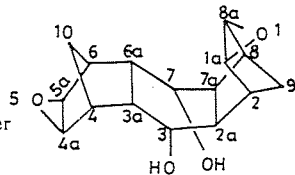


09.2-3 CRYSTAL AND MOLECULAR STRUCTURE OF (1a α , 2 β , 2a β , 3 α , 3a α , 4 α , 4a β , 5a β , 6 α , 6a α , 7 α , 7a β , 8 β , 8a α) - TETRADECAHYDRO-2,8:4,6-DIMETHANOANTHRA [2,3-b:6,7-b'] BISOXIRENE-3,7-DIOL MONOHYDRATE C₁₆H₂₀O₄·H₂O. By V. Ganesh and M. Seshasayee, Department of Physics, Indian Institute of Technology, Madras 600036, R. Bakthavatchalam and S.R. Ramadas, Department of Chemistry, Indian Institute of Technology, Madras 600036, India.

The above said compound belongs to a class of bridged polycyclic polyfunctional compounds. Such type of molecules have been claimed to be useful in polymer industry as curing agents for polyurethanes containing isocyanates (NCO) as terminal groups. The compound crystallizes in the monoclinic system with cell parameters: a = 16.100(1), b = 7.198(1), c = 12.858(2), β = 105.26(2)°. The space group is Cc with four molecules per unit cell. Three dimensional intensity data have been collected on a Nonius CAD-4 diffractometer with CuK α radiation. The structure is solved by direct methods and refined to a R value of 0.056 for 1290 unique reflections. All hydrogens have been located by difference Fourier synthesis. Intermolecular stability is ensured by both Van der Waal's forces and hydrogen bonds due to the water molecule.



09.2-4 CRYSTAL STRUCTURE OF TETRAMETHYLAMMONIUM DIHYDROGEN ORTHOPHOSPHATE MONOHYDRATE. By N.Ohama, M.Machida, T.Nakamura* and Y.Kunifujii*, Department of Physics, Kyushu University 33, Fukuoka 812, Japan; *School of Nursing and Medical Technology, University of Occupational and Environmental Health, Kitakyushu 807, Japan

This study has been carried out as the first case of a research series of the crystal structures of dihydrogen orthophosphates containing bulky univalent organic ions. Tetramethylammonium dihydrogen orthophosphate monohydrate, N(CH₃)₄H₂PO₄·H₂O is monoclinic, space group P2₁/c with a = 8.518(1), b = 12.897(2), c = 8.440(2) Å, β = 99.05(1)°, V = 915.6 Å³ and Z = 4. X-ray intensity data were collected at 296(1) K with an Enraf-Nonius CAD-4 diffractometer using MoK α radiation. The structure is determined by Patterson and Fourier syntheses and refined to R = 0.037 for 2023 unique reflections. The feature of the structure can be described as follows: H₂PO₄⁻ chains along the c axis are formed with PO₄ tetrahedra connected each other by two H bonds [O...O distances 2.543(2) and 2.606(2) Å, and O-H...O angles 171.1(8) and 175.6(8)°]; other two H bonds [O...O distances 2.809(2) and 2.875(2) Å, and O-H...O angles 167.7(8) and 167.5(8)°] between adjacent H₂PO₄⁻ chains are also formed with water molecules. Consequently a two-dimensional network of H bonds is constructed; there are no H bonds between the networks. N(CH₃)₄⁺ ions exist in the hollow space of the network.

09.2-5 ON THE CHANGE OF THE CRYSTAL STRUCTURE CAUSED BY THE CHEMICAL SUBSTITUTION AT 4- or 4,4'-POSITIONS OF trans-AZOBENZENES. By S. Kashino, T. Yamashita and M. Haisa, Department of Chemistry, Faculty of Science, Okayama University, Japan.

All the 4,4'-disubstituted trans-azobenzenes whose crystal structures have been determined so far adopt a space group P2₁/c, and in many cases the molecules retain the symmetry $\bar{1}$ in the crystals. Disordered structures have been observed in trans-azobenzene (C. J. Brown, Acta Cryst., 1966, 21, 146-152; J. A. Bouwstra, A. Schouten & J. Kroon, Acta Cryst., 1983, C39, 1121-1123) and in 4,4'-dimethyl-trans-azobenzene (C. J. Brown, Acta Cryst., 1966, 21, 153-158). The structures of 4-substituted-trans-azobenzenes have not been reported in spite of the carcinogenic interest. We have determined the structures of three 4-substituted-trans-azobenzenes based on the diffractometer data (Cu K α , T=295 K), and refined by full-matrix least-squares method. We will report the results and discuss on the structural change caused by the chemical substitution at 4- or 4,4'-positions of trans-azobenzenes. The structures determined are (I) 4-amino-trans-azobenzene [P2₁/n, Z=4, a=14.017(2), b=5.620(6), c=13.750(2) Å, β =98.34(1)°, d = 1.21, d_m=1.222 g/cm³, R=0.105 for 1405 reflections, disordered], (II) 4-dimethylamino-trans-azobenzene [P2₁, Z=4, a=7.412(2), b=27.532(7), c=6.065(2) Å, d_m=1.20, d_x=1.209 g/cm³, R=0.091 for 620 reflections], and (III) 4-diethylamino-azobenzene [P2₁, Z=2, a=10.880(3), b=7.576(6), c=8.913(2) Å, β =100.03(2)°, d_m=1.15, d_x=1.163 g/cm³, R=0.137 for 1214 reflections, disordered]. The structure of (I) is similar to that of trans-azobenzene, P2₁/c, Z=4. The molecules acquire $\bar{1}$ by disordering, and occupy the positions 2a and 2d. The two kinds of molecules are disordered furthermore with an occupancy ratio of 0.72 to 0.28. In (II) the molecular sheets are formed on (100), and the molecules are stacked along a.

The structure is similar to that of 4,4'-diethoxy-trans-azobenzene (P2₁/c, Z=4, a=9.77, b=7.59, c=20.57 Å, β =104.0°; J. L. Galigné, Acta Cryst., 1970, B26, 1977-1984), where the 2₁ along b in (II) changes to a c-glide. In (III) the space group descends to P2₁, a maximal subgroup of P2₁,2₁, and P2₁/c. There is a pseudo-mirror type disorder with an occupancy ratio of 0.72 to 0.28. The molecular sheets are formed on (010), and the molecules are stacked along b which corresponds to the a of (II). We will choose the structure of 4,4'-dichloro-trans-azobenzene, P2₁/c, Z=2 (H. Hope & D. Victor, Acta Cryst., 1969, B25, 1849-1853), as a reference to consider the structural change, because the structure is ordered and the molecule has $\bar{1}$ in the crystal. The structural change observed can be summarized as follows: (1) Change retaining the molecular symmetry $\bar{1}$. (1a) Change to a disordered structure without substantial change in the molecular orientation in the unit cell (e.g., 4,4'-dimethyl-trans-azobenzene). (1b) Change to a disordered structure with a loss of 2₁ at z=1/4. Two kinds of molecules occur in a new unit cell (e.g., trans-azobenzene). The molecular symmetry $\bar{1}$ is acquired by disordering when the molecule is non-centrosymmetric (e.g., I). (1c) Change to a different molecular orientation without disordering (e.g., 4,4'-dibromo-trans-azobenzene; A. G. Amit & H. Hope, Acta Chem. Scand., 1966, 20, 835-844). (2) Change to a structure with no molecular symmetry. The molecular orientation is also changed. (2a) Change without disordering (e.g., 4,4'-diethoxy-trans-azobenzene and II). (2b) Change with disordering (e.g., III). In the structures classified to (1) the space around the azo group is filled by the benzene rings of the neighbouring molecules, while in those classified to (2) the space is filled by the bulky substituents.