PS–06.02.16 EXPERIMENTAL AND COMPUTED GEOMETRIES: SHOULD THEY BE THE SAME? Istvan Hargittai* and Magdolna Hargittai, Institute of General and Analytical Chemistry, Technical University of Budapest, H-1521 Budapest and Structural Chemistry Research Group of the Hungarian Academy of Sciences at Eotvos 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 compatibility 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.

Computations produce "equilibrium geometries" with accuracies depending on the approximations used and on the nature of the molecule. The equilibrium geometry describes a hypothetically motionless molecule in the minimum position of the potential energy function. Experiments, on the other hand, do not 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 ways 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 to 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/fluxionality. But even for very rigid molecules these differences may exceed the accuracy of their 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. Küppers, Mineralogisches Institut Universität Kiel, Germany, and J. Eckert, LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

The two neighbouring carboxylic groups in quinolinic acid (pyridine-2,3-dicarboxylic acid) are linked by an extremely short asymmetric hydrogen bond (O...O: 2.398Å; O..H: 1.163 and 1.238Å) (Kvick et al. J. Chem. Phys. 60 (1974) 3866). Since the orientation of the molecules in the unit cell (space group P2$_1$/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: Colombo et al. J. Raman. Spectr. 15 (1984) 252 which has a similar structure). The bands at 1142 and 1570 cm^{-1} could then be assigned to the $\gamma(OH)$ and $\delta(OH)$ vibration of the intramolecular hydrogen bond, respectively, and those at 596 and 642 cm^{-1} most likely to $\nu_{as}(OH)$.

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PS–06.02.18 STRUCTURE OF 1,3-BISDIPHENYLENE-2-(p-CHLOROPHENYL)-ALLYL RADICAL AT ROOM TEMPERATURE: AN ORGANIC ANTIFERRO-MAGNET. By N. Azuma* and T. Ozawa, 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 titled radical (p-Cl-BDPA), however, undergoes phase transition to an antiferromagnetic state at T_N=3.25K (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 Kuhn, R. & Neugebauer, F. A. ((1964) Monatsh. Chem. 95, 3-23) was determined at 298K.

$C_{33}H_{20}Cl$, 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 Lp, absorption (ψ 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, R$_w$=0.036 with w=1/σ^2(F$_o$), and g.o.f.=1.48.

There are two crystallographically independent molecules consisting of a pair of enantiomers (racemic compound, Fig. 1). The coplanarity of their allyl groups is fairly good. They have clockwise and anti-clockwise propeller shape. The mean torsion angles of fluorene blades are about ±30° and the same angles of the chlorophenyl blades are about ±55°. When one views the molecular packing along the b axis (Fig. 2), the overlap between the aromatic rings seems simple at first sight. However, the packing is so complicated that one can hardly discriminate the mainly exchange-coupled chain from the subordinately coupled chains. This fact is in good accordance with the T_N, the highest among the organic free radicals. The elucidation of the magnetic chains and the exchange paths between the chains based on both the overlap integrals (strictly speaking, exchange integrals) between the singly occupied 2p$_z\pi$-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, 2728-2734) is under investigation and will be reported at the same time.
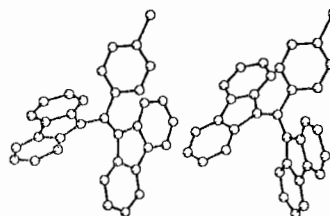

Fig. 1. Enantiomeric molecular structure of p-Cl-BDPA in the cell
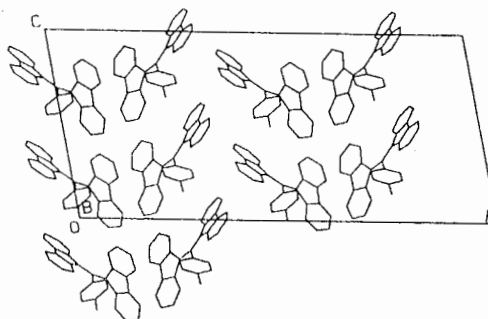

Fig. 2. Molecular packing of p-Cl-BDPA view down along b axis