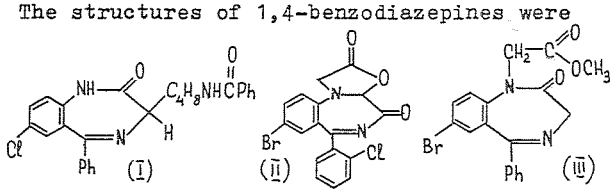
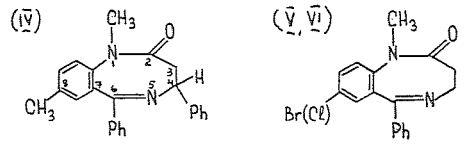
09.2–50 THE STRUCTURES OF SOME 1,4-BENZODIAZEPINES, 1,5-BENZODIAZOCINES AND ITS DERIVATIVES. By A.A.Dvorkin, Yu.A.Simonov and T.I. Malinowsky, Institute of Applied Physics of Academy of Sciences of Mold.SSR, Kishinev and S.A.Andronati and A.S.Yavorsky, Physics-Chemical Institute of Academy of Sciences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

The structures of 1,4-benzodiazepines were



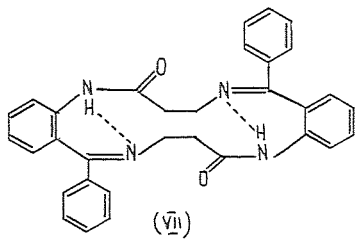
(I) (II) (III)

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



(IV) (V, VI)

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-



(VII)

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-phenoxymethyl-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, β=111.98°, Z=4, and compound II crystallizes in space group $P\bar{1}$ with a=12.034, b=11.648, c=13.080 Å, α=90.25, β=116.33, γ=96.44°, 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 CNC plane, well within the range observed in other nitroxypiperidine derivatives.

09.2–52 STRUCTURAL STUDIES OF PHENYLSULPHIDE 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, β=95.24°, 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, β=109.78°, Z=2, R=0.054 for 1387 reflexions, molecular symmetry C_i.
3. 4,4'-sulphonyl-bis/phenylene-S-thiobenzoate/: monoclinic $P2_1/a$, a=14.050, b=10.404, c=16.734 Å, β=110.57°, Z=4, R=0.049 for reflexions.
4. Triphenodithiazine: monoclinic $P2_1/a$, a=10.472, b=5.430, c=12.356 Å, β=107.61°, Z=2, R=0.0711 for 699 reflexions, molecular symmetry C_i.

*/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 lenghts 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.