05. PHYSICAL PROPERTIES AND STRUCTURE

05.1-22 X-RAY DIFFUSE SCATTERING STUDY OF SPATIAL CORRELATIONS IN PARA-TERPHERYL, by T.R. Welberry, Research School of Chemistry, Australian National University, Canberra, and S.L. Mair. CSIRO Division of Materials Science and Technology, Clayton, Victoria, Australia.

In the monoclinic (P2₁/a) room-temperature phase of paraterphenyl the triple-ringed molecules are approximately planar, but the rings are rotationally disordered about the long axis of the molecule (Rietveld, Maslen and Clews, 1970; see also Baudour, Cailleau and Yelon, 1977). At temperature Tc (~193 K) the molecules become rotationally ordered and non-oriental. The structure then is triclinic (P1) with a pseudo-monoclinic cell (Baudour, Delugeard and Cailleau, 1976; Baudour and Charbonneau, 1974), related to the high-temperature phase by an approximate doubling of the a and b cell dimensions.

X-ray diffuse scattering intensities have been measured around superlattice reflections in the monoclinic phase of paraterphenyl at temperatures near Tc at 200 K. Near Tc the superlattice reflections in the monoclinic phase of para-terphenyl undergoes an approximate doubling of the lattice parameter at Tc. Over the temperature range 200 K to Tc the superlattice reflections in the monoclinic phase of para-terphenyl become more intense and their positions shift to lower angles as the temperature decreases.


Order-disorder phase transitions are fairly common in molecular crystals, especially for those belonging to the class of n-donor:acceptor complexes. The complex studied in this work is the 1:1 donor-acceptor complex between acetylacetonic anhydride, TCPA, and acettrimethylammonium chloride, (CH₃NH₃)Cl, which is in fact monoclinic throughout the temperature range 100 K < T < 345 K but presents a transition to an orthorhombic phase at Tc = 345 K. The high temperature phase is characterized by orthorhombic distorted CuCl₄ octahedra due to the Jahn-Teller-effect of Cu-ions. The ferro/para-electric phase transition in Cu₃NH₃HgCl₄ at 830 K has been studied extensively. It has been shown that the Cu₃NH₃Hg group rotates almost freely in the high temperature monoclinic structure (space group C2) whereas these dipoles form an angle of about 10° with a threefold axis. Inelastic and quasielastic neutron scattering gave some evidence of a jump rotation at two orthorhombic phases around the C2-axis in the ferroelectric phase. The compound (CH₃NH₃)₂CuCl₄ is the first in this group of compounds with a nematic phase. The structure consists of isolated [CuCl₅]₂⁻ octahedra in space group C2 and one Cl⁻ ion is connected to the ammonium group via hydrogen bonds. The compound is paramagnetic down to 5 K.


Samples of peralkanoylated α- and β-glucopyranosides with alkoxy chains from C₂₁ to C₉₄ were investigated by X-ray diffraction to characterize their thermotropic liquid crystalline phase types. Various non-hexagonal columnar phases, D₀ and D₇, in Destre's terminology, (C. Destre, P. Poucher, R. Gasparoux, Nguyen Huu Tinh, A.-M. Levelut, and J. Malthete, Mol. Cryst. Liq. Cryst. 100 (1984) 121-146) and a nematic phase can be prepared depending on the phase preparation method. A preliminary photographic study of an α-C₁₄ oriented phase on a glass slide showed a second order ring at high angle (d₀₀² = 4.2 Å) corresponding to a columnar phase. Intercolumnar spacings inferred from low angle Bagg peaks increase regularly in a homologous series except for α-C₄₄ and α-C₅₄, which are anomalous. The e-series increases at 2.471(13) Å/CH₂ and the f-series at 2.1171(13) Å. The predicted core radius from the intercept of plots of chain length vs. intercolumnar distance is 16.619 Å for the e-series and 0.67 Å for the f-series, neglecting α-C₄₄ and α-C₅₄. Thus, it has been shown for the first time that chiral molecules with no aromatic core can be classified into the e or f phase types of both ordered and disordered types and that α-anomers of the series investigated may also have a nematic phase. Additionally, the columnar background structure is retained throughout the D₀ and D₇, and crystalline phases.