

Structure of Di-*p*-tolyl Diselenide, C₁₄H₁₄Se₂

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Abstract. $M_r = 340.19$, monoclinic, $P2_1/a$, $a = 15.344$ (4), $b = 6.189$ (3), $c = 13.951$ (4) Å, $\beta = 91.26$ (1)°, $V = 1325$ (1) Å³, $Z = 4$, $D_m = 1.69$, $D_x = 1.70$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 5.475$ mm⁻¹, $F(000) = 664$, $T = 293$ K, $R = 0.093$ for 1710 unique reflections. The Se–Se bond length is 2.328 (1) Å and the dihedral angle C–Se–Se–Se–C 80.3 (4)°. Some bonding and angular parameters seem to be correlated with the C–C–Se–Se torsion angle, as for the disulfides with the C–C–S–S torsion angle.

Introduction. Although several structures of diaryl dichalcogenides have been published, only three diaryl diselenides [(C₆H₅)₂Se₂ (Marsh, 1952), (*p*-ClC₆H₄)₂Se₂ (Kruse, Marsh & McCullough, 1957) and (C₆F₅)₂Se₂ (Woodard, Brown, Lee & Massey, 1976)] have been investigated by X-ray crystallography. The crystal structure determination of di-*p*-tolyl diselenide has been undertaken as part of a study of the diamagnetism of these compounds.

Experimental. Solutions in acetone give yellow prisms. D_m by flotation in aqueous HgCl₂. Crystal 0.80 × 0.44 × 0.40 mm. Preliminary Weissenberg and precession photographs displayed systematic absences consistent with space group $P2_1/a$ [and not $P2_1$ (Llabrès & Baiwir, 1974)]. Unit-cell dimensions by least squares from angle data for 10 general reflections ($31.0 < 2\theta < 35.6^\circ$). Hilger & Watts four-circle diffractometer, Zr-filtered Mo $K\alpha$ radiation, ω - 2θ scans [$(\sin\theta/\lambda)_{\text{max}} = 0.7034$ Å⁻¹]. Intensities corrected for Lorentz and polarization effects and, semi-empirically, for absorption (North, Phillips & Mathews, 1968), limit values of transmission factors 0.345 and 0.991. Index range h 0→21, k 0→8, l -19→19. Standard reflections (007 and 007) showed no significant variation. 4006 reflections measured [3591 with $I > 2\sigma(I)$ corresponding to 3385 unique with $R_{\text{int}} = 0.034$]; 1710 unique data [$I \geq 2.5\sigma(I)$] used in analysis. Structure solved by direct methods (MULTAN80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined anisotropically, except for H atoms, by full-matrix least squares on F (SHELX76; Sheldrick, 1976), $w = 6.9[\sigma^2(F_o) + 0.000134F_o^2]^{-1}$; H atoms in

calculated positions (C–H 1.08 Å) and three rotation parameters for methyl groups treated as rigid groups. In the final stages of refinement an empirical isotropic extinction parameter x was calculated according to the scheme $F_c = F_o(1 - 0.0001xF_o^2/\sin\theta)$, $x = 0.108 \times 10^{-2}$. $R = 0.093$, $wR = 0.063$, $(\Delta/\sigma)_{\text{max}} = 0.09$, max. and min. heights in final difference Fourier map 1.57 and

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²) with e.s.d.'s in parentheses

	$U_{\text{eq}} = \frac{1}{3} \text{trace } \bar{U}$			
	x	y	z	U_{eq}
Se(1)	0.3757 (1)	-0.2103 (2)	-0.1278 (1)	0.0507 (7)
Se(2)	0.3598 (1)	-0.1146 (2)	-0.2886 (1)	0.0583 (8)
C(1)	0.4774 (6)	-0.388 (2)	-0.1308 (6)	0.038 (6)
C(2)	0.4724 (7)	-0.599 (2)	-0.1708 (7)	0.057 (7)
C(3)	0.5468 (7)	-0.726 (2)	-0.1689 (7)	0.051 (7)
C(4)	0.6246 (7)	-0.655 (2)	-0.1285 (6)	0.047 (7)
C(5)	0.7022 (7)	-0.804 (2)	-0.1295 (7)	0.065 (8)
C(6)	0.6270 (7)	-0.453 (2)	-0.0874 (7)	0.052 (7)
C(7)	0.5541 (7)	-0.320 (2)	-0.0878 (7)	0.047 (7)
C(8)	0.2709 (7)	-0.312 (2)	-0.3330 (6)	0.047 (7)
C(9)	0.2916 (8)	-0.509 (2)	-0.3735 (7)	0.053 (7)
C(10)	0.2246 (9)	-0.639 (2)	-0.4074 (6)	0.056 (8)
C(11)	0.1402 (8)	-0.584 (2)	-0.4023 (6)	0.045 (7)
C(12)	0.0668 (8)	-0.732 (2)	-0.4356 (8)	0.072 (8)
C(13)	0.1203 (7)	-0.387 (2)	-0.3634 (7)	0.055 (7)
C(14)	0.1842 (7)	-0.252 (2)	-0.3281 (6)	0.055 (7)

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

Se(1)–Se(2)	2.328 (1)	C(7)–C(1)	1.37 (1)
Se(1)–C(1)	1.91 (1)	C(8)–C(9)	1.38 (1)
Se(2)–C(8)	1.92 (1)	C(9)–C(10)	1.38 (1)
C(1)–C(2)	1.42 (1)	C(10)–C(11)	1.34 (1)
C(2)–C(3)	1.39 (1)	C(11)–C(12)	1.52 (1)
C(3)–C(4)	1.38 (1)	C(11)–C(13)	1.38 (1)
C(4)–C(5)	1.51 (1)	C(13)–C(14)	1.37 (1)
C(4)–C(6)	1.37 (1)	C(14)–C(8)	1.38 (1)
C(6)–C(7)	1.39 (1)		
C(1)–Se(1)–Se(2)	101.2 (2)	C(4)–C(6)–C(7)	121.4 (10)
C(8)–Se(2)–Se(1)	102.0 (2)	C(6)–C(7)–C(1)	120.4 (9)
Se(1)–C(1)–C(2)	120.0 (8)	C(7)–C(1)–C(2)	119.3 (10)
Se(1)–C(1)–C(7)	120.6 (8)	C(8)–C(9)–C(10)	118.4 (10)
Se(2)–C(8)–C(9)	121.6 (9)	C(9)–C(10)–C(11)	123.4 (10)
Se(2)–C(8)–C(14)	119.4 (9)	C(10)–C(11)–C(12)	123.0 (10)
C(1)–C(2)–C(3)	118.4 (10)	C(10)–C(11)–C(13)	117.8 (10)
C(2)–C(3)–C(4)	122.1 (10)	C(12)–C(11)–C(13)	119.2 (10)
C(3)–C(4)–C(5)	118.4 (10)	C(11)–C(13)–C(14)	121.2 (10)
C(3)–C(4)–C(6)	118.4 (10)	C(13)–C(14)–C(8)	120.2 (10)
C(5)–C(4)–C(6)	123.1 (10)	C(14)–C(8)–C(9)	119.0 (10)

Table 3. Bond lengths (Å) and angles (°) in diaryl diselenides

Compound	Se—Se	Av. C—Se	Av. C—Se—Se	C—Se—Se—C	C—C—Se—Se	¹ C... ⁴ Se
Diphenyl diselenide ^(a)	2.29 (1)	1.93 (5)	106.1 (20)	82.0 (30)	{ 2.4 (30) 23.9 (30)	{ 3.43 3.46
Di- <i>p</i> -tolyl diselenide ^(b)	2.328 (1)	1.915 (10)	101.6 (2)	80.3 (4)	{ 89.9 (5) 73.2 (5)	{ 4.00 (1) 3.80 (1)
Bis(<i>p</i> -chlorophenyl) diselenide ^(c)	2.333 (15)	1.905 (100)	101.2 (20)	74.5 (30)	{ 74.4 (30) 55.0 (30)	{ 3.67 3.53
Bis(pentafluorophenyl) diselenide ^(d)	2.319 (4)	1.910 (15)	98.8 (6)	75.3 (10)	{ 77.0 (10) 72.2 (10)	{ 3.80 3.75

References: (a) Marsh (1952); (b) this work; (c) Kruse, Marsh & McCullough (1957); (d) Woodard, Brown, Lee & Massey (1976).

−1.58 e Å^{−3} near Se atoms. Neutral-atom scattering factors for Se from *International Tables for X-ray Crystallography* (1974), for C and H as in *SHELX76*. Drawing by *PLUTO* (Motherwell, 1972).

Discussion. A view of the molecule with the numbering system is shown in Fig. 1. Tables 1 and 2 give atomic parameters and molecular geometry.*

The benzene rings are planar to within the limits of experimental error and exhibit normal bond lengths and internal angles. While the methyl carbon C(5) is in plane with the benzene ring to which it is linked, the methyl carbon C(12) is 0.07 (1) Å out of its benzene plane. Se(1) and Se(2) deviate from their respective benzene-ring planes by 0.050 (1) and 0.068 (1) Å. In the packing there are no unusually close intermolecular contacts.

Shefter (1970), using a selection of crystallographic results, found that the C—C—S—S torsion angle in disulfides correlates with other structural features (among others S—S bond, C—S bond, C—S—S angle). All the compounds listed by Raghavan & Seff (1977), who update Shefter's (1970) compilation, support that observation. It seemed worthwhile to extend this observation to the diselenides (Table 3). When C—C—Se—Se is near 90°, the Se—Se bond length is longer than when C—C—Se—Se is near 0°, and falls very close to the value accepted for a pure σ bond between two Se atoms, *i.e.* 2.34 Å (Pauling, 1960). On the other hand, it seems that the C—Se—Se valency angle becomes greater when C—C—Se—Se is near 0°. The ¹C...⁴Se distances vary as the ¹C—C—Se—⁴Se angles, and these distances are somewhat shorter than the van der Waals contact distance [3.70 Å (Pauling, 1960)] when ¹C—C—Se—⁴Se is near 0° (Table 3); that could result from an attractive nonbonded 1,4 C—Se interaction, as proposed by Van Wart, Shipman & Scheraga (1975) for organosulfur compounds.

* Lists of structure factors, anisotropic thermal parameters, least-squares planes and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39650 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

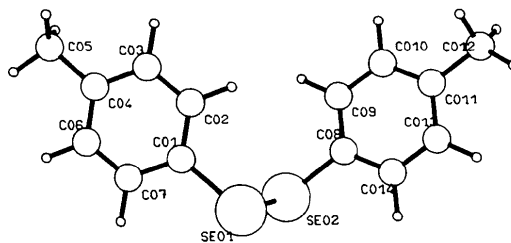


Fig. 1. Perspective view of the molecule showing the labeling scheme.

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References

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KRUSE, F. H., MARSH, R. E. & MCCULLOUGH, J. D. (1957). *Acta Cryst.* **10**, 201–209.
- LLABRÉS, G. & BAIWIR, M. (1974). *J. Appl. Cryst.* **7**, 299–300.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MARSH, R. E. (1952). *Acta Cryst.* **5**, 458–462.
- MOTHERWELL, W. D. S. (1972). *PLUTO*. A program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
- RAGHAVAN, N. V. & SEFF, K. (1977). *Acta Cryst.* **B33**, 386–391.
- SHEFTER, E. (1970). *J. Chem. Soc. B*, pp. 903–906.
- SHELDRIK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
- VAN WART, H. E., SHIPMAN, L. L. & SCHERAGA, H. A. (1975). *J. Phys. Chem.* **79**, 1436–1447.
- WOODARD, C. M., BROWN, D. S., LEE, J. D. & MASSEY, A. G. (1976). *J. Organomet. Chem.* **121**, 333–344.