

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.2-59 SOME STRUCTURES OF CYCLOPROPANE DERIVATIVES. By J.S.A.M. de Boer and H. Schenk, Laboratory of Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.

The geometry of cyclopropane rings is being influenced by π -donor and acceptor substituents. Donors result in vicinal bond shortening and distal bond lengthening, whereas acceptors show the opposite tendency.

In order to study this phenomenon the crystal structures of amino-cyclopropane (I), 1-methyl-1-aminocyclopropane (II), 1-phenyl-1-aminocyclopropane (III), cyanocyclopropane (IV), bicyclopropylidene (V), and dicyclopropylmethylenecyclopropane (VI) have been investigated. All compounds are liquids at room temperature and therefore crystals have been grown in a cooling device mounted on a Nonius CAD 4 diffractometer. The results of the various crystal structure determinations can be summarized in the following table of bondlengths:

	mean bondlength ring (Δ)	Δ -distal bond	Δ -vic bond 1	Δ -vic bond 2	C=C
I	1.490	+0.002	-0.001	-0.001	
II	1.502	+0.004	+0.000	-0.003	
III	1.510	-0.011	+0.006	+0.006	
IV	1.498	-0.022	+0.011	+0.011	
V	1.491	+0.048	-0.024	-0.025	1.305
VI	1.494	+0.049	-0.024	-0.025	1.325

From structures I and II it follows that the amino group does not influence the asymmetry in the bondlengths. From this and the results of structures III and IV we conclude that the effect induced by a phenyl group is significantly smaller than that of a cyano group. The influence of a double bond on the ring bondlengths is large, as can be seen from structures V and VI. The double bond in structure V has the same value as double bonds in allene compounds.

09.2-60 THE STRUCTURE OF TERTIARY DIPHENILIC ALCOHOLS. By A.N. Shnulin, B.Ju.Sultanov, Kh.S. Mamedov, Institute of Theoretical Problems of Chemical Technology, Institute of Inorganic and Physical Chemistry, the Academy of Sciences of the Azerbaijan SSR, Narimanov prospect, 29; Azerbaijan State University, P. Lumumba str. 23, Baku, USSR.

The structure of the title alcohols with general formula $\text{Ph}_2(\text{R})\text{COH}$ ($\text{R}=\text{H}, \text{CH}_3, \text{C}_2\text{H}_5$) both in solid and liquid states was studied by IR spectroscopy. The crystal structures of two alcohols with $\text{R}=\text{CH}_3$ and C_2H_5 are solved by single-crystal X-ray analysis. (Shnulin, Sultanov, Mamedov, J.Str.Chimii (1984), in print). In highly diluted solutions of CCl_4 the 1,1-diphenylmethanol isolated molecules are in two states. In one state an intramolecular hydrogen bonding such as $\text{OH}\dots\pi$ is formed, while free OH-groups are characteristic of the other state. The increase of concentration leads to the occurrence of associations being formed by means of intermolecular $\text{OH}\dots\text{OH}$ hydrogen bondings. In CCl_4 solution there exist simultaneously two crystalline modifications which are sharply different: one of them forms only regular planar hexagons, while the other exists as plates. The crystal structure ($a=b=17,27(17)$, $c=7,665(6)$ Å, space group $\text{P}4_2\text{C}$) of 1,1 diphenylethanol consists of associations in each of which there are included four molecules joined together by means of H-bonds between OH-groups. In the crystal structure there is carried out the type of organization in which hydrophilic molecular fragments such as OH-groups are securely hidden from their hydrophobic parts. In highly diluted solutions of CCl_4 the separated alcohol molecules are not tied with intramolecular $\text{OH}\dots\pi$ hydrogen bondings. When the concentration of the alcohol in CCl_4 solution is increased, dimer and tetramers appear. The crystal structure ($a=8,811(5)$, $b=11,891(7)$, $c=12,007(9)$ Å, $\beta=104,57(8)^\circ$, space group $\text{P}2_1/\text{C}$) of 1,1 diphenyl-

propanol-1 (DPhP) includes no intermolecular H-bonds of the type $\text{OH}\dots\text{OH}$, that is the crystal of given compound is a typical molecular crystal in which molecules are held together only by van der Waals forces. By means of X-ray analysis and IR spectroscopic studies it is shown that in crystalline state intramolecular $\text{OH}\dots\pi$ bonding takes place. The OH-group is tilted to one of benzoic rings accomplishing short contacts at distances 2,36(5) and 2,45(5) Å between hydroxylic hydrogen atom and two nearest carbon atoms. In IR spectrum of the crystalline DPhP there is observed a narrow asymmetrical and reasonably intensive band at 3548 cm^{-1} . Its asymmetry is expressed in form of wing at 3534 cm^{-1} and reflects the above indicated interactions with π -electrons of two carbon atoms. In IR spectrum of dilute solution of DPhP in CCl_4 the band at 3548 cm^{-1} disappears and is replaced by asymmetrical band with intensive peak at 3615 cm^{-1} and weak shoulder at 3552 cm^{-1} .

09.2-61 THE CRYSTAL AND MOLECULAR STRUCTURE OF ISONITROSOKETONS DERIVATIVES. By Tomasz A. Olszak, Andrzej Stępień, Mieczysław Grabowski, Department of Crystallography, Institute of Chemistry, University of Łódź, Nowotki 18, 91-416 Łódź, Poland, and Sylvain Lecocq, Laboratoire de Mineralogie Cristallographie, Université Claude Bernard (Lyon 1), 43 bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France.

This group of compounds has been obtained from the Dept. of Organic Chemistry of University of Łódź. Following compounds are investigated: 1-phenyl-2-hydroxyiminopropanon-1, 1-phenyl-2-hydroxyiminobutanon-1, 1-phenyl-2-hydroxyimino-3-methylbutanon-1. Each of listed compounds exists as Z and E isomer. The structural investigations have been undertaken due to interesting influence of hydrogen bonds on the stabilisation of the structure, and because of presence of conjugated bonds to find out if the proper isomers were obtained. Fig.1., shows the molecule and the idea of isomerisation.

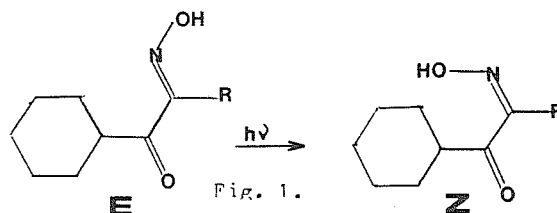


Fig. 1.