

mann: J.Signal-AM. (1974) 2, 457 and J.Molec. Structure (1975) 27, 67 and Theoret.Chim.Acta (1975) 36, 351 based on MO-theory. The polymethinic electron system corresponds to a defined spatial configuration of the molecules and a special intermolecular arrangement. Results of X-ray diffraction have contributed essentially to the general understanding and to the development of the theory. Significantly geometrical features of the polymethinic state are: equalisation of bond lengths and alternation of valence angles (Kulpe; Zedler; Dähne; Nolte: J.prakt.Chem. (1973) 315, 865); special intermolecular aggregation (Kulpe; Dähne; Ziemer; Schulz: Photogr.Sci.Eng. (1976) 20, 205); long bond lengths between Csp^2 atoms in coupled polymethines (Kulpe; Dähne: Acta Cryst. (1978) B34, 3616). In the last case canonic structures with the same sign of charge at neighbouring atoms are preferred as opposed to Pauling's rule (Pauling: Proc.nat.Acad.Sci.USA (1932) 18, 498). Special behaviour of the carbonyl group can be explained on the basis of the polymethine concept (Kulpe; Z.Chem. (1980) 20, 377 and Angew. Chem. in press). In photochromic azomethine imine-1,3-dipoles heteroatom polymethinic fragments are present causing strong intermolecular C-H...O hydrogen bonds (Kulpe; Seidel: Z.phys.Chem. in press). Nearly ideal polymethinic compounds are e.g. open chained cyanines and oxonols and coupled polymethines like substituted hydroxybenzoquinones, aminobenzoquinones, oxalates and oxamates (Fabian: J.prakt.Chem. (1978) 320, 316). Typical polymethine radicals with branched polymethinic fragments are Wurster's coloured salts (cf. 1.ref.). NMR spectroscopy provides further experimental verification of the polymethinic electron system (Radeglia: J.prakt.Chem. (1974) 316, 344).

09.2-01 THE CRYSTAL AND MOLECULAR STRUCTURE OF 3'-FLUOROBIPHENYL-4-CARBOXYLIC ACID. By A. Rawas and H.H. Sutherland, Physics Department, University of Hull, Hull, England.

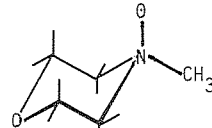
3'-Fluorobiphenyl-4-carboxylic acid, $C_{13}H_9O_2F$, is monoclinic, space group $P2_1/c$, with $a = 3.92(1)$, $b = 8.04(1)$, $c = 32.50(2) \text{ \AA}$, $\beta = 101.6(1)^\circ$, $Z = 4$, $D_m = 1.42$, $D_c = 1.43 \text{ Mg m}^{-3}$. The structure was solved by Patterson synthesis with $CuK\alpha$ x-ray data measured by densitometer and visually from equi inclination Weissenberg photographs. It was refined anisotropically by block diagonal least squares to $R = 0.08$ for 895 reflexions. The average C-C bond in the two phenyl rings is 1.390 \AA . The molecule is non planar; the two phenyl rings are rotated about the phenyl-phenyl bond by 36.3° and the acid group is rotated about its C-C bond by 3.6° . There is also distortion in the bond angle around C(3) with the internal angle of $124.5(1.2)^\circ$; the C-F bond is $1.363(13) \text{ \AA}$ and makes an angle of 2° with the phenyl plane.

Dimers formed from the molecules by an O-H...O bond of $2.623(15) \text{ \AA}$, pack in a herring bone arrangement with the fluorine atoms lying in sheets parallel to (001).

09.2-02 THE CRYSTAL AND MOLECULAR STRUCTURES OF SOME TERTIARY AMINE OXIDES.

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Recent investigations came to focus on tertiary amine oxides which look most promising for their cellulose dissolving power. To elucidate some of their structural characteristics, along with their possible mode of interactions with cellulose chains, a crystallographic investigation has been undertaken. Most attention has been devoted to N-methylmorpholine N-oxide (MMNO) : ($C_5H_{11}NO_2$).



- Anhydrous MMNO (MP=172°C) is monoclinic $P2_1/m$, ($a = 9.886(5)$, $b = 6.621(5)$, $c = 5.112(4)$, $\beta = 111.54(10)^\circ$, $Z = 2$). The structure has been refined to $R = 0.047$. The molecule is found to be in a perfect chair conformation and the $N \rightarrow O$ bond to be axially oriented with respect to the ring.

-MMNO, H_2O (MP=73°C) is monoclinic $P2_1/c$ ($a = 25.481(9)$, $b = 6.040(5)$, $c = 9.186(6)$, $\beta = 99.88(10)^\circ$, $Z = 8$). The structure has been refined to $R = 0.042$. Within the crystal, the water molecules are structured into a polymer-like fashion by the MMNO molecules through an extensive hydrogen bonding scheme. There exists a distinct segregation between the hydrophobic and the hydrophilic parts of the structure.

-MMNO, 2.5 H_2O (MP=36°C) is monoclinic $P2_1/c$, $a = 12.803(6)$, $b = 6.500(4)$, $c = 21.913(8)$, $\beta = 109.99(10)^\circ$, $Z = 8$. The structure has been refined to $R = 0.042$. An intricate network of 10 different hydrogen bonds holds the molecules in the crystal.

-MMNO : 1,2-trans-cyclohexanediol complex is monoclinic, $P2_1/c$, ($a = 6.137(3)$, $b = 10.153(4)$, $c = 21.015(6)$, $\beta = 94.33(10)^\circ$, $Z = 4$). The structure has been refined to $R = 0.042$. The geometry and conformation of MMNO are the same as those found in the other structures. The 1,2-trans-cyclohexanediol molecule is in a chair conformation and the hydroxylic oxygen atoms are in a diequatorial arrangement. The $N \rightarrow O$ structuring site of MMNO links through bifurcated hydrogen bonds contiguous 1,2-trans-cyclohexanediol molecules oriented into a polymer-like fashion.