C-166  09.  STRUCTURES OF ORGANIC AND COORDINATION COMPOUNDS

09.2-3  CRystAL AND MOLECULAR STRUCTURE

OF [N(N(CH3)4);H2P2O7]·H2O; a monoclinic system with cell parameters: a = 15.00(1), b = 7.198(1), c = 12.858(2), b = 105.28(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 CuKα radiation. The structure is solved by direct methods and refined to a R value of 0.056 for 2033 unique reflections. All hydrogens have been located by difference Fourier synthesis. Inter-molecular stability is ensured by both Van der Waals forces and hydrogen bonds due to the water molecule.

09.2-5  ON THE CHANGE OF THE CRYSTAL STRUCTURE CAUSED BY THE CHEMICAL SUBSTITUTION AT 4- or 4',5'-POSITIONS OF TRANS-azoBENZENES. By S. Kashiwagi, T. Yamashita and N. 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 1 in the crystals. Disordered structures have been observed in trans-azobenzenes (C. J. Brown, Acta Cryst., 1986, 42, 146-152; J. A. Bouwstra, A. Schouten & J. E. Koom, Acta Cryst., 1983, C39, 1112-1123) and in 4,4'-dimethyl-trans-azobenzene (C. J. Brown, Acta Cryst., 1986, 21, 153-158). The structures of 4-disubstituted-trans-azobenzenes have been determined by difference Fourier synthesis. Inter-molecular forces and hydrogen bonds due to the water molecule.

The above said compound belongs to a class of bridged polymeric 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. Tetramethylammonium dihydrogen orthophosphate monohydrate, N(CH3)4H2P2O7·H2O (228, 1877-1904), was selected for (I) because of its higher melting point (167.5 °C) and in 4,4'-dimethyl-trans-azobenzene (C. J. Brown, Acta Cryst., 1986, 21, 153-158). The structures of 4-disubstituted-trans-azobenzenes have been determined by difference Fourier synthesis. Inter-molecular forces and hydrogen bonds due to the water molecule.

This study has been carried out as the first step in the atomic structure determination of the azo group in the azobenzene molecule. The azo group is disordered in the crystals of 4,4'-dimethyl-trans-azobenzene. The structure is ordered and the molecule has 1 symmetry in the crystals. Disordered structures have been observed in trans-azobenzenes (C. J. Brown, Acta Cryst., 1986, 42, 146-152; J. A. Bouwstra, A. Schouten & J. E. Koom, Acta Cryst., 1983, C39, 1112-1123) and in 4,4'-dimethyl-trans-azobenzene (C. J. Brown, Acta Cryst., 1986, 21, 153-158). The structures of 4-disubstituted-trans-azobenzenes have been determined by difference Fourier synthesis. Inter-molecular forces and hydrogen bonds due to the water molecule.

The structure is similar to that of 4,4'-dithioxy-trans-azobenzene (P21/c, Z=2, a=9.77, b=7.59, c=20.57 Å, α=104.0°; J. L. Balagné, Acta Cryst., 1970, B26, 1123-1126), as a reference to consider the structural change, because the structure is ordered and the molecule has 1 symmetry in the crystal. The structural change observed can be summarised as follows: (1) Change retaining the molecular symmetry 1. (2a) Change to a disordered structure without substantial change in the molecular orientation in the unit cell (e.g., 4,4'-dimethyl-trans-azobenzene). (2b) Change to a disordered structure with a loss of 1 symmetry in the unit cell (e.g., 4,4'-dimethyltrans-azobenzene). The molecular symmetry 1 is acquired by disordering when the molecule is non-centrosymmetric (e.g., 1). (1c) Change to a different molecular orientation without disordering (e.g., 4,4'-dithioxy-trans-azobenzene; A. G. Anil & H. Hope, Acta Chem. Scand., 1966, 20, 635-644). (2) Change to a structure with no molecular symmetry. The molecular orientation is also changed. (2a) Change without disordering (e.g., 4,4'-dithioxy-trans-azobenzene) and (2b) Change with disordering (e.g., 4,4'-dimethyl-trans-azobenzene). 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.