06-Crystallography of Organic Compounds

PS-06.02.16 EXPERIMENTAL AND COMPUTED GEOMETRIES: SHOULD THEY BE THE SAME?
Jovan Hargittai* and Magdolna Hargittai, Institute of General and Analytical Chemistry, Technical University of Budapest, 1521 Budapest and Structural Chemistry Research Group of the Hungarian Academy of Sciences of Eötvös University, Pf. 117, H-143 Budapest, Hungary

Experimental structural parameters determined by different physical techniques are often compared in the literature with each other and with computed structures without allowing for the difference in their physical meaning. With enhanced accuracy of both the experimental and state-of-the-art computational structure determinations, the question of their comparability becomes increasingly important. Comparisons involving crystallographic data have to take account of the consequences of intermolecular interactions as well. If such comparisons are properly done, they can be an important source of information on such interactions in the crystal.

Comparative "free-energy geometries" with accuracies depending on the approximations used and on the nature of the molecule. The equilibrium geometry describes a hypothetical, motileless molecule in the minimum position of the potential energy (isomorphs). Experimental data, or others, are sometimes added, to provide directly equilibrium geometries. The meaning of the parameters, bond lengths and bond angles, as well as angles of torsion, determined experimentally, depend on the physical techniques used for their determination and on the way of averaging over molecular vibrations. These parameters can be compared with each other and with computed geometrical parameters only after appropriate corrections, bringing all parameters involved in the comparison in a common denominator.

How different a geometrical parameter may be from different techniques, depends also on the nature of the molecule, and above all on its rigidity/ductility. But even for very rigid molecules these differences may exceed the accuracy of the present-day determination. Examples of a broad range will be used for illustration.

PS-06.02.17 INELASTIC NEUTRON SCATTERING STUDY OF THE EXTREMELY SHORT INTRAMOLECULAR HYDROGEN BOND IN QUINOLINIC ACID. By H. Köppers, Mineralogisches Institut Universität Kiel, Germany, and J. Eckert, LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

The two neighboring carboxylic groups in quinolinic acid (pyridine-2,3-dicarboxylic acid) are linked by an essentially short asymmetric hydrogen bond (O..O.: 2.398 Å; O..H.: 1.163 and 1.238 Å) (Krick et al. J. Chem. Phys. 60 (1974) 3866). Since the orientation of the molecules in the unit cell (space group P21/c, Z = 4) is such that the hydrogen bonds point essentially in the same direction, we carried out inelastic neutron scattering (INS) experiments (filter difference spectrometer) on oriented single crystals in which the Q-vector was successively oriented parallel, perpendicular, in-plane, and out-of-plane with respect to the hydrogen bond. We also performed measurements on powder samples of the title compound and of a partially deuterated compound where the hydrogen atom in the short hydrogen bond and the one attached to the nitrogen atom were replaced by deuterium.

Many of the observed bands are caused by coupled vibrations of the hydrogen atoms attached to the benzene ring. These could be assigned by comparison with vibrational studies of other aromatic compounds (e.g., phthalic acid: Colombito et al. J. Raman Spectrosc. 15 (1984) 252 which has a similar structure). The bands at 1142 and 1570 cm⁻¹ could then be assigned to the ν(OH) and ν(OH) vibration of the intramolecular hydrogen bond, respectively, and those at 396 and 642 cm⁻¹ most likely to ν(NH).

Support from DFG is gratefully acknowledged. This work has benefited from the use of facilities at the Manuel Lujan Jr. Neutron Scattering Center, a national user facility funded by the US DOE.

PS-06.02.18 STRUCTURE OF 1,3-BISDIPHENYLENE-
2-(p-CHLOROPHENYL)-ALLYL RADICAL AT ROOM TEMPERATURE: AN ORGANIC ANTIFERROMAGNET. By N. Azuma* and T. Otsawa, Faculty of General Education, Ehime University, Matsuyama 790, Japan and J. Yamauchi, Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606, Japan.

The neutral organic free radical is characterized by a one-dimensional paramagnet. At the low temperature examined so far, most of the organic radicals show no magnetic phase transition into long-range ordered state. The radical (p-Cl-BDPA), however, undergoes planar transition into an antiferromagnetic state at TN=3.2 K (Yamauchi, J. et al. (1973) J. Phys. Soc. Jpn., 35, 443-446). This indicates appreciable exchange interaction between the magnetic chains. To know the molecular structure that rules the π-spin delocalization and to obtain information about the path of the exchange interaction, the X-ray crystal structure of p-Cl-BDPA prepared by the method of Kuhr, R. & Neugebauer, F. A. (1954) Monatsh. Chem. 95, 3-23 was determined at 298K. C13H13Cl1, monoclinic, Cc, Z=8, a=33.204(4), b=9.391(1), c=15.290(1) Å, β=101.223(7)°, CuKα, 2θ=123°. Corrected for f.p. absorption (ω scan), and secondary extinction. Checked the point group symmetry, m, based on the anomalous dispersion effect. Including anomalous dispersion and calculated hydrogen positions. R=0.035, Rw=0.036 with w=1/[ω²(f(ω))], and g.f. = 1.48.

There are two crystallographically independent molecules consisting of a pair of enantiomers (enamine compound, Fig. 1). The coplanarity of their ethyl groups is fairly good. They have clockwise and anti-clockwise propeller shape. The mean torsion angles of benzene rings are about ±30° and the angles of the chlorophenyl halides are about ±55°. When one views the molecular packing along the b axis (Fig. 2), the overlap between the aromatic rings seems to be first sight. However, the packing is so complicated that one can hardly discriminate the main exchange-coupled chain from the subordinately coupled chains. This fact is in good accordance with the TN, the highest among the organic free radicals. The elucidation of the magnetic chains and the exchange patterns between the chains based on the overlap integrals (strictly speaking, exchange integrals) between the singly occupied 2pπ-orbitals and the spin densities (theoretical: McConnell, H. M. (1963) J. Chem. Phys. 39, 1910; application: Azuma, N. et al. (1973) Bull. Chem. Soc. Jpn. 46, 2725-2734) is under investigation and will be reported at the same time.