

05.2-1 OPTICAL ACTIVITY AND CRYSTAL STRUCTURE. By A.M. Glazer<sup>1</sup>, M. Koralewski<sup>2</sup>, K. Stadnicka<sup>3</sup> and P.A. Thomas<sup>1</sup>.

<sup>1</sup>Clarendon Laboratory, Parks Road, Oxford OX1 3PU, U.K.

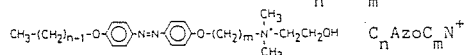
<sup>2</sup>Institute of Physics, Adam Mickiewicz University, ul. Grunwaldzka 6, 60780 Poznań, POLAND

<sup>3</sup>Faculty of Chemistry, Jagiellonian University, ul. Karasia 3, 30060 Kraków, POLAND

Recently it has been shown (A.M. Glazer and K. Stadnicka, J. Appl. Cryst. 19, 108, 1986; V. Devarajan and A.M. Glazer, Acta Cryst., A42, 560, 1986) that it is possible to explain the sign and even the magnitude of optical rotatory power in almost all the inorganic crystals for which the absolute configuration is known. Since these publications, further work has been carried out on several other materials, including  $\alpha$ -NiSO<sub>4</sub>·6H<sub>2</sub>O, TeO<sub>2</sub> and  $\beta$ -eucryptite, to determine absolute configuration by anomalous x-ray scattering and optical microscopy. In each case, we have been able to compute successfully the optical rotatory powers. In NiSO<sub>4</sub>·6H<sub>2</sub>O, the optical rotatory dispersion (ORD) is anomalous in that it changes sign twice with wavelength. The explanation for this lies in a competition between optical rotation due to d-d transitions in the Ni<sup>2+</sup> moiety and the effect of the oxygens, which produces a normal ORD as a "background". Even in this complicated case, it has been possible to calculate good values for the optical rotatory power. TeO<sub>2</sub> is a classic case where the sign of optical rotation is opposite to the screw axis in the structure, and is explained in terms of an interaction between oxygen atoms on neighbouring oxygen helices.

05.2-2 BILAYER STRUCTURES OF AZOBENZENE-CONTAINING AMPHIPHILES AND THEIR BATHO- OR HYPISO-CHROMIC SHIFTS IN ABSORPTION SPECTRA. By K. Okuyama, M. Shimomura, A. Hirabayashi, Faculty of Engineering, Tokyo University of Agriculture and Technology, Japan, T. Kajiyama, T. Kunitake, Kyushu University, Japan, and N. Yasuoka, Himeji Institute of Technology, Japan.

Bilayer-forming amphiphilic compounds have been proved very effective in ordering of functional groups by means of "crystal engineering" or Langmuir-Blodgett films. In this paper, bilayer structures of azobenzene-containing single-chain ammonium amphiphiles (C<sub>n</sub>AzoC<sub>m</sub>N<sup>+</sup>) were in-



vestigated by X-rays. Single crystals of C<sub>12</sub>AzoC<sub>5</sub>N<sup>+</sup>Br<sup>-</sup> were obtained from their solutions in water and ethanol, and are triclinic with the space group P $\bar{1}$ , Z=2, a=3.424, b=0.8525, c=0.6073nm,  $\alpha$ =73.45,  $\beta$ =88.03, and  $\gamma$ =93.32°. The structure is made up by regularly stacking bimolecular layers in which molecules incline about 30° to the layer surface. As expected from bathochromic shifts in absorption spectra, the azobenzene-chromophore shows a head-to-tail (J-like) aggregation between adjacent molecules. On the other hand, no single crystals of C<sub>8</sub>AzoC<sub>10</sub>N<sup>+</sup>Br<sup>-</sup> with hypsochromic shifts could be obtained, but ordered and self-supporting cast films were prepared from its aqueous bilayer dispersion. The most plausible bilayer model obtained from the X-ray analysis of this film is in good agreement with the structure proposed from the absorption spectroscopy, in which adjacent azobenzene-chromophores are aligned in parallel (H-aggregates). In both bilayer structures, molecular inclination angles to the layer surface were well explained in terms of the balance between cross-sections of the hydrophobic and hydrophilic parts of the amphiphile.

05.2-3 CIRCULAR DICHROISM OF Ca<sub>2</sub>Sr(C<sub>2</sub>H<sub>5</sub>CO<sub>2</sub>)<sub>6</sub> FAMILY CRYSTALS. By Y. Uesu, M. Sekiguchi and M. Inoue, Department of Physics, Waseda University, Tokyo.

We observed that a distinct difference exists between the signal of circular dichroism (CD) of ferroelectric Ca<sub>2</sub>Sr(C<sub>2</sub>H<sub>5</sub>CO<sub>2</sub>)<sub>6</sub> (DSP) and that of its isomorphous Ca<sub>2</sub>Pb(C<sub>2</sub>H<sub>5</sub>CO<sub>2</sub>)<sub>6</sub>. The results obtained at room temperature are indicated in Figure. Levo-rotatory crystals were chosen for all the measurements. CD of DSP has peaks at 275nm(A) and 229nm(B), while no signals are observed in a range from 235 to 800nm. On the other hand, CD of DLP is of quite different nature; it has much larger magnitude and more complicated structure than that of DSP. In addition to A and B bands, a broad peak(C) ranging from 230 to 253nm and a peak at 270nm(D) were newly observed. It should be noted that the sign of the D band is positive even though the crystal is levo-rotatory. Although the exact identification of these CD signals by associating them with specific electronic transitions of atoms or atomic groups are necessary, A and B bands which are common to DSP and DLP crystals, would be related to an electronic transition in propionate group. C and D bands observed only in DLP would have a close connection with a peculiar bonding nature of Pb atom.

These experimental results can be interpreted by the semi-empirical theory recently developed by Glazer and Stadnicka (J. Appl. Cryst. 1986, 19, 108).

Calculations of optical rotatory dispersions by the use of the Kramers-Kronig relation give satisfactory coincidence with the experiment in the case of DSP but not of DLP. The reason is not clear at present.

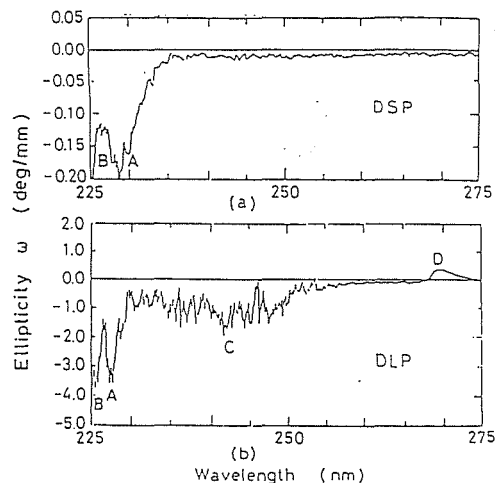


Figure. Circular dichroism of DSP(a) and DLP(b) crystals.