Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1215). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 887-889

An Orthorhombic Polymorph of 2,2′-Dipyridyl Diselenide†

SIMON DUNNE,[a] ELLAK VON NAGY-FELSOBUKI[b] AND MAUREEN MACKAY[c]

[a]*Department of Organic Chemistry, Royal Institute of Chemistry, S-100 44 Stockholm, Sweden,* [b]*Department of Chemistry, The University of Newcastle, Callaghan, NSW 2308, Australia, and* [c]*School of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia. E-mail: xraymm2@lure.latrobe.edu.au*

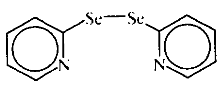
(*Received 1 August 1997; accepted 27 November 1997*)

Abstract

X-ray analysis has established the crystal structure of a non-centrosymmetric polymorph of 2,2′-dipyridyl diselenide, $C_{10}H_8N_2Se_2$, at ambient temperature. The molecular structure is very similar to the low-temperature structure of the centrosymmetric monoclinic form reported recently. The crystal packing in the two polymorphs is compared.

Comment

As part of an ongoing study of the dipyridyl chalcogenides exploring the factors governing the geometry of dichalcogenide linkages, we have determined the crystal structure of an orthorhombic polymorph of 2,2′-dipyridyl diselenide, (I), recrystallized from petroleum ether (b.p. 313–343 K). A non-centrosymmetric space group was indicated clearly by the statistical averages for the normalized structure amplitudes, for which the experimental $<|E^2-1|>$ value was 0.740 (Karle *et al.*, 1965). This was subsequently confirmed by successful refinement in the non-centrosymmetric space group $Pna2_1$. After we had completed our analysis, we became aware of a report of the crystal structure of a monoclinic form at 173 K (Kienitz *et al.*, 1996). The crystals of the monoclinic form were grown from diethyl ether/light petroleum (b.p. 303–313 K) at 243 K, and belonged to the centrosymmetric space group $P2_1/c$. We report here the crystal structure of the orthorhombic polymorph and compare it with that of the monoclinic form.



(I)

The molecular structures of the polymorphs are almost identical. The C—Se—Se—C torsion angles are 84.3 (2) and −83.6 (3)° in the monoclinic and orthorhombic forms, respectively, and the Se—Se bonds lie close to each pyridyl ring plane. In fact, in the monoclinic structure the two bonds lie within the ring planes as indicated by the torsion angles Se′—Se—C2—C3 −0.8 (6)° and Se—Se′—C2′—C3′ 0.6 (5)°. In the orthorhombic structure, the Se—Se bond lies within one of the ring planes [torsion angle Se1—Se1′—C2′—C3′ 0.6 (6)°], but it is significantly displaced from the other ring plane [Se1′—Se1—C2—C3 4.7 (6)°]. This appears to be the major conformational difference between the two polymorphs and must be a consequence of the different packing modes in the two crystal forms. It is of interest to note that in diphenyl diselenide the two torsion angles are 2.4 and 23.9° (Marsh, 1952) and in 4,4′-dinitrophenyl diselenide the Se—Se bond is significantly displaced from each aromatic plane as reflected in the torsion angles of 23.3° (Morris & Einstein, 1986); those of all other reported diaryl diselenides lie in the range 55–90°. A coplanar arrangement of the rings and the Se—Se bond should minimize unfavourable repulsions between the Se atom lone pairs and the π-electron system of the aromatic

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† Alternative name: 2,2′-diselenodipyridine.

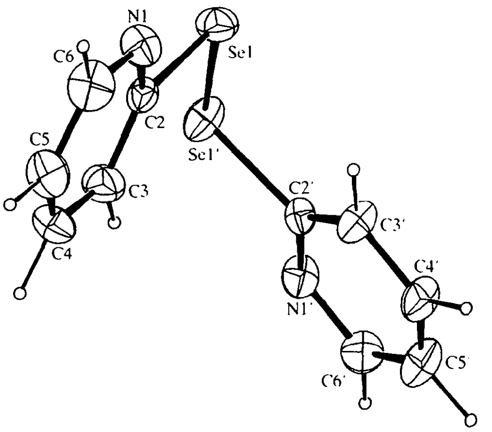
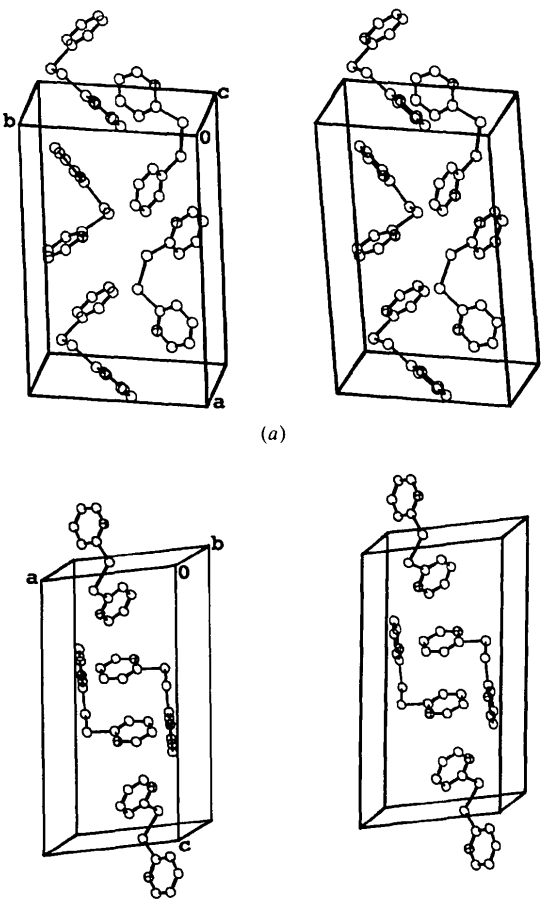


Fig. 1. A perspective view of the molecular structure of the orthorhombic polymorph of 2,2′-dipyridyl diselenide with displacement ellipsoids scaled to 50% probability. H atoms are represented by spheres of arbitrary radii.



(*a*)

(*b*)

Fig. 2. Stereoviews of the crystal packing in (*a*) the orthorhombic polymorph and (*b*) the monoclinic polymorph of 2,2′-dipyridyl diselenide.

rings, as would a perpendicular alignment, where a second minimum should exist. In the case of the diaryl disulfides, the distribution of the S—S—C—C(N) torsion angles is clustered tightly around both 0 and 90° (Shefter, 1970; Van Wart *et al.*, 1975) in line with this model. However, the distribution of diselenide conformations is not so restricted.

The crystal packing in the two polymorphs is illustrated in Fig. 2. In the orthorhombic structure, there is an almost complete overlap of the π-electron systems of the adjacent primed and unprimed rings of the molecules related by the axial glide plane perpendicular to the b axis; the interplanar angle is 12° and the interplanar spacing is about 3.6 Å. Moreover, the two molecules are also related by an approximate inversion centre (r.m.s. deviation 0.17 Å). There is no close overlap of the pyridyl rings in the monoclinic structure.

Although free rotation about the Se—C bonds is possible, the diselenide molecules maintain a virtually identical conformation in the two polymorphs. The cell dimensions of the monoclinic form are a = 10.129 (2), b = 5.7332 (12), c = 19.173 (3) Å and β = 101.493 (8)° (Kienitz *et al.*, 1996). As the short crystal axes in the two structures differ by only 0.020 (1) Å, it is not unreasonable to suppose that a perturbation of the molecular arrangements in the crystals in the directions normal to their short axes gives rise to the observed polymorphism.

Experimental

The title compound was prepared by a method similar to that reported by Kienitz *et al.* (1996) and was crystallized at ambient temperature (m.p. 323–324 K).

Crystal data

$C_{10}H_8N_2Se_2$
M_r = 314.1
Orthorhombic
$Pna2_1$
a = 17.492 (4) Å
b = 10.839 (2) Å
c = 5.753 (1) Å
V = 1090.7 (4) Å^3
Z = 4
D_x = 1.913 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 21–30°
μ = 8.16 mm^{-1}
T = 293 (2) K
Tabular
0.462 × 0.359 × 0.180 mm
Pale yellow

Data collection

Rigaku AFC diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (*SHELX*76; Sheldrick, 1976)
T_{min} = 0.067, T_{max} = 0.311
1021 measured reflections
1021 independent reflections

975 reflections with $I > 2\sigma(I)$
θ_{max} = 65°
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 6$
3 standard reflections every 50 reflections intensity decay: 0.65%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.088$
$S = 1.108$
1021 reflections
127 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0590P)^2 + 0.6984P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.003$
$\Delta\rho_{\text{max}} = 0.441$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.607$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0131 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (6)

Table 1. *Selected geometric parameters (Å, °)*

Se1—C2	1.942 (6)	Se1′—C2′	1.935 (5)
Se1—Se1′	2.298 (1)	N1′—C2′	1.322 (8)
N1—C2	1.324 (9)	N1′—C6′	1.372 (9)
N1—C6	1.343 (10)	C2′—C3′	1.373 (9)
C2—C3	1.356 (11)	C3′—C4′	1.392 (9)
C3—C4	1.411 (11)	C4′—C5′	1.345 (13)
C4—C5	1.378 (12)	C5′—C6′	1.361 (13)
C5—C6	1.348 (13)		
C2—Se1—Se1′	102.7 (2)	C2′—Se1′—Se1	103.5 (2)
C2—N1—C6	116.6 (7)	C2′—N1′—C6′	116.5 (6)
N1—C2—C3	125.8 (6)	N1′—C2′—C3′	125.2 (5)
N1—C2—Se1	109.8 (5)	N1′—C2′—Se1′	110.3 (4)
C3—C2—Se1	124.4 (5)	C3′—C2′—Se1′	124.4 (5)
C2—C3—C4	116.6 (7)	C2′—C3′—C4′	116.8 (7)
C5—C4—C3	118.0 (7)	C5′—C4′—C3′	119.1 (7)
C6—C5—C4	120.2 (7)	C4′—C5′—C6′	121.3 (7)
N1—C6—C5	122.8 (8)	C5′—C6′—N1′	121.1 (8)

Data collection: *Rigaku AFC Software* (Rigaku Corporation, 1974). Cell refinement: *Rigaku AFC Software*. Data reduction: *Rigaku AFC Software*. Program(s) used to solve structure: *SHELX*76 (Sheldrick, 1976). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1189). Services for accessing these data are described at the back of the journal.

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