

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

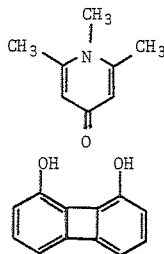
09.2-39 HYDROGEN BONDING INTERACTIONS FOR 1,8-BIPHENYLENEDIOL AND DERIVATIVES. By J. Hine, K. Ahn, S.-M. Linden and J.C. Gallucci, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, U.S.A.

The crystal structures of 1,8-biphenylenediol(I), of the 1:1 adduct of this diol with 1,2,6-trimethyl-4-pyridone (II), and of 1,8-dimethoxybiphenylene(III) have been determined at low temperatures to investigate the hydrogen bonding possibilities in these systems.

Crystal data (MoK α radiation): I, orthorhombic, Pca2 $_1$, at -123°C, a=14.056(2), b=4.952(1), c=24.134(3) Å, Z=8, R(F)=0.048 for the 1985 F $_o^2$ values. II, monoclinic, P2 $_1$ /n, at -123°C, a=7.639(1), b=22.130(4), c=9.411(1) Å, β =90.66(1)°, Z=4, R(F)=0.048 for 2188 reflections with F $_o^2$ >3 σ (F $_o^2$). III, monoclinic, P2 $_1$ /c, at -114°C, a=15.378(3), b=13.360(3), c=10.896(2) Å, β =109.57(1)°, Z=8, R(F)=0.041 for 3011 reflections with F $_o^2$ >3 σ (F $_o^2$).

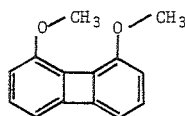
Molecule I crystallizes to form linear chains of intermolecular hydrogen bonds. These chains lie in planes approximately perpendicular to the molecular plane. Each oxygen atom is involved in a donor and acceptor interaction with O-H...O distances ranging from 2.752(3) to 2.828(3) Å.

The two components of the 1:1 adduct (II) are almost coplanar and both hydroxy groups of one diol molecule form strong hydrogen bonds to the same basic oxygen atom of the 1,2,6-trimethyl-4-pyridone to form a cyclic unit; the O-H...O distances are 2.545(3) and 2.548(3) Å.



(II)

In molecule III both O-CH $_3$ bonds lie close to the plane of the biphenylene ring. One of these bonds is situated such that the intramolecular O...CH $_3$ distance is 3.000(3) Å.



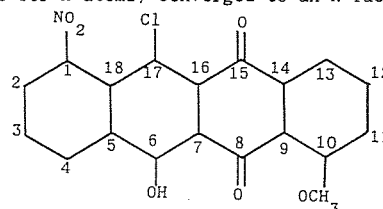
(III)

09.2-40 THE CRYSTAL AND MOLECULAR STRUCTURE OF 5-CHLORO-12-HYDROXY-4-NITRO-10-METHOXY-6a,7,10,10a-TETRAHYDRONAPHTHACEN-6,11-DIONE. By M.A. Hoyos, S. Martinez Carreras and S. Garcia Blanco, Dpt. Geologia, U.A.M., Madrid-34, Spain and Dpt. R-X, Inst. Rocasolano, C.S.I.C., Madrid, Spain.

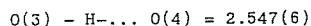
Crystal data C $_{19}$ H $_{14}$ O $_5$ NCl; Mr=387.77; P $\bar{1}$; a=9.216 (2), b=9.668(3), c=10.089(2)Å; α =82.81(3), β =108.08(2), γ =99.88(2)°; V=839.2(4)Å 3 ; Z=2; D $_x$ =1.535 Mg m $^{-3}$; λ (MoK α)=0.7172Å, μ =2.61 cm $^{-1}$; F(000)=400.

Red plate-like crystal. Nonius CAD-4 diffractometer, graphite-monochromated MoK least-squares fit of 25 reflections to obtained cell dimensions. 2381 independent observed reflections with I>2 σ (I), θ -2 θ scan technique, two periodically monitored reflections with no significant intensity variation, Lp correction, absorption ignored. Structure solved with MULTAN (Germain, Main and Woolfson 1971) except one oxygen for the nitro group and the C atom of the methyl group, that were located by Fourier map. All H-atoms located in difference syntheses.

Full-matrix refinement of a scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms) converged to an R factor of 0.067.



The structure may be described as isolated molecules of C $_{19}$ H $_{14}$ O $_5$ NCl, separated by ordinary van der Waals distances reflecting only non-bonded interactions between molecules. The bond distances and angles are normal for this type of compound and show no unexpected values. The hydroxylic H(O $_3$) is involved in a strong intramolecular hydrogen bond



The molecule is not planar. The equation of the "best" plane for the 18 carbon atoms of the molecule is:

$$0.787X - 0.056Y - 0.614Z = 6.612$$

Atoms C(8), C(9), C(14), C(15) deviate strongly from the plane.

The planarity of the anion carbon rings varies: The A ring is planar within the limits of experimental error, while in the other rings the deviations from the best plane are more significant. The degree of aromaticity of the rings diminishes in the order A > B > D > C.

The presence of a symmetry center results in a mean separation between the carbon atoms C(6)-C'(3), C(6)-C'(2) of 3.46Å. These are the atoms involved in a charge-transfer.