

Acta Cryst. (1995). **C51**, 2402–2404

4,4'-Dimethyl-1,1'-bi(1,2,3,5-diselenadiazole)

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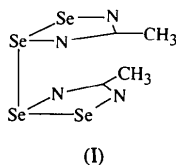
(Received 3 January 1995; accepted 10 May 1995)

Abstract

The radical units Se₂N₂CMe dimerize with long Se···Se distances of 3.159(3) and 3.187(3) Å to give the title compound, C₄H₆N₄Se₄. There are two crystallographically independent dimers in the unit cell. The dimers adopt a twisted conformation with parallel ring planes. One ring is rotated on the axis between ring centers by approximately 90° from the eclipsed position to give Se—Se—Se—Se torsion angles of 86.81(15) and 88.95(17)°. Se—Se bond lengths within the radicals vary from 2.306(3) to 2.330(3) Å.

Comment

Interest in the solid-state structure of the title compound arose from a program (Cordes, Haddon & Oakley, 1992) of studies on the use of neutral π radicals in forming new molecular conductor materials.



The conformation of the dimers is similar to that found for the CF₃ (Höfs *et al.*, 1985), Me (Banister, Hansford, Hauptman, Wait & Clegg, 1989) and NMe₂ (Cordes, Goddard, Oakley & Westwood, 1989) derivatives of the dithia (S instead of Se) radicals. Apparently, the steric requirements of the methyl groups prevent an eclipsed cofacial alignment of the monomers, even with the longer dimer linkages provided by the Se···Se interactions.

The dihedral angles between the planes of the heterocyclic rings in the dimers are 2.6(3) and 3.8(3)°. The Se—Se distances in these radicals are within 0.035 Å of the values found for the phenyl analog (Del Bel Bel-luz *et al.*, 1989), the hydrogen analog (Cordes *et al.*, 1992) and the 2-, 3- and 4-cyanophenyl analogs (Cordes,

Haddon, Hicks, Oakley & Palstra, 1992). The 3.159(3) and 3.187(3) Å Se···Se distances of the dimers are 0.1 to 0.2 Å shorter than the corresponding distances in the above mentioned analogs, which are all cofacially dimerized with two Se···Se linkages. In all of these structures there are also inter-dimer Se···Se contacts of less than the van der Waals separations; contacts less than 3.7 Å in the current structure are included in Table 2. The packing diagram (Fig. 2) shows that these interactions produce a structure that is layered with respect to the heterocyclic rings and the methyl groups.

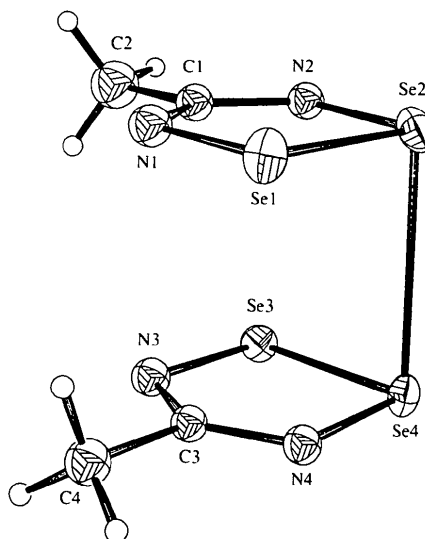


Fig. 1. An ORTEPII (Johnson, 1976) drawing (30% ellipsoids) of one of the two independent dimers, showing the numbering scheme.

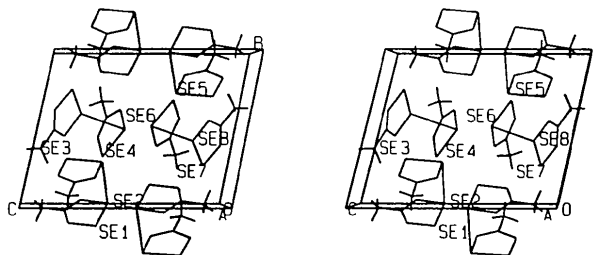


Fig. 2. Stereo projection of the unit-cell contents onto the *yz* plane.

Experimental

Preparation of the title compound, (I), was by reduction of the corresponding diselenadiazoline cation with triphenylantimony; the cation was prepared by the condensation of acetamide with selenium dichloride. Crystals were grown by sublimation *in vacuo*.

Crystal data

C₄H₆N₄Se₄
M_r = 425.96

Mo K α radiation
 λ = 0.71073 Å

Acta Crystallographica Section C
ISSN 0108-2701 ©1995

Triclinic
 $P\bar{1}$
 $a = 8.6495 (14) \text{ \AA}$
 $b = 9.857 (2) \text{ \AA}$
 $c = 12.375 (3) \text{ \AA}$
 $\alpha = 102.11 (2)^\circ$
 $\beta = 89.77 (2)^\circ$
 $\gamma = 104.65 (2)^\circ$
 $V = 996.7 (4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 2.84 \text{ Mg m}^{-3}$

Data collection

Enraf-Nonius CAD-4
 diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 ψ scans of 3 reflections
 $T_{\min} = 0.40$, $T_{\max} = 0.99$
 3712 measured reflections
 3493 independent reflections
 1803 observed reflections
 $[I > 3\sigma(I)]$

Refinement

Refinement on F
 $R = 0.047$
 $wR = 0.064$
 $S = 0.98$
 1803 reflections
 137 parameters
 H-atom parameters not
 refined
 $w = 1/[\sigma^2(F) + 0.0025F^2]$

Cell parameters from 25
 reflections
 $\theta = 8.00\text{--}12.00^\circ$
 $\mu = 14.5 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Thin needle
 $0.48 \times 0.22 \times 0.07 \text{ mm}$
 Black

$R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 24.92^\circ$
 $h = -10 \rightarrow 9$
 $k = 0 \rightarrow 11$
 $l = -14 \rightarrow 14$
 3 standard reflections
 frequency: 60 min
 intensity decay: 1.4%

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.14 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.98 \text{ e \AA}^{-3}$
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV, Table
 2.2B)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Se1—Se2	2.330 (2)	N1—C1	1.35 (2)
Se1—N1	1.799 (14)	N2—C1	1.36 (2)
Se2—N2	1.798 (13)	N3—C3	1.36 (2)
Se3—Se4	2.308 (2)	N4—C3	1.32 (2)
Se3—N3	1.787 (13)	N5—C5	1.32 (2)
Se4—N4	1.806 (12)	N6—C5	1.36 (2)
Se5—Se6	2.330 (3)	N7—C7	1.32 (2)
Se5—N5	1.798 (13)	N8—C7	1.35 (2)
Se6—N6	1.776 (15)	C1—C2	1.45 (3)
Se7—Se8	2.306 (3)	C3—C4	1.48 (2)
Se7—N7	1.793 (13)	C5—C6	1.52 (3)
Se8—N8	1.779 (15)	C7—C8	1.52 (2)
Se1...Se4 ⁱ	3.339 (3)	Se2...Se5 ⁱⁱ	3.560 (3)
Se1...Se6 ⁱ	3.666 (3)	Se6...Se6 ⁱⁱⁱ	3.630 (4)
Se2—Se1—N1	90.8 (4)	Se7—N7—C7	115.3 (11)
Se1—Se2—N2	91.8 (4)	Se8—N8—C7	114.8 (12)
Se4—Se3—N3	91.6 (4)	N1—C1—N2	125.4 (14)
Se3—Se4—N4	91.6 (4)	N1—C1—C2	117.5 (15)
Se6—Se5—N5	89.8 (4)	N2—C1—C2	117.0 (14)
Se5—Se6—N6	93.0 (5)	N3—C3—N4	128.2 (13)
Se8—Se7—N7	91.2 (4)	N3—C3—C4	115.7 (14)
Se7—Se8—N8	91.8 (5)	N4—C3—C4	116.1 (13)
Se1—N1—C1	116.5 (11)	N5—C5—N6	129.0 (15)
Se2—N2—C1	115.5 (10)	N5—C5—C6	116.5 (15)
Se3—N3—C3	114.2 (11)	N6—C5—C6	114.4 (15)
Se4—N4—C3	114.2 (10)	N7—C7—N8	127.0 (15)
Se5—N5—C5	115.6 (11)	N7—C7—C8	117.9 (14)
Se6—N6—C5	112.7 (12)	N8—C7—C8	115.1 (15)

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $-x, 1 - y, 1 - z$.

The data crystal was sealed in an epoxy-filled capillary tube. The scan widths were $(1.0 + 0.35\tan\theta)^\circ$, with scan speeds of $4\text{--}16^\circ \text{ min}^{-1}$. The total exposure time was 25.8 h. The structure was solved by direct methods. The H atoms were constrained to idealized (C—H 0.95 \AA) positions where the orientation of the methyl group was determined by difference maps. Each H atom was assigned an isotropic U value of 0.01 \AA^2 plus U of the attached C atom.

Data collection: *CAD-4-PC* (Enraf-Nonius, 1993). Cell refinement: *CAD-4-PC*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *NRCVAX TABLES* (Version of Jan 94).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1120). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

	$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$			
	x	y	z	U_{eq}
Se1	0.0681 (2)	−0.14452 (19)	0.59643 (16)	0.0410 (10)
Se2	0.3083 (2)	0.0108 (2)	0.56611 (16)	0.0406 (10)
Se3	0.23855 (18)	0.29859 (18)	0.81770 (15)	0.0345 (10)
Se4	0.16599 (18)	0.28013 (18)	0.63484 (14)	0.0339 (9)
Se5	0.3604 (2)	0.68378 (19)	0.35278 (16)	0.0407 (10)
Se6	0.1840 (2)	0.5106 (2)	0.42745 (17)	0.0489 (12)
Se7	0.1304 (2)	0.25361 (19)	0.12919 (16)	0.0410 (11)
Se8	−0.01901 (19)	0.4132 (2)	0.19734 (18)	0.0464 (12)
N1	0.1311 (15)	−0.1230 (15)	0.7387 (12)	0.039 (3)
N2	0.3803 (14)	0.0366 (14)	0.7070 (11)	0.032 (3)
N3	0.0506 (14)	0.1824 (14)	0.8380 (11)	0.035 (3)
N4	−0.0308 (14)	0.1690 (14)	0.6491 (11)	0.031 (3)
N5	0.4826 (14)	0.5610 (14)	0.3107 (11)	0.034 (3)
N6	0.2959 (17)	0.3818 (17)	0.3859 (13)	0.048 (4)
N7	0.2648 (15)	0.3860 (15)	0.0701 (12)	0.038 (3)
N8	0.1099 (16)	0.5515 (16)	0.1429 (13)	0.045 (4)
C1	0.2786 (17)	−0.0365 (17)	0.7717 (14)	0.032 (4)
C2	0.331 (2)	−0.015 (2)	0.8869 (18)	0.058 (5)
C3	−0.0529 (17)	0.1374 (16)	0.7471 (13)	0.028 (4)
C4	−0.2112 (19)	0.0423 (19)	0.7615 (15)	0.041 (4)
C5	0.4295 (19)	0.4333 (19)	0.3337 (15)	0.038 (4)
C6	0.526 (2)	0.325 (2)	0.2937 (17)	0.055 (5)
C7	0.2329 (18)	0.5133 (19)	0.0876 (14)	0.035 (4)
C8	0.344 (2)	0.631 (2)	0.0418 (16)	0.048 (5)

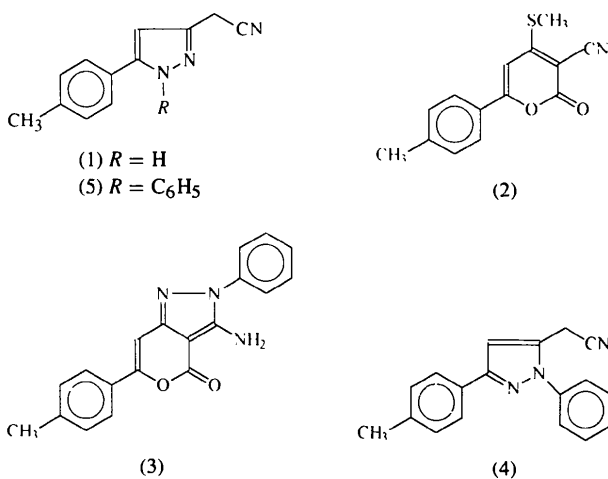
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Acta Cryst. (1995). **C51**, 2404–2406

5-Cyanomethyl-3-(4-methylphenyl)-1-phenylpyrazole

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(Received 1 March 1995; accepted 13 June 1995)

Abstract

The title nitrile, 3-(4-methylphenyl)-1-phenylpyrazole-5-acetonitrile, C₁₈H₁₅N₃, is one of the products obtained from the reaction of 3-cyano-6-(4-methylphenyl)-4-methylthio-2-oxo-2H-pyran with phenylhydrazine. The asymmetric unit contains two almost identical molecules differing only in the orientations of the phenyl and methylphenyl groups with respect to the planar pyrazole nucleus.

Comment

Owing to the widespread applications of pyrazole derivatives in medicinal, agricultural and synthetic chemistry (Kurowski, Dunky & Geddawi, 1986; Rosiere & Grossman, 1951; Seki, Watanabe & Suga, 1988; Chauhan, Singh & Chatterjee, 1993), we have synthesized a large number of novel compounds containing the pyrazole nucleus. One of our compounds, (1), showed significant anti-invasive activity against solid tumours. In order to establish the structure–activity relationship, several analogues of (1), including the title compound, (4), have been synthesized.

The reaction of 3-cyano-6-(4-methylphenyl)-4-methylthio-2-oxo-2H-pyran, (2), with phenylhydrazine produced two *N*-phenylpyrazoles. One of these was unequivocally identified as (3) from a detailed analysis of its spectral data. However, the position of the phenyl ring in the second compound remained unclear; that is, the compound was either (4) or (5). This X-ray investigation was undertaken to remove this ambiguity.

The asymmetric unit contains two molecules of (4), one of which is illustrated in Fig. 1. The corresponding bond lengths for these two molecules are the same within experimental error and in each case the pyrazole nucleus is flat. The main difference between these molecules is in the orientation of the peripheral aromatic groups relative to the plane of the pyrazole nucleus. In the first molecule the phenyl and methylphenyl groups are inclined at angles of 59.5 (1) and 15.7 (2)^o, respectively, relative to the plane of the pyrazole ring; the corresponding values for the second molecule are 51.8 (1) and 17.1 (2)^o. All of the bond lengths and angles are unexceptional; specifically the cyanide group is essentially linear with an average C—C—N angle of 179.3 (5)^o. There are no unusual intermolecular interactions.

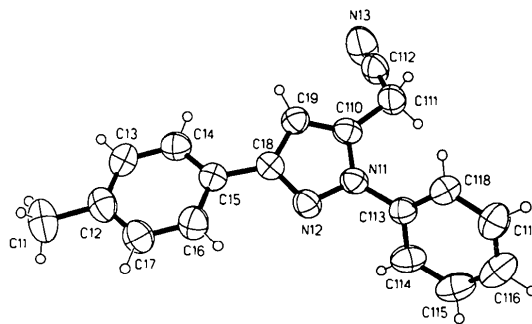


Fig. 1. View of one molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 30% probability level. The second molecule has an analogous numbering scheme.