

09.1-6 AN INVESTIGATION OF THE TORSIONAL ANGLES IN THE TRIFLUOROACETATE GROUP. By R.W.H. Small, Chemistry Department, The University, Lancaster, U.K.

A number of structures involving the trifluoroacetate group (either as an ion or covalently bound) have recently been determined. A consistent pattern amongst these has been a) a wide range of torsional conformations of the CF_3 group b) unusually large U_{ij} values for the fluorines c) evidence of disorder involving alternative conformations of the CF_3 groups. With the carboxyl group as planar and symmetrical and the CF_3 group as three-fold symmetrical, there will be a six-fold barrier to the relative rotation of these groups. Trueblood & Dunitz (Acta Cryst. 1983, B39, 120-133) have interpreted the atomic vibration tensors in a limited number of structures of this type involving the CF_3 group in terms of a weak force constant for internal libration.

In the results presented here, the emphasis is on the range of observed conformations. On account of symmetry, the possible range of unique torsion angles is restricted to 30 degrees. The distribution, within that range, of the angles in about 50 separate determinations of the trifluoroacetate group will be described. The results will be discussed in relation to theoretical studies of the barrier to rotation of the CH_3 group.

09.2-1 X-RAY STUDIES ON HYDROGENATED QUINOLINE-STRUCTURE OF 2-PHENYL 3-METHYL 4-HYDROXYL PERHYDROQUINOLINE. By M. Krishnaiah and L.Ramamurthy, Department of Physics, Sri Venkateswara University, Tirupati 517 502. India; K. Venkatesan, Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012. India and B.M.Gatehouse, Department of Chemistry, Monash University, Clayton, Victoria, Australia, 3168.

Quinoline derivatives have attracted considerable interest in view of their conformations with substituents. The title compound $C_{16}H_{23}NO$ is a quinoline molecule with Phenyl,

Methyl, Hydroxyl groups as substituents. The crystal structure has been investigated to understand the conformation of hydrogenated quinoline in general and to resolve the controversy over whether the hydrogen atom of N is 'axial' or 'equatorial' in particular.

The colourless crystals are orthorhombic in spacegroup $Pbca$ with $a=43.036(2)$, $b=12.344(3)$ and $c=10.451(3) \text{ \AA}$; $V=5522 \text{ \AA}^3$, $Z=16$, $D_c=1.174$ and $D_m=1.16 \text{ g cm}^{-3}$. Based on 1773 (significant) diffractometer data collected using $Cu-K\alpha$ radiation, the structure was solved by a combination of direct and Fourier methods and refined to R-value of 0.089 with anisotropic temperature factors for non-hydrogen atoms. The most important findings is that the two crystallographically distinct molecules are epimers with D and L companion, because the hydrogen atom attached to N is 'equatorial' in one molecule and 'axial' in another in the asymmetric unit. In each quinoline the cyclohexane and piperidine rings are trans-fused in chair form. The structure is stabilized by O-H...N type weak and strong hydrogen bonds.

09.2-2 CRYSTAL AND MOLECULAR STRUCTURE OF 2-(α -PHENYLETHYL)-3 METHYL-3 CARBONOMETHOXY-1 OXOCYCLOHEXANE ($C_{17}H_{22}O_3$). M. Vlasi, Quantum Chemistry Laboratory, Catholic University of Louvain, Place Louis Pasteur 1, Belgium and S.G. Biswas, Dept. of Physics, Visva-Bharati University, Santiniketan, W. Bengal, India.

In a synthetic approach toward some C-9 methyl hydrofluorene synthon for plant hormones, gibberellins, the diastereoisomeric esters had been prepared. Since the stereostructures of these esters could not definitely be assigned from 1H NMR the X-ray investigation was undertaken to establish their precise molecular architectures.

The intensities of X-ray reflexions were measured on a CAD-4 diffractometer using graphite monochromated $Cu-K\alpha$ radiation with $|F| \geq 2.5|F|$ and $\theta \leq 110^\circ$. The intensity data were corrected for Lorentz and polarisation factors but no absorption corrections were made.

Crystal data (Isomer I), Orthorhombic, $a=8.786(6)$, $b=11.008(7)$, $c=31.856(22) \text{ \AA}$; space group $Pcab$, $Z=8$, $D_c=1.18 \text{ g cm}^{-3}$, $D_m=1.23 \text{ g cm}^{-3}$, $F(000)=592$, m.p.= $73^\circ C$, $R=0.061$ with 1640 measured reflexions.

Crystal data (Isomer II) Monoclinic, $a=6.234(3)$, $b=12.928(7)$, $c=20.375(16) \text{ \AA}$, $\beta=97.76(3)$; space group $P2_1/c$ $Z=4$, $D_c=1.20 \text{ g cm}^{-3}$, $D_m=1.26 \text{ g cm}^{-3}$, $F(000)=1184$, m.p.= $81^\circ C$, $R=0.063$ with 1812 measured reflexions.

Both the structures were solved by MULTAN84 and refined by full-matrix least square method (SHELX 76). The computed bond lengths and angles were fairly within the range of chemically expected values and the non-bonded contacts were always greater than the sum of the Vander Waals radii. A comparative view of the asymmetric units of the stereoisomers is shown in Figure - 1 (projected). Their architectures substantially differ from one another. Torsion angle computations as well as Dreiding model-building reveal some interesting features of these stereoisomers and these results are expected to guide the direction of future syntheses of intermediates which could perhaps lead to the synthesis of plant hormones.

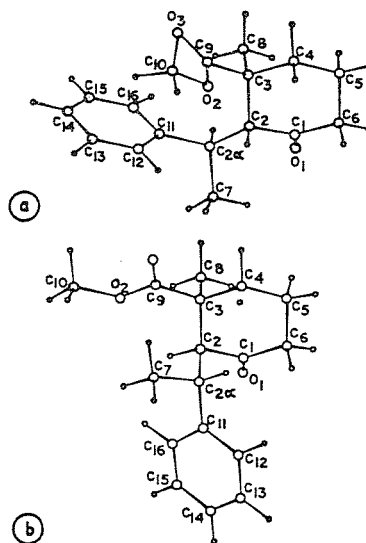


Figure -1

(a) - Isomer I

(b) - Isomer II