

09.2-13 CRYSTAL STRUCTURE OF ION-RADICAL SALTS OF SEVERAL PHENOTHIAZINE DERIVATIVES. By T. UCHIDA and K. KOZAWA, Department of Industrial and Engineering Chemistry, Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278 JAPAN

- (1) Phenothiazine cation radical hexachloroantimonate hydrate, $C_{12}H_9NS \cdot SbCl_6 \cdot H_2O$, $M_r = 551.8$, $F(000) = 1100$.
- (2) 3,7-Dichlorophenothiazine cation radical hexachloroantimonate, $C_{12}H_7NSCl_2 \cdot SbCl_6$, $M_r = 602.6$, $F(000) = 578$.
- (3) Phenothiazine cation radical tetrachloroantimonate, $C_{12}H_9NS \cdot SbCl_4$, $M_r = 462.8$, $F(000) = 892$.
- (4) N-Methylphenothiazine cation radical hexachloroantimonate, $C_{13}H_{11}NS \cdot SbCl_6$, $M_r = 547.7$, $F(000) = 530$.
- (5) Benzo[c]phenothiazine cation radical tetrachloroantimonate 1,2-dichloroethane hemisolvate, $C_{16}H_{11}NS \cdot SbCl_4 \cdot \frac{1}{2}C_2H_4Cl_2$, $M_r = 562.4$, $F(000) = 2192$.
- (6) Benzo[a]phenothiazine cation radical pentatellurate, $C_{16}H_{11}NS \cdot TeCl_5$, $M_r = 554.2$, $F(000) = 1068$.

Phenothiazine (or its derivative) is readily oxidized by Lewis acids to form cation radical salts in the crystal. These complex compounds are classified into three groups by the behavior of cations. (i) The cation exists as monomer. (ii) Two or four cation molecules overlap together and make dimer or tetramer. (iii) The cations form "one-dimensional" columnar structure. In the latter two groups, electronic absorption bands were observed at about 1000 nm or more longer wave length range.

The crystal data are shown in Table 1.

Table 1. Crystal data

Compound	(1)	(2)	(3)
Space group	C2/c	$P\bar{1}$	$P2_1/c$
a (Å)	14.488 (3)	9.978 (3)	12.119 (5)
b (Å)	11.902 (2)	12.279 (4)	18.116 (3)
c (Å)	10.996 (2)	8.340 (3)	7.517 (1)
α (°)	90	103.96 (3)	90
β (°)	98.20 (1)	96.92 (2)	107.79 (2)
γ (°)	90	80.21 (2)	90
V (Å ³)	1876.7 (6)	973.8 (6)	1571.4 (8)
Z	4	2	4
R	0.066	0.071	0.061
Reflections	1429	3434	1502
Cation	monomer	monomer	1-D
Anion	monomer	monomer	inf. chain

Compound	(4)	(5)	(6)
Space group	C2/m	$P2_1/a$	$P2_1/a$
a (Å)	11.025 (2)	14.151 (4)	10.966 (2)
b (Å)	11.452 (3)	21.877 (3)	19.929 (5)
c (Å)	8.607 (2)	14.069 (4)	8.719 (2)
β (°)	121.46 (2)	106.49 (2)	90.37 (2)
V (Å ³)	927.0 (5)	4176 (2)	1905 (1)
Z	2	8	4
R	0.032	0.073	0.064
Reflections	1048	3158	2139
Cation	monomer	1-D	dimer
Anion	monomer	tetramer	dimer

09.2-14 STRUCTURE OF SOME SESAMIN-TYPE LIGNANS. by Bodil Honore Eriksen and Rita Grenbek Hazell, Chemical Institute, Aarhus University, DK-8000 Århus C, Denmark.

Three sesamin-type compounds have been investigated. They have been extracted from the strong tasting plants wormwood (*Artemisia absinthium* L) (yangambin and epiashantin) and black pepper (*Piper nigrum* L) (ashantin). They have a tetrahydrofurofuran nucleus diagonally substituted by aryl groups, ashantins by a 3,4,5 methoxy-phenyl group and a (3,4 methylenedioxy)phenyl group, yangambin by two 3,4,5 methoxy-phenyl groups.

Epiashantin ($C_{24}H_{30}O_7$) extracted from *Artemisia absinthium* roots crystallizes in space group $P2_1^2$ with unit cell $a = 12.187$, $b = 5.527$, $c = 15.090$ Å, $\beta = 110.66^\circ$, $Z = 2$. It was refined to $R = 0.035$.

Ashantin ($C_{22}H_{24}O_7$) obtained from *Piper nigrum* fruits belongs to space group $P2_1^2$, with unit cell $a = 10.412$, $b = 7.399$, $c = 25.626$ Å, $Z = 4$. R-value 0.044.

Yangambin ($C_{24}H_{30}O_8$) from *Artemisia absinthium* roots also belongs to space group $P2_1^2$ with unit cell $a = 12.556$, $b = 5.524$, $c = 31.700$ Å, $Z = 4$. R-value 0.033.

All three structures were solved by direct methods but not without difficulty. In the case of one ashantin two molecular fragments were recognized in the best solution from MULTAN shifted by half a C-C bond either way from the true position. For yangambin all E-maps looked too bad to give a recognizable shift, but in one a fragment consisting of a phenyl ring with four atoms attached was promising enough to be put into TRADIR of the DIRDIP program system, which gave the solution.

The molecules appear flat and stretched out, but there are differences around the tetrahydrofurofuran grouping. In ashantin from *Artemisia absinthium* the 3,4,5 methoxy-phenyl group is cis (axial) to the other 5-ring, all the other aryl groups in the three compounds are attached in the trans (equatorial) positions.

09.2-15 RESONANCE STABILIZATION IN ALPHA-FURIL. By S.C. Biswas, Siddhartha Ray, X-ray Crystallography Laboratory, Department of Solid State Physics, Indian Association for the Cultivation of Science, Calcutta 700032 and Aloka Podder, Crystallography and Molecular Biology Division, Saha Institute of Nuclear Physics, Calcutta 700060.

The results of x-ray crystallographic studies on the single crystals of alpha-furil, the furanyl analog of benzil and an important member of symmetrically substituted alpha-dicarbonyls, confirms the orientation of both the ring and its adjacent carbonyl oxygen atoms in (O,O-cis) position as the furyl group contributes a polarity vector to the resultant molecular dipole moment.

The conformational analysis of the crystal structure of alpha-furil shows evidence of maximum resonance stabilization in the molecule as the angle of torsion between the ring(C-O) and the carbonyl(C=O) bonds gives a zero value. The molecule packs in the space group $Fdd2$ which is very unusual for a flexible molecular crystal, with cell lengths of 30.471, 8; 14.851, 5 and 3.750, 8 Å with eight molecules per unit cell. The molecule retains the two fold symmetry to minimize the vibrational energy component of its total free energy with the packing coefficient of 0.77 and density = 1.488 gm cm⁻³.

The results of MO calculations support the molecular structure.