

09.2-22 CRYSTAL AND MOLECULAR STRUCTURE OF 2-HYDROXY-4-METHOXY- ω, ω -DICHLOROACETOPHENONE. By D. Chattopadhyay and S. K. Mazumdar, Crystallography & Molecular Biology Division, Saha Institute of Nuclear Physics, Sector I, Block 'AF', Bidhannagar, Calcutta-700 064, India.

Acetophenone is known to have photochemical properties. Aminoacetophenones possess some degree of local anaesthetic activity (Haisa, Kashino, Yuasa & Akigawa, *Acta Cryst.* (1976) **B32**, 1326). The X-ray analysis of the title compound has been carried out as a part of our programme of studies on various substituted acetophenones.

Crystal and experimental data: $C_9H_8O_3Cl_2$, crystallized from ethanol, $M_r=235.08$, orthorhombic, $P2_12_12_1$, $a=6.981(1)$, $b=11.901(3)$, $c=12.061(3)$ Å, $Z=4$, $D_m=1.553$, $D_x=1.557$ Mg m^{-3} , $F(000)=480$, $\lambda=0.7107$ Å, $\mu=0.624$ mm $^{-1}$. The structure, solved by direct methods, was refined to a final R of 0.042 with 946 'observed' reflections [$I > 3\sigma(I)$]. All hydrogen atoms were located and their parameters were refined.

The C(phenyl)-C(carbonyl) bond is considerably shorter than those in *p*-hydroxyacetophenone (Vainshtein, Lobanova & Gurskaya, *Krystallografiya* (1974) **19**, 531), *p*-aminoacetophenone (Haisa *et al.* (1976)) and in 3-chloro-4-amino- ω, ω -dichloroacetophenone (A. De, unpublished). The angle *ipso* to the dichloroacetyl group is significantly shorter than the sp^2 angle. These observations indicate conjugation between the phenyl ring and the carbonyl group. Substituents *ortho* (hydroxy) and *para* (methoxy) to the dichloroacetyl group, having +R effects favour the conjugation; this is further corroborated by the shortening of the two C(sp^2)-O bonds as compared to those in *p*-hydroxyacetophenone (Vainshtein *et al.* (1974)) and *p*-hydroxyacetanilide (Haisa, Kashino & Maeda, *Acta Cryst.* (1974) **B30**, 2510). The Cl-C-Cl bond angle at the dichloroacetyl moiety is comparable with similar angles in Chloramphenicol (Acharya, Sake Gowda & Post, *Acta Cryst.* (1979) **B35**, 1360) and 3-chloro-4-amino- ω, ω -dichloroacetophenone (A. Dey, unpublished). Four of the endocyclic bond angles in the phenyl ring agree well with those in *p*-aminoacetophenone; the angle *ipso* to the methoxy group is larger in the present structure while that at C3 is smaller (Haisa *et al.* (1976)). An intramolecular O-H...O(carbonyl) hydrogen bond favours the *endo* conformation of the molecule; this may have aided the coplanarity of the carbonyl moiety and the phenyl ring although such coplanarity is also found in acetophenone (Tanimoto, Kobayashi, Nagakura & Saito, *Acta Cryst.* (1973) **B29**, 1822) and *p*-aminoacetophenone (Haisa *et al.* (1976)).

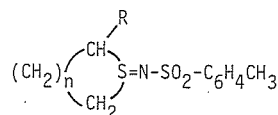
09.2-23 THE CRYSTAL STRUCTURES OF OVERCROWDED CONDENSED POLYCYCLIC AROMATIC HYDROCARBONS. By I. Oonishi, S. Fujisawa and J. Aoki, Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274, and Y. Ohashi and Y. Sasada, Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan.

We have been studying the synthesis and structure of a series of overcrowded condensed polycyclic aromatic hydrocarbons, which are stereochemically interesting because they exhibit great steric hindrance between hydrogen atoms. Recently, X-ray analysis of violanthrene B(I) was undertaken to compare the crystal and molecular structure with those of II and III (Bull. Chem. Soc. Jpn., (1978) **51**, 2256 and (1982) **55**, 3424). Crystals of I, $C_{34}H_{18}$, are monoclinic, and space group $P2_1/c$, with the lattice constants $a=25.98(1)$, $b=3.307(5)$, $c=19.975(8)$ Å, $\beta=96.55(3)^\circ$, and $Z=4$. The structure was solved by the direct method and refined by a block-diagonal least-squares method to an R value of 0.76 on the basis of 1242 reflections. The molecules are largely distorted from a planar structure due to the repulsion between the hydrogen atoms attached to the carbon atoms indicated by asterisk. The steric repulsion is mainly released by the enlargement of the C-C-C angle and twisting of the two C-C bonds opposite to each other. In the present molecules, they are 124° and 37.3° , respectively.



09.2-24 X-RAY STUDY OF THE CONFORMATION OF 2-ALKYL-THIOLANE AND 2-ALKYL-THIANE-1-TOSYLIMIDES. A. Kálmán, T. Koritsánszky, *Central Research Institute for Chemistry HAS, H-1525, Budapest POB 17, Hungary*; I. Jalsovszky, F. Ruff and A. Kucsman, *Institute of Organic Chemistry, Eötvös University, H-1445, Budapest POB 325, Hungary*

The diastereomers of 2-alkyl-thiolane-1-tosylimides ($n=2$, R=Me, Et, *i*-Pr and *t*-Bu) and the corresponding thiane derivatives ($n=3$) have been prepared by stereoselective syntheses and their structures have been assigned by ^{13}C NMR spectroscopy.



In the case of 2-alkyl-thiane-1-tosylimides even the orientation of both substituents has been established, showing that 2-alkyl-substituents assume invariably the *equatorial* position, while the 1-tosylimino group is *equatorial* in the *trans* diastereomers, but *axial* in the *cis* compounds. These observations have been substantiated by the X-ray analyses of several compounds e.g. the 2-methyl diastereomers (II and III) reported here. Although the parent compound I exhibits conformational disorder around the S(VI)-N bond, the conformers bear the NTs group only in *axial* position: I: $C_5H_{10}S=N-Ts$,

II: *cis*-2-Me-($C_5H_9S=N-Ts$), III: *trans*-2-Me-($C_5H_9S=N-Ts$)

For the thiolane derivatives, however, the actual orientation of the 1-N-Ts and 2-alkyl substituents could not be inferred from the NMR spectra owing to the flexibility of the five-membered rings. These informations have been obtained from X-ray studies of the following thiolane derivatives: IV: $C_4H_8S=N-Ts$, V: *trans*-2-Me($C_4H_7S=N-Ts$),