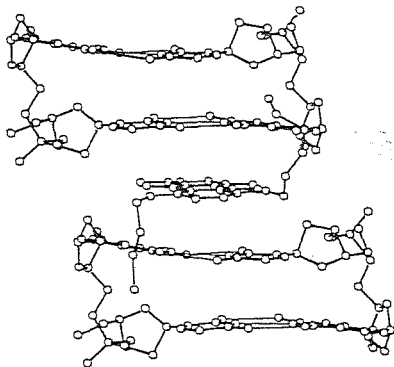The interactions observed in the crystals show an interesting correlation with the pharmacological activity of mitoxantrone related drugs.

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 $[Cu(bpy)_2(ONO)]NO_3$ has been determined at 20, 100, 165, and 296K. It is found that the molecular geometry of the CuN_4O_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 $[Cu(bpy)_2(ONO)]NO_3$ 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 CuN_4O_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 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 OXO^- group ($OXO^- = CH_3CO_2-$, etc.).

04.1-2   STRUCTURE-FUNCTION RELATIONSHIPS IN $Z-PR_3$ 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 R_3P-Z bonding in tertiary phosphine-metal complexes (Z = metal), phosphine oxides (Z = O) and PPN^+ salts (Z = N) from analysis of structural data. The P-Z bond is usually depicted as having both σ and π interactions. The nature of the π 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 π-bonding, but recently this view has been challenged and the importance of the P-R σ^* 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 Z = metal, rests on comparison of pairs of complexes where the structures of $[L_nM-PR_3]$ and $[L_nM-PR_3]^+$ are known. In cases where the effect of oxidation on metal-phosphine bonding is largely limited to the M-P π bond the M-P bond is lengthened and P-R bonds shortened. These changes together with others in the PR_3 geometry support the "new" view of metal-PR_3 bonding. The second approach which is more widely applicable, rests on comparison of the geometries of large numbers of $Z-PPh_3$ 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 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 14,15β-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 14,15β-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.

Present work intends to quantify the degree of isostruc-turality of these pairs by means of packing coefficients, hydrogen bond parameters and analysis of the corresponding atomic coordinates of eleven steroids possessing a common flexible 14-iso-aethiocholane skeleton. E.g. scillarenin (reported by us earlier as 3β,14-dihydroxy--14β-bufa-4,20,22-trienolide, Ribár et al (1983) J.Chem. Res.(S) 90) is quasi-isostructural with bufalin (Rohrer et al (1982) Acta Cryst. B38, 1865) although there is a quite relevant difference between the puckering of their A rings.
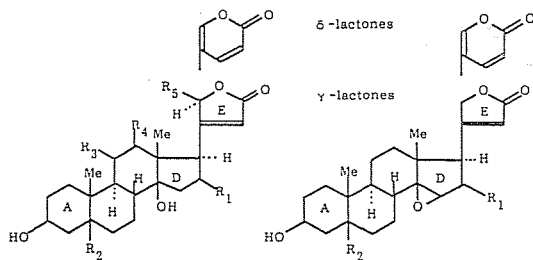

Fig. 1. Eleven steroids having a common sp. gr. $P2_12_12_1$

γ -lactones
DIGITOXIGENIN*   DIGIREZIGENIN
METHYLDIGITOXIGENIN: R_c= Methyl
5β-HYDROXYGITOXIGENIN: R_1^2=R_2= OH

δ -lactones
BUFALIN   CINOBUFAGIN: R_1= O-Acetyl
BUFOTALIN: R_1= O-Acetyl   CINOBUFOTALIN: R_1= O-Acetyl
GAMABUFOTALIN: R_2= OH R_2= OH
ARENOBUFAGIN: R_3=OH, R_4= O=
SCILLARENIN: Δ ^{24},5-ANHYDROBUFALIN
* No special indication is given if R_i = H.

04.1-4   CONFORMATION OF DIPHENYLSULPHIDE DERIVATIVES

By M. Ratajczak-Sitarz, A. Katrusiak and Z. Kałuski, Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

In the present paper we would like to discuss the conformation of diphenylsulphide derivatives, the basic structures in the chemistry of alkyl-aryl-sulphuric compounds. A diphenylsulphide molecule (1) contains two rigid fragments - phenyl rings - which can rotate about its "soft" S-C bonds.
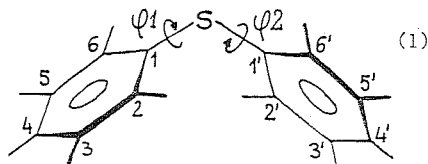
The conformation of the molecule can be conviniently described by torsion angles C(1')-S-C(1)-C(2) [$\psi 1$] and C(1)-S-C(1')-C(2') [$\psi 2$] or, in other words, by the angles between the plane containing atoms C(1)-S-C(1') and the planes of the phenyl rings. The rotations of the phenyl rings about the S-C bonds are limited by the steric hindrances due to the intramolecular van der Waals contacts. A simple computer program was written to evaluate these contacts as a function of $\psi 1$ and $\psi 2$. In that program the steric hindrances in the diphenylsulphide molecule were defined by means of van der Waals radii, thus the conformations accepted of the two phenyl rings larger than the sums of the appropriate van der Waals radii [1.6 for carbon and 1.0 Å for hydrogen atom]. It was demonstrated that the steric hindrances in this molecule is due to the interactions of ortho-hydrogen atom H(2) [or H(6)] with atoms H(2'), C(2'), C(1'), C(6') and H(6').

In the plot presented below the dotted area show the possible values of $\psi 1$ and $\psi 2$. The plot also shows the conformations of four diphenylsulphide derivatives determined experimentally:
(1.) diphenylsulphide, $\psi 1$= $\psi 2$=55.6° (Rozsondai et al., Acta Chim. Budapest 1977, 94, 321);
(2.) 4,4-thiodibenzylothiol, $\psi 1$= $\psi 2$=33.4° (Ratajczak--Sitarz et al., Acta Cryst. C - in press);
(3.) 1,4-bis(phenylthio)benzene, $\psi 1$=14.9°, $\psi 2$=59.2° (Andreetti et al., Cryst. Struct. Comm. 1981, 10, 789);
(4.) crystalline phase of poly-p-phenylenesulphide, $\psi 1$= $\psi 2$=45° (Tabor et al., Eur. Polym. J. 1971, 7, 1127).
In three of these structures the phenyl rings are related by the twofold axis passing through the central S atom and, consequently, $\psi 1$ and $\psi 2$ have the same values. The plot shows that angles $\psi 1$ and $\psi 2$ in all above structures fall in the region least limited by steric hindrances, where $\psi 1$ and $\psi 2$ have the same sign. The close van der Waals contacts were found only in the molecule of 4,4-thiodibenzylothiol: H(2)...C(2') of 2.71(6) Å.

04.1-5   THE RELATIONSHIP BETWEEN THE Br···O SEPARATION AND Br-C-C=O TORSION ANGLE IN ALPHA-BROMO-CYCLOHEXANONE RINGS.

By Michael Laing, Department of Chemistry, University of Natal, Durban, South Africa.

The Br-C-C=O torsion angle in an α-bromocyclohexanone ring can have several values: it can be 0° or 120° in an ideal chair, while in an ideal boat it can be 0°, 60° or 120°. If the ring is an ideal twist boat, then torsion angles of 30° and 90° are possible. However, with the flexible boat form any torsion angle between 0° and 180° is possible. A series of structures containing the α-bromocyclohexanone system (Sommerville, Laing, Acta Cryst., 1976 B32, 2683, 2685, 2687; 1978, B34, 1736), showed that there was a discontinuity in the relationship between the Br-C-C=O torsion angle and Br···O distance at about 50°, below which the Br···O distance remained effectively constant at about 3.0Å, (Fig). This effect is caused by the non-compressibility of the van der Waals radii of the Br and O atoms. Analysis of the parameters of all compounds of this class in the Cambridge Data File shows the same phenomenon. Below a torsion angle of about 50° the Br···O distance is approximately constant. This is a result of the internal Br-C-C and C-C-O angles being forced open to accomodate the compression strain as the torsion angle is reduced. An approximate value of the Br···O distance can be estimated for any torsion angle θ by the equation:

$$d^2 = R - S\cos\theta + T\cos^2\theta$$
where R = 11.73, S = 3.62, T = 0.75

TORSION ANGLE θ IN DEGREES