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.

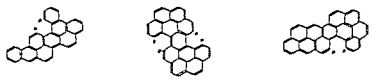
Acetophenone is known to have photochemical properties. Aminoacetophenones possess some degree of local anaesthetic activity (Haisa, Kashino, Yuasa & Akigawa, Acta Cryst. (1976) B32, 1326). The X-ray analysis of the title compound has been carried out as a part of our programme of studies on various 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 Mgm^{-3}, F(000)=480, λ=0.7107 Å, μ=0.624 mm^{-1}. The structure, solved by direct methods, was refined to a final R of 0.042 with 946 'observed' reflections [$I \geq 3\sigma(I)$]. 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 (1976)) and in 3-chloro-4-amino-ω,ω-dichloroacetophenone (A. De, unpublished).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 (1979) B35, 1360) and 3-chloro-4-amino-ω,ω-dichloroacetophenone (A. Dey, unpublished).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.

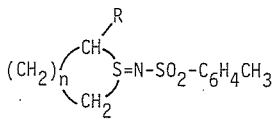
We have been studying the synthesis and structure of a series of overcrowded condensed polycyclic aromatic hydrocarbons, which are stereochemically interesting because they exhibit great steric hindrance between hydrogen atoms. Recently, X-ray analysis of violanthrene B(I) was undertaken to compare the 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=25.88(1), b=3.807(5), c=19.975(8) Å, β=96.55(3)°, 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.



I II III

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 Á. 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),

VI: *cis*-2-Et-(C_4H_7S=N-Ts), (struct.anal. is in progress)

VII: *trans*-2-Et-(C_4H_7S=N-Ts), *VIII*: *cis*-2-*t*-Bu(C_4H_7S=N-Ts)

In *IV* the tosylimino group assumes *axial* position and the conformation of the five-membered ring is near to a half-chair form with a C_2 symmetry axis bisecting the C(2) atom. [The puckering parameters (Cremer & Pople, J.Amer.Chem.Soc., *97*, 1354 (1975) are listed below.]

As it has been shown by g.e.d., the thiolane ring with bivalent sulfur atom exhibits much greater puckering amplitude and a twofold axis bisecting the S(1) atom [Náhlovská, Náhlovsky & Seip, Acta Chem.Scand. (1969) *23*, 3534.] In the *cis* compound *VIII* the NTs substituent retains its *axial* position, while the 2-*t*-Bu group is *equatorial*, the twofold axis of the distorted half-chair form shifted toward the C(4) atom. In the *trans* isomers *V* and *VII* the NTs group can be found in *pseudo-axial* position, while the 2-Me and 2-Et groups with similar torsion angles assume *pseudo-equatorial* orientations. In both cases the thiolane rings appear in similar envelope conformations with a mirror (C_s) plane approximately bisecting the C(4) atom, and only their puckering amplitudes differ considerably.

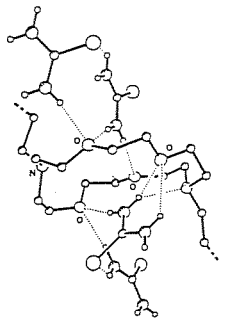
	q(Å)	φ(°)	C_s	C_2
IV	0.41	40.7	-	C(2)
V	0.45	100.3	C(4)	-
VII	0.37	104.6	C(4)	-
VIII	0.46	199.0	-	C(4)
thiolane (g.e.d.)	0.47	270.0	-	S(1)

The bonding of "cyclic N-tosyl sulfilimines" investigated agree well with the corresponding parameters of other sulfilimines as summarized recently by Kálmán, Párkányi & Kucsman (Acta Cryst. (1980) *B36*,1440. Apart from *III*, the amount of rotations about S(VI)-N and S(VI)-C_{ar} bonds fall in the range expected on the basis of a conformational study of N-substituted arylsulfonamides [Kálmán, Czugler & Argay, Acta Cryst. (1981) *B37*, 886].

09.2–25 A 14:1 ADDUCT BETWEEN THIOUREA AND AN N,N'-DISUBSTITUTED MACROCYCLIC AMINO-POLYETHER. By G. Weber and G.M. Sheldrick, Institut für Anorganische Chemie der Universität, D-3400 Göttingen, Fed. Rep. of Germany

In all complexes between (thio)urea and annular oligoethers so far studied by X-ray methods (Harkema, van Hummel, Daasvatn & Reinhoudt, Chem. Commun. (1981), 368; Weber, Acta Cryst. (1982) B38, 2712, and J. Incl. Phen., in press), one (thio)urea molecule is attached at either side of the ligand, thus giving rise to 2:1 core adducts.

The present compound N,N'-didecyl-1,7,10,16-tetraoxa-4,13-diaza-cyclooctadecane.14 thiourea (Pc, a = 28.425(9), b = 16.326(6), c = 9.802(4) Å, β = 94.20(4)°, R = 0.069) is the first example of a (thio)urea/crown ether complex containing a 4:1 core adduct (see Fig.). Its irregular pattern of hydrogen bonds is associated with an irregular conformation of the macrocycle. The remaining ten thiourea molecules are involved in an intricate system of bridging N-H..S linkages.

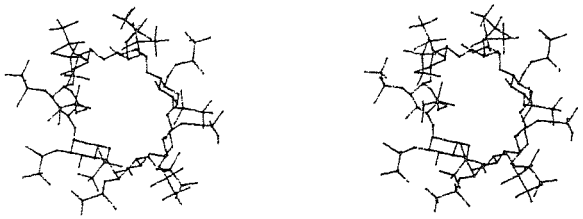


The 4:1 core adduct

09.2–26 THE CRYSTAL STRUCTURE OF per-2,6-O-*t*-BUTYL-DIMETHYL-SILYL-β-CYCLODEXTRIN. Heinz Pöhlmann, Emil Eckle, Gottfried Geiger and John J. Stezowski, Institut für Organische Chemie, Biochemie und Isotopenforschung der Universität Stuttgart, Pfaffenwaldring 55, 7000 Stuttgart 80, FRG.

Because of the potential that selectively modified cyclodextrins would be suitable as medium molecular weight enzyme models, there has been great interest in their chemical substitution. The redundancy in their chemical structure introduces considerable complication into the preparation of pure derivatives. Wife et al[1,2] have characterized the chemistry of a series of cyclodextrin silyl adducts (*t*-butyl-dimethyl substituents) that provide the potential for the preparation of monosubstituted β-cyclodextrins with the substituent on a secondary hydroxyl group. The selectivity of their procedure is very likely the result of steric interactions between the silyl-substituents. We report the crystal structure of one of what we expect to be a small series of derivatives that we plan to study in an effort to elucidate the steric principals involved.

The title compound crystallizes with space group symmetry $P2_1$ with a = 15.206(4), b = 34.236(6), c = 18.622(5) and β = 98.27(2) for a crystal at ∿120 K; Z = 2 for $C_{126}H_{266}O_{35}Si_{14}$ (no clearly defineable solvent has yet been found). The present R value is 0.137 for 10530 contributing data.



A stereoscopic projection of per-2,6-O-*t*-butyl--dimethyl-silyl-β-cyclodextrin.

[1]R. L. Wife, D. E. Reed and H. C. Volger in "Proceedings of the First International Symposium on Cyclodextrins, J. Szejtli (Ed) Akademiai Kiado, Budapest, 1982 pp 289-300.

[2]R. L. Wife, D. E. Reed, D. P. Leworthy, D. M. Barnett, P. D. Regan and H. C. Volger, ibid. pp 301-325.