-TTF Salts

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Abstract

The crystal structures of 3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium hexafluorophosphate chloroacetyl chloride solvate, (1), C₁₀H₈S₈^{1/2+} · ½PF₆⁻ · ½C₂H₂Cl₂O, 3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium hexafluorophosphate tetrahydrofuran solvate, (2), C₁₀H₈S₈⁺ · PF₆⁻ · ½C₄H₈O, and 3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium perchlorate, (3), C₁₀H₈S₈⁺ · ClO₄⁻, have been determined. Compounds (1) and (2) crystallize in the *P* $\bar{1}$ space group. The structure of (1) consists of layers of BEDT-TTF ions separated by planes of PF₆⁻ ions and chloroacetyl chloride molecules. The BEDT-TTF ions are stacked in a face-to-face manner with short S ··· S contacts linking these stacks. Compound (2) consists of layers of BEDT-TTF face-to-face dimers with PF₆⁻ ions and tetrahydrofuran (THF) molecules filling cavities separating these layers. As in compound (1), there are short S ··· S contacts between dimers resulting from the side-by-side mode of packing. Compound (3) crystallizes in the *C*2/*m* space group and consists of layers of BEDT-TTF ions, stacked in a staggered side-by-side manner with one type of S ··· S contact, separated by layers of perchlorate ions.

Comment

Cation radical salts of the organic donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) are of current interest as several compositions are examples of conducting and superconducting molecular solids (Adrian &