

The Crystal and Molecular Structure of *trans*-Selenophthene

BY A. CHIESI VILLA, M. NARDELLI AND C. PALMIERI

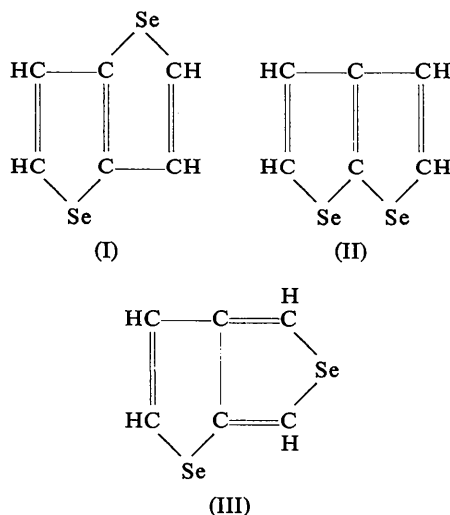
Istituti di Chimica Generale e di Strutturistica Chimica, Università degli Studi, Parma, Italy

(Received 29 July 1968)

The crystal structure of *trans*-selenophthene has been determined by means of three-dimensional Fourier methods (final $R=11.6\%$). Bond lengths in the asymmetric unit of the molecule are $C(1)-C(2)=1.35$ (3), $C(2)-C(3)=1.42$ (2), $C(3)-C(3')=1.36$ (2), $C(1)-Se=1.93$ (2), $C(3')-Se=1.87$ (1) Å. The structure is compared with that of isostructural *trans*-thiophthene.

Introduction

When selenophene is prepared from acetylene and selenium, residues are obtained which contain the *trans* (I), *cis* (II) and *iso* (III) forms of selenophthene:



These isomers were recognized by Umezawa and co-workers (Tamamushi, Akiyama & Umezawa, 1939; Umezawa, 1939), who assigned the above structures from a study of dipole moments.

No X-ray structural work has ever been carried out on these compounds, so it seemed interesting to examine one of these structures, as a part of our research programme on crystal structures of heterocyclic compounds, to provide a contribution to the structural knowledge of organic selenium compounds. In particular the *trans* form was considered as its structure could be compared with that of *trans*-thiophthene studied by Cox, Gillot & Jeffrey (1949).

Experimental

Crystals suitable for X-ray work were obtained by crystallization from ethanol. Crystal data deduced from rotation and Weissenberg photographs and refined by a least-squares procedure from powder dif-

fractometer data are as follows (the e.s.d.'s given in parentheses are in units of the last decimal figure):

$$C_6H_4Se_2, M=234.0;$$

$$a=10.324 (3), b=10.071 (8), c=6.084 (1) \text{ \AA};$$

$$U=632.6 \text{ \AA}^3; Z=4; D_x=2.46 \text{ g.cm}^{-3};$$

$$\mu=155.2 \text{ cm}^{-1} (\text{Cu } K\alpha); F(000)=432.$$

Space group: *Pbca* uniquely defined from systematic absences.

From these data it appeared the crystals were isostructural with those of thiophthene and this deduction was supported by the fact that the odd layer lines of the [100] rotation photograph were weak as observed also for thiophthene, indicating the heaviest atom to have a z coordinate of approximately $\frac{1}{4}$.

To collect three-dimensional intensity data, integrated equi-inclination Weissenberg photographs were taken up to the ninth and eleventh layers along [100] and [101] respectively (multiple film technique). Because the crystals are unstable under X-rays, the samples were changed every two or three layers. Structure amplitudes were obtained from the photometrically measured intensities after correction for Lorentz and polarization factors, using the Rollett & Sparks (1960) procedure to put the intensities on the same relative scale, and the Wilson's (1942) method to establish the absolute scale and the overall B value. To correct for absorption, the samples were considered spheres with a mean radius of 0.05 cm. The total number of independent non-zero reflexions was 508 (possible 707).

Structure analysis and refinement

The first step of the structure analysis was a structure factor calculation carried out with the use of the atomic coordinates for thiophthene found by Cox *et al.* (1949). A relatively low value (36.2%) for the R index was obtained, indicating once more that the two compounds are isostructural. Four cycles of isotropic least-squares with an overall thermal parameter lowered the R index only to 26.2% and no further improvement was achieved, even after introducing anisotropic thermal parameters. At this point it was quite clear that something was wrong concerning the atomic coordi-

Potters, Loopstra, MacGillavry & Veenendaal (1955) for C.

Discussion

Bond distances and angles in the selenophthene molecule are quoted in Table 4 and in Fig. 1, which shows a projection of the structure on (001). The standard deviations are calculated from the formulae of Ahmed & Cruickshank (1953) for bond lengths, and of Darlow (1960) for angles, the effects of error in cell parameters being accounted for following Darlow & Cochran (1961).

Comparison with thiophthene shows that the C-C bond distances are practically the same in the two compounds, in particular the shortening of the C(3)-C(3') bond is confirmed. It is doubtful that the difference between the two C-Se distances, which is possibly significant [$\Delta/\sigma = (l_1 - l_2)/(\sigma_1^2 + \sigma_2^2)^{1/2} = 2.68$, significance test of Cruickshank & Robertson, 1953], has a real significance considering that the longer value in selenophthene corresponds to the shorter value in thiophthene. If allowance is made for the increased size of selenium with respect to sulphur, it seems that π delocalization is not much different in the two molecules.

The general rule by which the bond angle on the hetero-atom decreases with increasing atomic number, is observed; the values found for Se and S agree well with the corresponding ones found in α -selenophene- (87.1°) and in α -thiophene- (91.3°) carboxylic acids (Nardelli, Fava & Giraldi, 1962). Of course, the variation of the bond angle on the hetero-atom, passing from the sulphur to the selenium compounds, produces sensible variations in the other angles in the ring; this fact and the e.s.d.'s can justify the differences observed for the corresponding angles in the two compounds.

The selenium atom lies 0.051 \AA out of the plane through C(1)C(2)C(3') (the equation of the plane is: $0.6193x + 0.3443y - 0.7057z = -0.0150$) and this displacement, which is statistically significant ($\Delta/\sigma_{\perp} = 29.48$) seems to be also real considering that it is similar to that (0.065 \AA) found in α -selenophene-carboxylic acid. It is interesting to observe that a similar but smaller

displacement ($0.02-0.03 \text{ \AA}$) can be calculated from the coordinates given for thiophthene by Cox *et al.* (1949)* and has been found in α -thiophene-carboxylic acid (0.028 \AA) and in β -thiophene-carboxylic acid (0.020 \AA) (Hudson & Robertson, 1964). Nevertheless, it is important to observe that there is a weighted least-squares plane through all the atoms of the molecule (its equation is: $0.6329x + 0.3611y - 0.6849z = 0$) from which the atoms are not significantly displaced.

Packing of the molecules is shown in the clinographic projection of Fig. 2. The angles formed by the normal to the plane of the molecule and the crystallographic axes are 52° to [100], 70° to [010] and $45\frac{1}{2}^\circ$ to [001] the corresponding angles for thiophthene being respectively: 50° , $71\frac{1}{2}^\circ$ and $45\frac{1}{2}^\circ$. There are no intermolecular contacts shorter than the sums of van der Waals radii, the most significant ones being:

$$\begin{aligned} \text{Se} \cdots \text{C}(2'') &= 3.58 \text{ \AA} \\ \text{Se} \cdots \text{C}(3'') &= 3.87 \\ \text{Se} \cdots \text{C}(2''') &= 3.46 \\ \text{Se} \cdots \text{C}(1''') &= 3.63 \\ \text{C}(1) \cdots \text{C}(1''') &= 3.60 \\ \text{C}(1) \cdots \text{C}(1^{\text{iv}}) &= 3.60 \\ \text{C}(1) \cdots \text{C}(2''') &= 3.58 \end{aligned}$$

$$\begin{aligned} \text{''} & \bar{x}, \frac{1}{2} + y, -\frac{1}{2} - z \\ \text{''' } & \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z \\ \text{iv} & \frac{1}{2} - x, \bar{y}, z - \frac{1}{2}. \end{aligned}$$

All calculations were performed in the Olivetti Elea 6001/S computer of the Centro di Calcolo Elettronico della Università di Parma. The work was done with the financial support of the Consiglio Nazionale delle Ricerche (Roma). The authors are indebted to the late Professor L. Chierici who kindly supplied samples of selenophthene.

* The plane through C(1)C(2)C(3), calculated from the coordinates indicated by *D* in the paper, has the equation $-0.6400x + 0.3205y - 0.6983z = -1.6438$ and the distance of S from this plane is -0.029 \AA

Table 2. Atomic peak heights ($\text{e.}\text{\AA}^{-3}$), curvatures ($\text{e.}\text{\AA}^{-5}$) and e.s.d.'s

		ρ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{kl}	A_{hl}	A_{hk}
Se	obs	59.3	458	568	537	-22	-16	-15
	calc	60.2	463	561	535	-18	-10	-13
C(1)	obs	6.5	43	59	54	-1	7	14
	calc	6.7	46	59	54	0	8	12
C(2)	obs	7.5	44	66	53	-7	-1	-1
	calc	7.1	43	65	54	-10	0	-2
C(3)	obs	7.8	57	65	70	-7	-12	-10
	calc	7.7	56	64	72	-6	-11	-9
	e.s.d.	0.3	4	4	4	2	2	2

Table 4. Comparison of the dimension of the selenophthene and thiophthene molecules

	X=Se	X=S
C(1)-C(2)	1.35 (3) Å	1.36 (2) Å
C(2)-C(3)	1.42 (2)	1.41 (2)
C(3)-C(3')	1.36 (2)	1.36 (3)
C(1)-X	1.93 (2)	1.72 (1)
C(3')-X	1.87 (1)	1.74 (1)
C(1)XC(3')	86.1 (8)°	91.2°
XC(1)C(2)	111.4 (1.8)	116.5
C(1)C(2)C(3)	114.2 (1.4)	111.7
C(2)C(3)C(3')	117.0 (1.1)	114.3
C(3)C(3')X	111.1 (1.0)	110.2
C(2')C(3')X	131.8 (1.6)	135.5

References

AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
 COX, E. G., GILLOT, R. J. J. H. & JEFFREY, G. A. (1949). *Acta Cryst.* **2**, 356.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
 CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698.
 DARLOW, S. F. (1960). *Acta Cryst.* **13**, 683.
 DARLOW, S. F. & COCHRAN, W. (1961). *Acta Cryst.* **14**, 1250.
 HUDSON, P. & ROBERTSON, J. H. (1964). *Acta Cryst.* **17**, 1497.
 NARDELLI, M., FAVA, G. & GIRALDI, G. (1962). *Acta Cryst.* **15**, 737.
 ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.
 TAMAMUSHI, B., AKIYAMA, H. & UMEZAWA, S. (1939). *Bull. Chem. Soc. Japan*, **14**, 318.
 THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.
 UMEZAWA, S. (1939). *Bull. Chem. Soc. Japan*, **14**, 363.
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.

Acta Cryst. (1969). **B25**, 1378

The Crystal Structure of Tetra(pyridine oxide)copper(II) Perchlorate

BY J. D. LEE, D. S. BROWN AND B. G. A. MELSOM*

Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire, England

(Received 5 July 1968)

The crystal structure of tetra(pyridine oxide)copper(II) perchlorate $\text{Cu}(\text{PyO})_4(\text{ClO}_4)_2$ has been determined from three-dimensional X-ray diffraction data. Crystals are monoclinic with space group $P2_1/c$, and cell dimensions $a=9.65$, $b=14.30$, $c=10.85$ Å, $\beta=122^\circ 0'$. The structure was refined by Fourier and full-matrix least-squares methods on 1468 independent observed reflexions to $R=10.4\%$. The structure is centrosymmetrical about the copper. Oxygen atoms from four pyridine oxide molecules form a square planar arrangement around the copper with Cu-O distances of 1.93 Å and 1.92 Å. The perchlorate ions occupy approximately octahedral positions, but are not involved in any coordination with the copper since the closest oxygen-metal approach is 3.38 Å.

Introduction

As part of a series of investigations into the role of polyanions in copper(II) complexes the structure of tetra(pyridine oxide)copper(II) perchlorate has been determined. Dark green coloured crystals in the form of hexagonal plates were prepared by Dr B. J. Hathaway (University of Essex).

A crystal of dimensions 0.4 mm × 0.3 mm × 0.2 mm was used for X-ray analysis. Three-dimensional Weissenberg data were collected for the crystal rotating about its b and c axes, allowing the observation of 1468 independent X-ray reflexions. Intensities were measured visually and converted to $|F|^2$ and $|F|$ by applying Lorentz and polarization corrections. No corrections were made for absorption or extinction.

Crystal data

$\text{Cu}(\text{C}_5\text{H}_5\text{NO})_4(\text{ClO}_4)_2$, $M=642.9$.

Monoclinic, $a=9.65$, $b=14.30$, $c=10.85$ all ± 0.02 Å, $\beta=122^\circ 0' \pm 30'$.

$U=1269.7$ Å³, $Z=2$, $D_m=1.66$ g.cm⁻³, $D_c=1.681$ g.cm⁻³.

$F(000)=654$, $\text{Cu } K\alpha$, $\lambda=1.542$ Å, $\mu=38.4$ cm⁻¹.

Absent reflexions, $h0l$ when $l=2n+1$, $0k0$ when $k=2n+1$; Space group $P2_1/c$.

Structure analysis

Since there are only two molecules of the complex in each unit cell, it was assumed that the molecules were centrosymmetric, with the copper atoms occupying special positions at 0,0,0 and $0, \frac{1}{2}, \frac{1}{2}$. The positions of the light atoms were located from three-dimensional Patterson and Fourier sections. Several interpretations were possible, but all except one of the possibilities

* Present address: British Petroleum Research Centre, Sunbury on Thames, Middlesex.