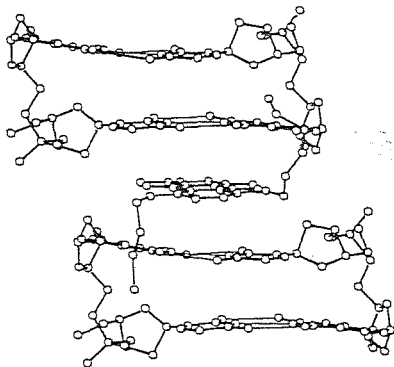


The interactions observed in the crystals show an interesting correlation with the pharmacological activity of mitoxantrone related drugs.



04.1-1 THE FIRST DETERMINATION OF THE ENERGY DIFFERENCE BETWEEN SOLID STATE CONFORMERS BY X-RAY DIFFRACTION: 1. THE CRYSTAL STRUCTURE OF THE PSEUDO-JAHN-TELLER COMPLEX (NITRITO)BIS(2,2'-BIPYRIDYL)COPPER(II) NITRATE AT 20, 100, 165, AND 296 K. 2. THE POSSIBILITY OF USING X-RAY DIFFRACTION TO CHARACTERIZE ADIABATIC POTENTIAL ENERGY SURFACES AND RELATIVE LIGAND STRENGTHS. By Charles J. Simmons, Chemistry Department, University of Puerto Rico, Rio Piedras, Puerto Rico 00931; Brian J. Hathaway, Chemistry Department, University College, Cork, Ireland; Bernard D. Santarsiero, Chemistry Department, California Institute of Technology, Pasadena, California 91125; Abraham Clearfield, Chemistry Department, Texas A&M University, College Station, Texas 77843.

The crystal structure of  $[\text{Cu}(\text{bpy})_2(\text{ONO})]\text{NO}_3$  has been determined at 20, 100, 165, and 296 K. It is found that the molecular geometry of the  $\text{CuN}_4\text{O}_2$  chromophore is temperature dependent: the Cu-O bonds are 2.051(2) and 2.536(2) Å at 20 K and 2.230(5) and 2.320(5) Å at 296 K. The distortional behavior of  $[\text{Cu}(\text{bpy})_2(\text{ONO})]\text{NO}_3$  and other similar systems is rationalized in terms of a pseudo-Jahn-Teller formalism. The proposed adiabatic potential energy surface, which is consistent with both theory and the crystallographic results, consists of a double-minimum ground state, which, depending on crystal-packing forces, may or may not be equivalent. A methodology which uses the observed metrical data from the structures of the  $\text{CuN}_4\text{O}_2$  chromophore from 20-296 K and Boltzmann statistics will be presented which allows an accurate determination of the energy difference between the two conformers (77  $\text{cm}^{-1}$ ).

A formalism which allows these energy surfaces to be calculated from crystallographic and ESR data will be discussed. The energy gap between the ground and first-excited electronic states for an undistorted complex, obtainable from the calculations, is proportional to the ligand strength of the  $\text{OXO}^-$  group ( $\text{OXO}^- = \text{CH}_3\text{CO}_2^-$ , etc.).

04.1-2 STRUCTURE-FUNCTION RELATIONSHIPS IN Z- $\text{PR}_3$  COMPOUNDS. By B.J. Dunne, R.B. Morris and A.G. Orpen, Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.

We have sought to understand  $\text{R}_3\text{P-Z}$  bonding in tertiary phosphine-metal complexes ( $\text{Z} = \text{metal}$ ), phosphine oxides ( $\text{Z} = \text{O}$ ) and  $\text{PPN}^+$  salts ( $\text{Z} = \text{N}$ ) from analysis of structural data. The P-Z bond is usually depicted as having both  $\sigma$  and  $\pi$  interactions. The nature of the  $\pi$  component has been a subject of debate, notably for transition metal-phosphine complexes. Traditionally the phosphorus 3d orbitals have been invoked as the site of phosphorus  $\pi$ -bonding, but recently this view has been challenged and the importance of the P-R  $\sigma^*$  orbitals postulated on the basis of molecular orbital calculations (e.g. D.S. Marynick, *J. Am. Chem. Soc.*, 1984, 106, 4064).

We have tested this theory by two analytical approaches to illustrate data. The first, which concerns the case where  $\text{Z} = \text{metal}$ , rests on comparison of pairs of complexes where the structures of  $[\text{L}_n\text{M-PR}_3]$  and  $[\text{L}_n\text{M-PR}_3]^+$  are known. In cases where the effect of oxidation on metal-phosphine bonding is largely limited to the M-P  $\pi$  bond the M-P bond is lengthened and P-R bonds shortened. These changes together with others in the  $\text{PR}_3$  geometry support the "new" view of metal- $\text{PR}_3$  bonding. The second approach which is more widely applicable, rests on comparison of the geometries of large numbers of Z- $\text{PPh}_3$  structures taken from the Cambridge Structural Database (CSD). These show patterns of structural deformations which relate the nature of Z, the length of the P-Z bond, and other geometrical parameters of the  $\text{PPh}_3$  unit. The observed correlations may be understood with the aid of qualitative molecular orbital theory.

04.1-3 ON THE LATTICE PACKING RULES REVEALED BY THE PAIRS OF QUASI-ISOSTRUCTURAL CARDENOLIDES AND ANALOGOUS BUFADIENOLIDES. A. Kálmán, Gy. Argay and V. Fülöp Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, POB 17, Hungary; B. Ribár and D. Lazar, Institute of Physics, Faculty of Sciences, 21000 Novi Sad, POB 204, Yugoslavia.

Quasi-isostructural relationship between two or more related steroid crystals first was recognized when we reported (Kálmán et al (1984) *Croat. Chem. Acta* 57, 519) the X-ray analysis of digirezigenin (Fig. 1) formed from digitoxigenin via 14,15 $\beta$ -epoxy-ring-closure. Although this alters the puckering of ring D (Karle & Karle (1969) *Acta Cryst.* B25, 434) the packing (e.g. hydrogen bonds) of the crystal lattice remains unaltered:

	a(Å)	b(Å)	c(Å)	packing coeff.
digitoxigenin:	7.250(2)	15.015(4)	18.464(8)	0.693
digirezigenin:	7.288(2)	14.686(3)	18.480(3)	0.691

Continuing X-ray studies of the analogous bufadienolides isolated also from Ch'an Su, the dried venom of the Chinese toad (Fig. 1) we found a second isostructural pair formed by gamabufotalin and arenobufagin which differ in a 12-oxo group (Kálmán et al (1987) *Acta Cryst.* in press). This was followed by the observation that the 5-OH group of cinobufotalin also does not spoil the lattice found for cinobufagin (Declercq et al (1977) *Abstr. of ECM-4 Oxford*, p. 279). In contrast with this the related bufotalin is not isostructural with them, since its 14-OH takes part in hydrogen bonding. Consequently, in this case the closure of 14,15 $\beta$ -epoxy ring has to destroy the already existing molecular packing. In other words: quasi-isostructural pairs or groups (e.g. methyl-digitoxigenin (Prasad & Gabe (1983) *Acta Cryst.* C39, 273) is also isostructural with digitoxigenin) may exist only if the alteration of the molecular structures does not disturb the existing hydrogen bonding of the system.