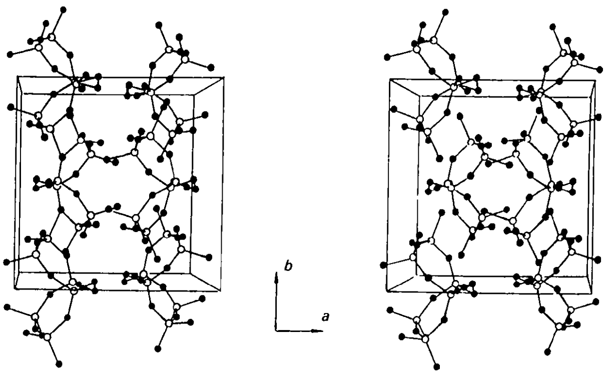

Fig. 2. Stereopair showing the molecular packing in (II).

compensates the increase of conformational energy caused by this enlargement of the angle.

The mean Si—O bond length of 1·608 (3) Å in (II) is somewhat smaller than the value of 1·625 Å which is usual for sterically non-overloaded tetrasiloxanes with nearly the same values of the SiOSi bond angles (Shklover & Struchkov, 1980). It emphasizes the absence of significant strain in the siloxane ring in (II); on the contrary, in molecule (I) a small lengthening of the Si—O bonds and a noticeable decrease of the bond angles at the O atoms are observed in comparison with the usual angles in tetrasiloxanes. Other bond lengths and bond angles in (II) are ordinary.

The crystal structure of (II) is very loose; there is only one intermolecular contact less than 4 Å: C(6)···C(2)($\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$) of 3·907 (7) Å. The layers of molecules, which are coplanar to the crystallographic *ab* and *bc* planes, are clearly distinguished (Fig. 2). It is possible that the mobility of these layers is the cause for crystals of (II) becoming shapeless without a decrease of rigidity in 2–3 days at room temperature.

References

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A27, 368–376.

Gerr, R. G., Yanovsky, A. I. & Struchkov, Yu. T. (1983). *Kristallografiya*, **28**, 1029–1030.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Ovchinnikov, Yu. E., Shklover, V. E., Struchkov, Yu. T., Astapova, T. V. & Zhdanov, A. A. (1986). *Z. Anorg. Allg. Chem.* **533**, 159–164.

Shklover, V. E. & Struchkov, Yu. T. (1980). *Usp. Khim.* **49**, 518–556.

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Structure of a Planar Organic Compound: 2,1,3-Benzoselenadiazole (Piaselenole)

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Abstract. $C_6H_4N_2Se$, $M_r = 183{\cdot}11$, orthorhombic, $Pna2_1$, $a = 12{\cdot}553$ (4), $b = 12{\cdot}414$ (3), $c = 3{\cdot}941$ (1) Å, $V = 614{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}98$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 6{\cdot}46$ cm^{-1}, $F(000) = 352$, $T = 288$ K. Final $R = 0{\cdot}044$ for 747 observed reflections. The molecule is planar within experimental error. The mean N—Se distance is 1·784 (5) Å, and a pseudo C_{2v} axis is observed in the molecule.

Introduction. The structure determination of the title compound (received through the courtesy of Dr Wirz of Universität Basel, Switzerland) was undertaken as part of a series of studies of carcinogenic heterocyclic planar chromophoric organic compounds, seeking structure–function correlations because these compounds are important for their selective intercalation in DNA and for chemotherapeutic uses. Structural elucidation of these series of compounds may also explain physical properties, such as cleavage and melting point, and may clarify salient features of the effect of intermolecular binding forces.

The primary synthesis and chemical characterization reports concerning piaselenole and others were published by Hinsberg (1889) and Zincke & Schwartz (1899); the 2D structure was reported by Luzzati (1951) and subsequently further NMR studies and molecular orbital calculations have been undertaken (Rettig & Wirz, 1976). This paper presents a complete

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3D structural elucidation of the molecule in the crystalline state.

It is hoped that the indications of the electronic structure obtained from the crystallographic information can serve as a starting point for the theoretical studies of piazthiol, benzofurazane, indole, azolopyridazines and the structural analogs of these series of compounds, where correlation of changes in chemical configuration with changes in structure should facilitate further understanding of their chemical reactivity.

Experimental. $C_6H_4N_2Se$ crystallized from ethanol in the form of transparent needles at room temperature; dimensions 0·15 × 0·10 × 0·25 mm. 25 reflections (to $\theta = 15{\cdot}2°$) for measurement of lattice parameters. 1028 [747 with $I > 2\sigma(I)$] unique reflections on Syntex $P3$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω–2θ scan, $2\theta \leq 50°$, range of h, k and l 0 to 17, 0 to 17 and 0 to 6 respectively. Data corrected for Lorentz–polarization factors but not for absorption; structure solved by Patterson method. Full-matrix least-squares refinement on F with anisotropic temperature factors using weighting scheme $w = 1/\sigma^2(F)$ (Seal & Roy, 1981) produced $[(\Delta/\sigma)_{\max} = 0{\cdot}26]$ $R = 0{\cdot}044$, $wR = 0{\cdot}048$ with $S = 1{\cdot}396$. The N2 z coordinate was held fixed as required by the space group during refinement. The values of $w|\Delta F^2|$ showed no systematic variation. All the H atoms were generated and refined isotropically. Final difference Fourier map showed max. and min. peaks of 0·2 and $-0{\cdot}3$ e Å^{-3} respectively. It is noted that an anisotropic final refinement using an f'' multiplier did not show any significant changes in molecular geometry. The maximum differences in average bond lengths and bond angles appeared to be 0·004 Å and 0·3° respectively for non-hydrogen atoms. Atomic scattering factors are from *International Tables for X-ray Crystallography* (1974). All calculations carried out on a Burroughs 6700 computer. Programs used from *XRAY ARC* (*World List of Crystallographic Computer Programs*, 1973), modified for the B6700 computer.

Atomic parameters are listed in Table 1* and bond lengths and angles in Table 2.

Table 1. *Final atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic values of the anisotropic thermal parameters for non-*H *and* H *atoms*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}/B_{\rm iso}$(Å^2)
Se	0·95740 (5)	0·13914 (5)	0·23369 (84)	3·785
N2	0·8547 (5)	0·2272 (5)	0·3846	4·033
N3	0·8886 (4)	0·0190 (5)	0·3435 (19)	3·729
C4	0·7970 (5)	0·0496 (5)	0·4816 (21)	3·112
C5	0·7782 (5)	0·1637 (5)	0·4983 (22)	3·123
C6	0·6789 (5)	0·2020 (6)	0·6373 (23)	4·031
C7	0·6079 (5)	0·1297 (7)	0·7507 (46)	4·796
C8	0·6264 (5)	0·0173 (6)	0·7324 (48)	4·348
C9	0·7185 (6)	−0·0232 (6)	0·6031 (25)	3·820
H6	0·6608 (65)	0·2838 (70)	0·6646 (329)	3·977
H7	0·5393 (68)	0·1719 (87)	0·8087 (387)	4·703
H8	0·5676 (64)	−0·0356 (79)	0·8057 (354)	4·289
H9	0·7345 (76)	−0·0989 (75)	0·5893 (321)	3·848

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Se—N2	1·792 (6)	Se—N3	1·777 (6)
N2—C5	1·321 (9)	N3—C4	1·328 (9)
C4—C5	1·438 (9)	C4—C9	1·420 (10)
C5—C6	1·442 (10)	C6—C7	1·341 (12)
C7—C8	1·416 (11)	C8—C9	1·359 (12)
N2—Se—N3	94·7 (3)	Se—N2—C5	106·8 (4)
Se—N3—C4	106·3 (5)	N3—C4—C5	116·3 (6)
N3—C4—C9	123·9 (7)	C5—C4—C9	119·8 (6)
N2—C5—C4	116·9 (6)	N2—C5—C6	124·2 (6)
C4—C5—C6	118·9 (6)	C5—C6—C7	118·7 (8)
C6—C7—C8	122·2 (10)	C7—C8—C9	121·5 (10)
C4—C9—C8	118·8 (8)		

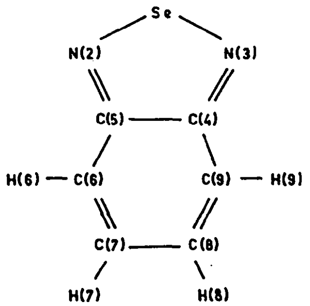

Fig. 1. Chemical diagram of the piaselenole molecule.

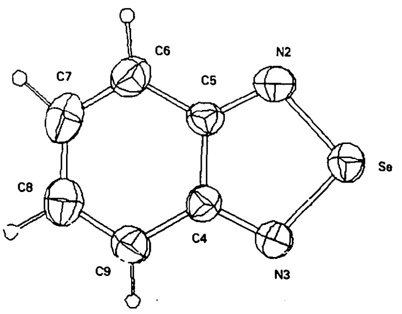

Fig. 2. A view of the molecule down the c axis with 50% thermal probability ellipsoids.

Discussion. Fig. 1 shows the chemical diagram of the title compound and Fig. 2 gives a view of the molecule. The C5—N2 and C4—N3 bond lengths, 1·321 (8) and 1·328 (9) Å, exhibit double-bond character and are in accordance with the chemical reactivity. The C6—C7 and C8—C9 bonds, 1·341 (12) and 1·359 (12) Å, are

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, least-squares-planes data and dihedral angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51202 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

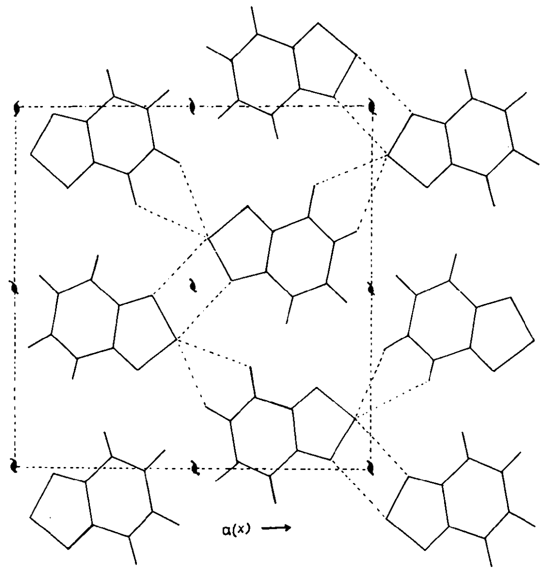

Fig. 3. Packing diagram of piaselenole molecules viewed down the *c* axis with an intricate network of short contacts.

also relatively shorter than the C=C double-bond distance. The other bond lengths including the Se—N bonds [1·792 (6) and 1·777 (6) Å] and angles are within the normal range found in similar heterocyclic systems. The molecules are planar with largest deviations from the least-squares plane of 0·017 (7) Å at N2 and N3 on opposite sides of the molecular plane. The small departure from C_{2v} symmetry of the molecule may be due to molecular packing forces. This is similar to that observed in the crystal structure of piaselenole–piaselenolium pentaiodide (Gieren, Hubner, Lamm, Neidlein & Droste, 1985) where protonation at one N of the SeN_2 unit also destroyed the molecular symmetry and led to significant changes in bond lengths and bond angles. In our case the probable partial protonation at the N atom results in lengthening of one Se—N bond. The crystal structure is characteristic of similar kinds of compounds like dibenzofuran (Banerjee, 1973) and indole (Roychowdhury & Basak, 1975) with a packing arrangement of pairs of localized molecules related by twofold symmetries and a network of short contacts. In piaselenole the Se···N contact distance in the parallelogram (Fig. 3) is 3·154 (4) Å. This distance is significantly shorter [2·972 (5) and 2·691 (4) Å] in the piaselenole–piaselenolium pentaiodide structure.

References

Banerjee, A. (1973). *Acta Cryst.* B**29**, 2070–2074.

Gieren, A., Hubner, T., Lamm, V., Neidlein, R. & Droste, D. (1985). *Z. Anorg. Allg. Chem.* **523**, 33–44.

Hinsberg, O. (1889). *Ber. Dtsch. Chem. Ges.* **22**, 2895–2902.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Luzzati, P. V. (1951). *Acta Cryst.* **4**, 193–200.

Rettig, W. & Wirz, J. (1976). *Helv. Chim. Acta*, **59**, 1054–1074.

Roychowdhury, P. & Basak, B. S. (1975). *Acta Cryst.* B**31**, 1559–1563.

Seal, A. & Roy, S. (1981). *Indian J. Phys.* **55**A, 414–416.

World List of Crystallographic Computer Programs (1973). *J. Appl. Cryst.* **6**, 309–346.

Zincke, E. C. T. & Schwartz, P. (1899). *Justus Liebigs Ann. Chem.* **307**, 28–49.

Acta Cryst. (1989). C**45**, 75–77

Structure of *endo,exo*-9,11-Dibromotricyclo[6.3.1.0^{2,7}]dodeca-2(7),3,5-trien-10-one

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Abstract. $C_{12}H_{10}Br_2O$, $M_r = 330{\cdot}04$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}045\,(2)$, $b = 9{\cdot}837\,(3)$, $c = 19{\cdot}487\,(7)$ Å, $V = 1159\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}89$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 69{\cdot}02$ cm^{-1}, $F(000) = 640$, $T = 295$ K, $R = 0{\cdot}053$ for 1348 observed reflections. The compound studied has a benzene ring fused to a bicyclo[3.2.1]octane ring. The two Br atoms are bonded to the seven-membered ring in *endo* and *exo* positions at two C atoms. Oxygen is also bonded to the same ring with a double C=O bond.

Introduction. Benzobarrelene (1,4-dihydro-1,4-ethenonaphthalene) is a molecule of considerable potential mechanistic interest in view of the di-π-methane rearrangement (Hixon, Mariano & Zimmerman, 1973). By the introduction of a substituent in a vinyl location the symmetry of the benzobarrelene skeleton is destroyed. On this basis, vinyl substituted benzobarrelenes gain more importance by elucidation of the mechanism of the $(2\pi + 2\pi)$-cycloaddition reaction and di-π-methane rearrangement. Recently, an

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