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3,5-Diphenyl-2-(2-pyridylamino)-1-thia-6,6aλ^4-diselenapentalene

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Abstract

Crystals of the title compound, $C_{22}H_{16}N_2SSe_2$, contain two crystallographically independent molecules in the unit cell. The Se—Se and Se—S bonds are long [Se—Se 2.465 (2), 2.488 (2); Se—S 2.498 (3), 2.495 (3) Å] and the Se—Se—S bond angle is wide [173.6 (4), 174.09 (4)°]. All other bond angles in the triheteropentalene framework are intermediate between those of corresponding single and double bonds. The pyridine ring and the phenyl substituents are twisted out of the plane of the triheteropentalene unit.

Comment

The title compound, (1), was obtained by the cyclo-addition of 2-pyridylisothiocyanate to 3-benzylidene-5-phenyl-3H-1,2-diselenole, (2), a member of a new class of heterocyclic compounds, according to a new synthesis of 1,6,6aλ^4-triheteropentalenes (Rose, 1991). The structure determination was carried out to determine whether the cycloaddition had produced (1) or the isomeric compound (3).
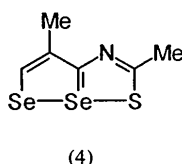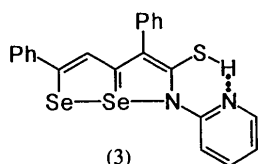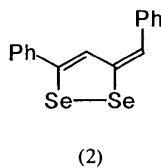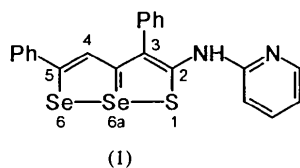
Crystals of (1) contain two independent molecules (A and B) in the unit cell. (1) shows the characteristic structural features of 1,6,6aλ^4-triheteropentalenes. The Se—Se bond lengths [2.465 (2) Å in molecule A, 2.488 (2) Å in B] are greater than the standard length of a two-centre two-electron Se—Se covalent bond (2.34 Å; Allen, Kennard et al., 1987) by 5.3 (A) and 6.4% (B). Likewise, the Se—S bonds [2.498 (3) in A, 2.495 (3) Å in B] are longer than the two-centre two-electron Se—S covalent bond (2.193 Å; Allen, Kennard et al., 1987) by 14 (A) and 13.8% (B). The Se—Se—S bond angle is wide [173.6 (4) in A, 174.09 (4)° in B], tending towards a collinear arrangement of the heteroatom sequence.
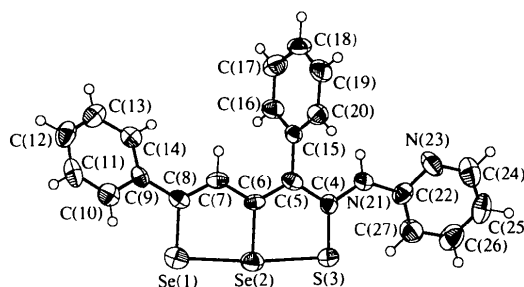

Fig. 1. *ORTEP* (Johnson, 1965; Davenport, Hall & Dreissig, 1992) diagram of molecule A showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

The C(8)—Se(1) bond length [1.854 (5) in A, 1.861 (5) Å in B] and the C(6)—Se(2) bond length [1.879 (5) in A, 1.873 (5) Å in B] are intermediate between the length of a C—Se single bond (1.97 Å; Allen, Kennard et al., 1987) and the estimated length of a C—Se bond in tetramethyl selenourea [1.863 (4) Å; Foss & Maartmann-Moe, 1987]. The C(4)—S bond length [1.681 (6) in A, 1.682 (6) Å in B] is almost the same as the C—S bond length in thioureas (1.68 Å; Allen, Kennard et al., 1987). The Se—Se, Se—S, C—Se and C—S bond lengths and the Se—Se—S bond angle in (1) are very similar to the corresponding dimensions in the heterocycle (4) (Allen, Boeyens et al., 1987). The pyridine ring and the phenyl substituents are twisted out of the plane of the triheteropentalene unit.

(1)   (2)

(3)   (4)

Experimental

The title compound was recrystallized from cyclohexane as red needle-shaped crystals, m.p. 482–483 K.

Crystal data

$C_{22}H_{16}N_2SSe_2$ Mo $K\alpha$ radiation
$M_r = 498.35$ $\lambda = 0.71067$ Å

$C_{22}H_{16}N_2SSe_2$

Triclinic
$P\bar{1}$
$a = 8.586\,(8)$ Å
$b = 15.286\,(11)$ Å
$c = 15.606\,(8)$ Å
$\alpha = 94.57\,(4)°$
$\beta = 92.31\,(4)°$
$\gamma = 100.58\,(4)°$
$V = 2004\,(3)$ Å^3
$Z = 4$
$D_x = 1.652$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 9–17°$
$\mu = 3.761$ mm^{-1}
$T = 295\,(2)$ K
Flat needle
$0.5 \times 0.2 \times 0.06$ mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scan (North, Phillips & Mathews, 1968)
  $T_{min} = 0.70$, $T_{max} = 1.00$
11147 measured reflections
9951 independent reflections

3833 observed reflections
  $[F_o > 4\sigma(F_o)]$
$R_{int} = 0.05$
$\theta_{max} = 30°$
$h = -12 \rightarrow 12$
$k = -21 \rightarrow 21$
$l = -1 \rightarrow 15$
3 standard reflections
  frequency: 60 min
  intensity decay: random

Refinement

Refinement on F^2
$R(F) = 0.055$
$wR(F^2) = 0.1576$
$S = 0.895$
9951 reflections
488 parameters
$w = 1/[s^2(F_o^2) + 0.0799P)^2]$
  where $P = [\max(F_o^2,0) + 2F_c^2]/3$

$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.813$ e Å^{-3}
$\Delta\rho_{min} = -0.715$ 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* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Se(1A)	0.4853 (1)	-0.0253 (1)	0.2077 (1)	0.065 (1)
Se(2A)	0.6717 (1)	0.1191 (1)	0.2261 (1)	0.050 (1)
S(3A)	0.8539 (2)	0.2668 (1)	0.2273 (1)	0.048 (1)
C(4A)	0.7570 (6)	0.2982 (4)	0.1427 (3)	0.038 (1)
C(5A)	0.6144 (7)	0.2423 (4)	0.1061 (3)	0.039 (1)
C(6A)	0.5587 (6)	0.1587 (4)	0.1359 (3)	0.034 (1)
C(7A)	0.4228 (6)	0.1001 (4)	0.0982 (3)	0.037 (1)
C(8A)	0.3714 (7)	0.0153 (4)	0.1206 (3)	0.035 (1)
C(9A)	0.2337 (6)	-0.0474 (3)	0.0798 (3)	0.036 (1)
C(10A)	0.1409 (7)	-0.1108 (4)	0.1258 (4)	0.049 (2)
C(11A)	0.0128 (8)	-0.1663 (4)	0.0873 (5)	0.057 (2)
C(12A)	-0.0255 (8)	-0.1657 (5)	0.0022 (5)	0.060 (2)
C(13A)	0.0604 (7)	-0.1074 (5)	-0.0459 (4)	0.054 (2)
C(14A)	0.1893 (7)	-0.0483 (4)	-0.0068 (4)	0.044 (2)
C(15A)	0.5245 (6)	0.2726 (4)	0.0337 (3)	0.036 (1)
C(16A)	0.5193 (7)	0.2353 (4)	-0.0488 (3)	0.043 (2)
C(17A)	0.4361 (7)	0.2653 (5)	-0.1137 (4)	0.056 (2)
C(18A)	0.3630 (7)	0.3357 (5)	-0.0975 (4)	0.058 (2)
C(19A)	0.3670 (8)	0.3760 (5)	-0.0163 (4)	0.059 (2)
C(20A)	0.4454 (7)	0.3442 (4)	0.0503 (4)	0.046 (2)
N(21A)	0.8086 (6)	0.3764 (3)	0.1068 (3)	0.047 (1)
C(22A)	0.9429 (7)	0.4426 (4)	0.1246 (4)	0.046 (2)
N(23A)	0.9228 (7)	0.5200 (4)	0.0970 (4)	0.060 (2)
C(24A)	1.0458 (10)	0.5859 (5)	0.1086 (5)	0.072 (2)
C(25A)	1.1878 (9)	0.5815 (5)	0.1473 (5)	0.068 (2)
C(26A)	1.2084 (8)	0.5019 (6)	0.1726 (4)	0.067 (2)
C(27A)	1.0859 (8)	0.4304 (5)	0.1626 (4)	0.058 (2)
Se(1B)	-0.0913 (1)	-0.0609 (1)	0.2891 (1)	0.059 (1)
Se(2B)	0.1025 (1)	0.0785 (1)	0.2726 (1)	0.045 (1)
S(3B)	0.2876 (2)	0.2246 (1)	0.2703 (1)	0.050 (1)
C(4B)	0.2171 (7)	0.2700 (4)	0.3589 (3)	0.041 (1)
C(5B)	0.0873 (7)	0.2215 (4)	0.3991 (3)	0.037 (1)
C(6B)	0.0226 (6)	0.1325 (4)	0.3690 (3)	0.034 (1)
C(7B)	-0.1041 (6)	0.0818 (4)	0.4084 (3)	0.039 (1)
C(8B)	-0.1689 (7)	-0.0057 (4)	0.3846 (3)	0.037 (1)
C(9B)	-0.2936 (7)	-0.0593 (4)	0.4300 (4)	0.038 (1)
C(10B)	-0.4012 (8)	-0.1308 (4)	0.3874 (4)	0.050 (2)
C(11B)	-0.5164 (8)	-0.1800 (4)	0.4299 (5)	0.060 (2)
C(12B)	-0.5292 (8)	-0.1616 (5)	0.5154 (5)	0.062 (2)
C(13B)	-0.4268 (8)	-0.0932 (5)	0.5598 (4)	0.056 (2)
C(14B)	-0.3085 (7)	-0.0420 (4)	0.5184 (4)	0.042 (2)
C(15B)	0.0219 (6)	0.2668 (4)	0.4747 (3)	0.037 (1)
C(16B)	0.0407 (7)	0.2423 (4)	0.5557 (4)	0.048 (2)
C(17B)	-0.0233 (8)	0.2846 (5)	0.6247 (4)	0.066 (2)
C(18B)	-0.1015 (8)	0.3515 (5)	0.6131 (5)	0.061 (2)
C(19B)	-0.1177 (8)	0.3793 (5)	0.5328 (5)	0.064 (2)
C(20B)	-0.0590 (7)	0.3359 (4)	0.4624 (4)	0.053 (2)
N(21B)	0.2828 (6)	0.3547 (3)	0.3952 (3)	0.054 (1)
C(22B)	0.4085 (7)	0.4167 (4)	0.3732 (4)	0.047 (2)
N(23B)	0.3973 (6)	0.5001 (4)	0.4021 (4)	0.059 (2)
C(24B)	0.5169 (10)	0.5645 (5)	0.3882 (5)	0.078 (2)
C(25B)	0.6451 (9)	0.5530 (6)	0.3461 (6)	0.083 (2)
C(26B)	0.6596 (9)	0.4691 (6)	0.3185 (5)	0.083 (2)
C(27B)	0.5407 (8)	0.3981 (5)	0.3334 (5)	0.070 (2)

Table 2. *Selected geometric parameters* (Å, °)

Se(1A)—C(8A)	1.854 (5)	Se(1B)—C(8B)	1.861 (5)
Se(1A)—Se(2A)	2.465 (2)	Se(1B)—Se(2B)	2.488 (2)
Se(2A)—C(6A)	1.879 (5)	Se(2B)—C(6B)	1.873 (5)
Se(2A)—S(3A)	2.498 (3)	Se(2B)—S(3B)	2.495 (3)
S(3A)—C(4A)	1.681 (6)	S(3B)—C(4B)	1.682 (6)
C(4A)—C(5A)	1.427 (8)	C(4B)—C(5B)	1.417 (8)
C(5A)—C(6A)	1.402 (8)	C(5B)—C(6B)	1.408 (8)
C(6A)—C(7A)	1.410 (7)	C(6B)—C(7B)	1.409 (8)
C(7A)—C(8A)	1.369 (8)	C(7B)—C(8B)	1.366 (8)
C(8A)—Se(1A)—Se(2A)	90.6 (2)	C(8B)—Se(1B)—Se(2B)	90.5 (2)
C(6A)—Se(2A)—Se(1A)	89.2 (2)	C(6B)—Se(2B)—Se(1B)	88.8 (2)
C(6A)—Se(2A)—S(3A)	85.2 (2)	C(6B)—Se(2B)—S(3B)	85.4 (2)
Se(1A)—Se(2A)—S(3A)	173.60 (4)	Se(1B)—Se(2B)—S(3B)	174.09 (4)
C(4A)—S(3A)—Se(2A)	93.9 (2)	C(4B)—S(3B)—Se(2B)	93.4 (2)
C(5A)—C(4A)—S(3A)	119.6 (4)	C(5B)—C(4B)—S(3B)	120.5 (5)
C(6A)—C(5A)—C(4A)	121.2 (5)	C(6B)—C(5B)—C(4B)	120.5 (5)
C(5A)—C(6A)—C(7A)	122.5 (5)	C(7B)—C(6B)—C(5B)	122.0 (5)
C(5A)—C(6A)—Se(2A)	119.9 (4)	C(8B)—C(7B)—C(6B)	125.1 (5)
C(7A)—C(6A)—Se(2A)	117.5 (4)	C(7B)—C(8B)—Se(1B)	117.7 (4)
C(8A)—C(7A)—C(6A)	124.4 (5)		
C(7A)—C(8A)—Se(1A)	118.2 (4)		

Se(1A)—C(8A)—C(9A)—C(10A)	32.8 (7)
C(4A)—C(5A)—C(15A)—C(16A)	108.3 (6)
C(5A)—C(4A)—N(21A)—C(22A)	-177.2 (6)
C(4A)—N(21A)—C(22A)—C(27A)	25 (1)
Se(1B)—C(8B)—C(9B)—C(10B)	-29.0 (7)
C(4B)—C(5B)—C(15B)—C(16B)	-110.1 (6)
C(5B)—C(4B)—N(21B)—C(22B)	178.7 (6)
C(4B)—N(21B)—C(22B)—C(27B)	-30 (1)

Data collection and reduction were carried out using standard Enraf–Nonius routines. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) and refined by full-matrix least-squares methods using *SHELXL93* (Sheldrick, 1993). H atoms were placed in geometrically calculated positions and allowed to refine, riding on the atoms to which they are attached and with a common isotropic displacement parameter. The labelled structure diagrams were produced using *ORTEP* (Johnson, 1965) as modified by Davenport, Hall & Dreissig (1992).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1131). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Structure with Through-Space Cyclopropyl π-Interaction

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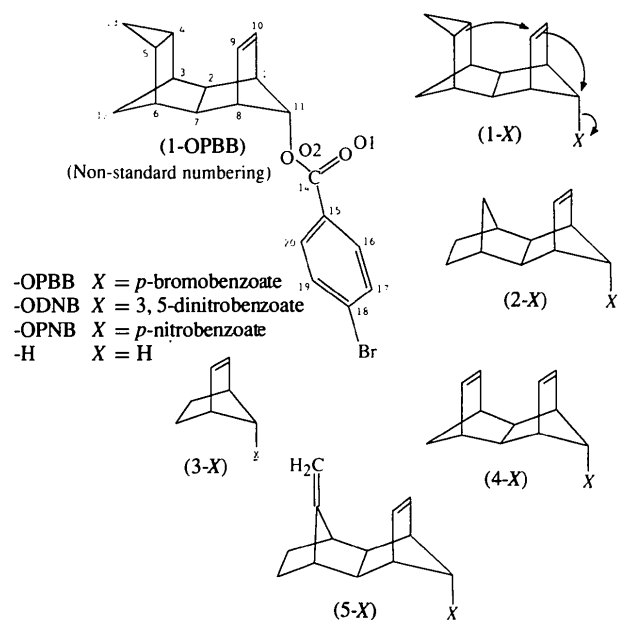*Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA*

Abstract

The crystal structure determination of *endo,endo*-pentacyclo[7.2.1.1^{3,7}.0^{2,8}.0^{4,6}]tridec-10-en-*anti*-12-yl *p*-bromobenzoate, $C_{20}H_{19}BrO_2$ (1-OPBB), is reported. The molecule consists of norbornene with an *anti-p*-bromobenzoate substituent at the methano bridge, and with an *endo*-norbornyl unit *endo*-fused to the ethano bridge. The norbornyl unit also has an *exo*-cyclopropyl ring on the two-C-atom bridge opposite the ring

† Deceased, 8th July 1991.

fusion. Interbridge steric interactions are discussed, and some comparisons are made with other norbornenyl derivatives.

Comment

A variety of compounds having cyclopropyl π-orbital interactions have been studied theoretically and spectroscopically (Hoffmann, Hauel & Landmann, 1983; Martin & Mayer, 1983; Elsässer, Hassenrück, Martin, Mayer, Lutz & Prinzbach, 1991). The cyclopropyl π-interaction in hydrocarbon (1-H) is substantial (Prinzbach, Sedelmeier & Martin, 1977). The magnitude of the interaction is very dependent on the orbital geometries and is linked to reactivity in anchimerically assisted solvolysis reactions (March, 1992).

(1-OPBB)
(Non-standard numbering)

-OPBB X = *p*-bromobenzoate
-ODNB X = 3,5-dinitrobenzoate
-OPNB X = *p*-nitrobenzoate
-H   X = H

(1-X)

(2-X)

(3-X)

(4-X)

(5-X)

Solvolysis reactions have been followed via ^{1}H NMR spectroscopy for a few norbornenyl 3,5-dinitrobenzoate structures at 383 K in 80% dioxane-D_8/20% D_2O (*v/v*) (Lloyd, 1985). Under these conditions, esters (1-ODNB), (2-ODNB), (4-ODNB) and (5-ODNB) undergo solvolysis reactions 480, 28, 160 and 30 times faster, respectively, than the already enormously reactive *anti*-7-norbornenyl ester (3-ODNB). The rate enhancement of (1-ODNB) over (3-ODNB) is likely due (at least in part) to 'π'-electron donation from a cyclopropyl Walsh HOMO [see electron arrows for (1-ODNB) above] to the reaction center (C11 LUMO) via relay through the C9=C10 π bond (HOMO). The ribbon topologies require that the through-space interactions should destabilize the reactant and stabilize the transition state leading to the carbocation intermediate for (1-ODNB) relative to (3-ODNB) (Inagaki, Fujimoto