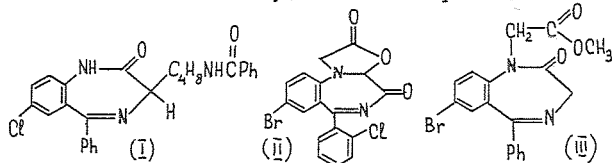


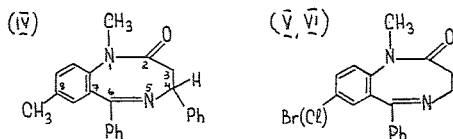
09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.2-50 THE STRUCTURES OF SOME 1,4-BENZODIAZEPINES, 1,5-BENZODIAZOCINES AND ITS DERIVATIVES. By A.A.Dvorkin, Yu.A.Simonov and T.I. Malinowsky, Institute of Applied Physics of Academy of Sciences of Mold.SSR, Kishinev and S.A.Andronati and A.S.Yavorsky, Physics-Chemical Institute of Academy of Sciences of Ukr.SSR, Odessa, USSR.

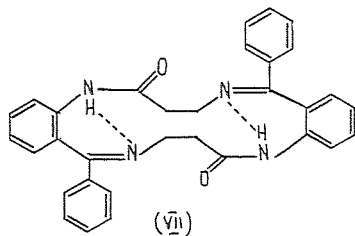
The structures of 1,4-benzodiazepines were



determined by the X-ray method. In all three cases the structures are molecular ones. The structure (I) is built up of molecular dimers by two H-bonds. The 7-membered ring has a "boat" conformation. The bond lengths and angles are in agreement with those found in diazepam, oxazepam (Camerman & Camerman, J. Amer. Chem. Soc. (1972) 94, 268 and G.Gilli, V.Bertolasi, H.Sacerdoti & P.A.Borea, Acta Cryst. (1977) B33, 2664) and others. The molecular structure with "bath" conformation is realized in 1,5-benzodiazocines, which are



analogous of 1,4-benzodiazepines. We have found in (IV) an unusual C-N=1.450Å bond, which is shorter than in other similar compounds. It can be explained by the influence of the electron-donor substituent in 8-position. The structure of the compound (VII) has been determined as well. The 16-membered hetero-



cycle contains a C_2 -axis and is stabilized by two intramolecular H-bonds. The molecule consists of nearly flat fragments with "bath" conformation.

09.2-51 CRYSTAL STRUCTURE OF A PIPERIDINE NITROXYL AND ITS FREE AMINE. By M. Cygler, Dept. of Crystallography, Inst. of Chemistry, University of Łódź, 91-416 Łódź, Nowotki 18, Poland.

Crystal structures of 4-phenoxyethyl-4-hydroxy-2,2,6,6-tetramethylpiperidine (I) and its N-oxyl derivative (II) have been determined. Compound I crystallizes in space group $P2_1/c$ with $a=13.666$, $b=10.449$, $c=11.491$, $\beta=111.98^\circ$, $Z=4$, and compound II crystallizes in space group $P1$ with $a=12.034$, $b=11.648$, $c=13.080$ Å, $\alpha=90.25$, $\beta=116.33$, $\gamma=96.44^\circ$, $Z=4$ with two molecules in the asymmetric unit. Both structures have been solved by direct methods and refined to $R=0.052$ and 0.056 for I and II respectively. Molecules of I and II adopt very similar conformations in the solid state with a chair form of the piperidine ring, axial orientation of the hydroxyl group and with the equatorial substituent at C(4) in an extended conformation. The phenyl ring is nearly perpendicular to the mean plane of the piperidine ring. The arrangements of molecules in the crystals of I and II are very similar but the lack of exact equivalence of the two independent molecules in II lowers the symmetry from monoclinic to triclinic. The networks of H-bonds are topologically equivalent in both crystals. Molecules are joined in chains along the c-axis. The N-O group in II makes an angle of 18° with the C-N-C plane, well within the range observed in other nitroxypiperidine derivatives.

09.2-52 STRUCTURAL STUDIES OF PHENYL-SULPHIDE DERIVATIVES. By Józef Garbarczyk, Department of Chemistry, Technical University, Poznan, Poland.

The crystal structures of the following compounds have been determined:

- 1.4,4'-dimercaptodiphenylenesulphide: monoclinic $P2_1/n$, $a=5.752$, $b=25.767$, $c=7.954$ Å, $\beta=95.24^\circ$, $Z=4$, $R=0.080$ for 1237 reflexions.
- *2.4,4'-bis(phenylthio)-benzene: monoclinic $P2_1/a$, $a=5.794$, $b=18.185$, $c=7.590$ Å, $\beta=109.78^\circ$, $Z=2$, $R=0.054$ for 1387 reflexions, molecular symmetry C_2 .
- **3.4,4'-sulphonyl-bis(phenylene-S-thiobenzoate)/monoclinic $P2_1/a$, $a=14.050$, $b=10.404$, $c=16.734$ Å, $\beta=110.57^\circ$, $Z=4$, $R=0.049$ for reflexions.
- 4.Triphenodithiazine: monoclinic $P2_1/a$, $a=10.472$, $b=5.430$, $c=12.356$ Å, $\beta=107.61^\circ$, $Z=2$, $R=0.0711$ for 699 reflexions, molecular symmetry C_2 .

*In collaboration with Prof. G.D.Andretti, University of Parma, Italy, Cryst. Struct. Com.1981/** /Details of the analyses of compound 3, have been submitted to Die Makrom. Chem. for publication/.

The present work is a part of our study on the relationship between structure and thermal properties of sulphur containing polymers. The investigated compounds are model molecules for related polymers.

It was found that the bond lengths S—C are within a range 1.744 to 1.785 Å and C—S—C angles within a range 99 to 106° . It is interesting that in triphenodithiazine these values are maintained in spite of the fact a sulphur atom is a part of six-membered ring.

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

The results obtained show a deformation of phenyl rings: the angles at C atoms bonded with a sulphur atom are smaller than those at neighbouring carbon atoms. Comparison of the molecular structures of 1, 2 and 3 indicates that the investigated compounds have various angles between phenyl planes. Difference in conformation of 1 and 2 and in particularly asymmetric structure of 3 was explained on the basis of energetic calculations. It was determined that in 3, for example, the energetic barrier during rotation around C-S bond is relatively low /approx. 2-3 kcal/mol/. It indicates a possibility of a conformational change in the compounds in diluted solution and at rising temperature. The determines valence angles, bond lengths as well as angles determining molecular structures are different from those found for poly-p-phenylenesulphide.

The arrangement of molecules in unit cells confirms that only these model compounds which, similarly to related macromolecules, have not molecular symmetry C_1 can be used for the study of intermolecular interactions in polymers.

half forming the asymmetric unit.

The structure was solved using the direct method and then refined by least squares method using full matrix approximation with anisotropic thermal parameters for individual atoms to $R_w = 0.05$.

The dimer was found to have a centre of symmetry at the middle point of the bond connecting the two dimer halves. In each dimer half the thienyl ring was found to be coplanar with the pyridazinone ring. The deviations from this planarity were calculated for each atom.

09.2-53 Crystal Structure of 4,5-dihydro-6-(2-thienyl)-3(2H)pyridazinoneazine, $C_{16}H_{16}N_6S_2$.

By

G. Will, I. S. Ahmed Farag and M. El-Kordy.

(National Research Centre, Dokki, Cairo.)

The compound was prepared from a direct unusual reaction of 6-(2-thienyl)-2,3,4,5-tetrahydropyridazin-3-one with hydrazine hydrate. The crystals of this compound are monoclinic with unit cell constants: $a=5.567(1)_0$; $b=7.857(2)$; $c=19.194(10) \text{ \AA}$; $\beta=99.97(3)$ and $z=2$. The systematic absences and the statistical distribution of the normalized structure amplitudes showed that the unit cell should acquire a centre of symmetry and hence the space group was considered to be $P 2_1/c$. The molecule behaves in the structure as a dimer with

09.2-54 COMPARATIVE STUDY OF THE HIGH PRESSURE AND LOW TEMPERATURE $(\text{IMTSF})_2\text{PF}_6$ STRUCTURES.

J. Gaultier, C. Hauw, B. Gallois
Laboratoire de Cristallographie et de Physique Cristalline
LA 144 CNRS, 351, Cours de la Libération - 33405 TALENCE
CEDEX (France)

The crystal structure of $2 \text{ C}_{10}\text{H}_{12}\text{Se}_4^{1/2+} \cdot \text{PF}_6^-$, a unidimensional organic conductor which exhibits superconductivity at 12 Kbars below 0.9 K, has been determined respectively at 4 K and under an 7 Kbars hydrostatic pressure.

The space group and the crystal packing are the same than at ambient pressure and room temperature (Thorup et al 1981, Acta Cryst, B37). However the intra and interstack distances are perturbed. In particular, Se-Se distances of great interest for the understanding of conducting properties, decrease strongly. Thus, the dimensional character is increased.

	1 Kbar 300 K	7 Kbars 300 K	1 bar 4 K
Intrastack Se-Se distances			
d_1	3,66 \AA	3,56 \AA	3,55 \AA
d_2	3,63 \AA	3,56 \AA	3,53 \AA
Interstack Se-Se distances			
d'_1	3,88 \AA	3,74 \AA	3,71 \AA
d'_2	3,93 \AA	3,78 \AA	3,74 \AA
d'_3	3,96 \AA	3,83 \AA	3,86 \AA
Shortest Se-F distance			
d'_4	3,23 \AA	3,09 \AA	3,06 \AA

At room temperature, the PF_6^- anion is disordered. Under pressure, this disorder strongly weakens and at 4 K, the anion is perfectly ordered.