

05.1-22

X-RAY DIFFUSE SCATTERING STUDY OF SPATIAL CORRELATIONS IN PARA-TERPHENYL. 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 (P2<sub>1</sub>/a) room-temperature phase of para-terphenyl 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  $T_c$  (=193K) the molecules become rotationally ordered and non-coplanar. 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 para-terphenyl for the temperature range  $T_c + 1$  to  $T_c + 121$  K. Near  $T_c$  the correlation lengths along the a, b and c directions, estimated from the peak shapes within the Ornstein-Zernike formalism, are found to be in the approximate ratios 2:6.5:1, respectively. The two larger correlations are along the directions in which the unit cell undergoes an approximate doubling of the lattice parameter at  $T_c$ . Over most of the temperature range the correlation lengths are proportional to  $(T - T_c)^{-1/2}$ , corresponding to the predictions of mean-field theory, but within 4 K of  $T_c$  a critical exponent,  $\nu$ , greater than 0.5 is indicated.

Baudour J.L., Cailleau H. and Yelon W.B. (1977) Acta Cryst. B33, 1773-80.

Baudour J.L. & Charbonneau G.P. (1974) Acta Cryst. B30, 1379.

Baudour J.L., Delugeard Y. & Cailleau H. (1976) Acta Cryst. B32, 150-4.

Rietveld H.M., Maslen E.N. & Clews C.J.B. (1970) Acta Cryst. B26, 693-706.

05.1-23

ORDER-DISORDER PHASE TRANSITIONS: THE CRYSTAL STRUCTURE OF THE 1:1 DONOR:ACCEPTOR COMPLEX BETWEEN ANTHRACENE AND TETRACHLOROPHTHALIC ANHYDRIDE AS A FUNCTION OF TEMPERATURE. By John J. Stezowski\* and Rolf-Dietrich Stigler\*, W. Mühle† and J. U. von Schütz† Institut für Organische Chemie, Biochemie und Isotopenforschung und †Physikalisches Institut, Teilinstitut 3 der Universität Stuttgart, D-7000 Stuttgart 80, FRG.

Order-disorder phase transitions are fairly common in molecular crystals, especially for those belonging to the class of  $\pi$ -donor:acceptor complexes. The complex between anthracene, A, and tetrachlorophthalic anhydride, TCPA, is a very interesting example of such a system. The specific heat,  $C_p(T)$ , measurements by differential scanning calorimetry techniques, reveal two phase transitions, one at 257 K and another at 194 K; the  $C_p$  vs. T curves are consistent with second order phase transitions. We have determined the crystal structure for this complex at three temperatures: 296, 230, and 120 K; that is for an example of the structure in each of the three phases accessible with our low temperature apparatus (Syntex LT-1). All three phases display P1 symmetry: lattice parameters are at 296 K:  $a = 16.441(3)$ ,  $b = 8.913(1)$ ,  $c = 6.834(1)$  Å,  $\alpha = 101.77(1)$ ,  $\beta = 91.06(1)$  and  $\gamma = 102.29(1)^\circ$ ; at 230 K:  $a = 16.425(5)$ ,  $b = 8.863(3)$ ,  $c = 13.539(5)$  Å,  $\alpha = 101.62(3)$ ,  $\beta = 90.73(3)$  and  $\gamma = 102.54(3)^\circ$  and at 120 K:  $a = 16.401(3)$ ,  $b = 8.810(2)$ ,  $c = 13.417(3)$  Å,  $\alpha = 101.60(2)$ ,  $\beta = 90.62(2)$  and  $\gamma = 102.76(2)^\circ$ . The doubling of the c-axis length on passing from the room temperature phase to the phase at 230 K, gives rise to two symmetry independent D:A complexes per asymmetric unit. The TCPA molecules display two fold orientational disorder in the room temperature phase, which persists in the 257-194 K phase. In this phase, the 'D:A:D:A' stacks contain symmetry nonequivalent adjacent D:A units. Upon crossing the second phase boundary (T = 194 K), the TCPA molecules reorient to give an ordered structure.

05.1-24

STRUCTURAL PHASE TRANSITIONS IN CHLOROALKYLAMMONIUM-METALLATES. By H. Fuess, I. Pabst, M. Körfer, H. Ben Chozlen and M. Czjzek, Institut für Kristallographie, University Frankfurt, Federal Republic of Germany.

Several chloroalkylammoniummetallates of di-, tri-, and tetravalent metals have been investigated by diffraction and spectroscopy.

Structural phase transitions were detected in  $[(C_2H_5)_2NH_2]_2SnCl_6$  (P2<sub>1</sub>  $\xrightarrow{330K}$  P2<sub>1</sub>/n) and  $[(C_2H_5)_4N]_2SnCl_6$  (C2/c  $\xrightarrow{264K}$  P2<sub>1</sub>/c). The octahedral coordination of the Sn-ions is not affected by the change in crystal structure.

A continuous transition previously described in the literature could not be confirmed for  $(CH_3NH_3)_2CuCl_4$  which is in fact monoclinic throughout the temperature range  $100 < T < 348K$  but presents a transition to an orthorhombic phase at  $T_c = 348K$ . The high temperature phase is characterized by orthorhombic distorted  $CuCl_6$  octahedra due to the Jahn-Teller-effect of Cu-ions. The ferro/paraelectric phase transition in  $CH_3NH_3HgCl_3$  at 61°C has been studied extensively. It has been shown that the  $CH_3NH_3^+$  group rotates almost freely in the high temperature monoclinic structure (space group C2) whereas these dipoles form an angle with the threefold axis in the trigonal ferroelectric phase (sp. gr. P3<sub>2</sub>). D-NMR-measurements on single crystals between 80K and 340 showed that the angle between the long axis of the  $CH_3NH_3^+$ -group and the polar threefold axis is gradually increasing. Inelastic and quasielastic neutron scattering gave some evidence of a jump rotation model of the  $CH_3$ - and  $NH_3$ -groups around the C-N-axis in the ferroelectric phase. The compound  $(CH_3NH_3)_4YbCl_7$  is the first in this group of compounds with a rare earth ion. The structure consists of isolated  $[YbCl_6]^{3-}$  octahedra in space group C2 and one Cl-ion is connected to the ammonium group via hydrogen bonds. The compound is paramagnetic down to 5K.

05.1-25

CHARACTERIZATION OF THE PHASE TYPES OF A SERIES OF PERALKANOYLATED GLUCOPYRANOSIDES: CHIRAL, NONAROMATIC, DISK SHAPED MOLECULES WHICH FORM COLUMNAR PHASES. By Nancy L. Morris, Richard G. Weiss, and Geoffrey B. Jameson, Department of Chemistry, Georgetown University, Washington, D.C. 20057.

Samples of peralkanoylated  $\alpha$ - and  $\beta$ -glucopyranosides with alkanoyl chains from C<sub>10</sub> to C<sub>18</sub> were investigated by X-ray diffractometry to characterize their thermotropic liquid crystalline phase types. Various non-hexagonal columnar phases, D<sub>rd</sub> and D<sub>ro</sub> in Destrade's terminology, (C. Destrade, P. Foucher, H. Gasparoux, Nguyen Huu Tinh, A.-M. Levelut, and J. Malthete, Mol. Cryst. Liq. Cryst., 106 (1984) 121-146) and a nematic phase can be prepared depending on the phase preparation method. A preliminary photographic study of an  $\alpha$ -C<sub>16</sub> oriented phase on a glass slide showed a second order ring at high angle ( $d_{002} = 4.2\text{Å}$ ) corresponding to stacking of disks. Intercolumnar spacings inferred from low angle Bragg peaks increase regularly in a homologous series except for  $\alpha$ -C<sub>10</sub> and  $\alpha$ -C<sub>11</sub>, which are anomalous. The  $\alpha$ -series increases at 2.67(15)Å/CH<sub>2</sub> and the  $\beta$ -series at 2.17(7)Å/CH<sub>2</sub>. The predicted core radius from the intercept of plots of chain length vs. intercolumnar distance is 10.0(9)Å for the  $\beta$ -series and 0.0(7) for the  $\alpha$ -series, neglecting  $\alpha$ -C<sub>10</sub> and  $\alpha$ -C<sub>11</sub>. Thus, it has been shown for the first time that chiral molecules with no aromatic core can produce oriented, columnar phases of both ordered and disordered types and that  $\alpha$ -anomers of the series investigated may also have a nematic phase. Additionally, the columnar background structure is retained throughout the D<sub>rd</sub>, D<sub>ro</sub>, and crystalline phases.