ments, autour des axes BrS, SO(mét.), et de l'axe binaire sont : $-\partial W/\partial \alpha i$ (i=1,2,3) et la force d'attraction entre molécules : $-\partial W/\partial y$. Les accélérations s'expriment en fonction des moments d'inertie Ji (i=1,2,3) et de la masse moléculaire M :

$$\alpha''_i = d^2\alpha_i/dt^2 = -\partial W/\partial \alpha_i/J_i \quad , \quad y'' = d^2y/dt^2 = -\partial W/\partial y/M.$$

Supposant les accélérations constantes, les accroissements des paramètres αi, y, dans un intervalle court τ (≠10^{-14} sec), s'écrivent :

$$\Delta\alpha_i = \alpha''_i\tau^2/2 + \alpha'_i\tau \quad , \quad \Delta y = y''\tau^2/2 + y'\tau \quad ,$$

α'i et y' désignant les vitesses. La nouvelle conformation αi+Δαi, y+Δy est prise comme point de départ d'un nouveau calcul. Au bout d'un certain nombre de cycles, les molécules viennent en contact et prennent la conformation étendue trouvés dans le cristal, soit α1=100°, α2=10°, α3=0°, y=5Å (W=-40 kcal/mole).

Les fonctions de Van der Waals entre atomes non liés ont été empruntées à P.de Santis, E.Giglio, A.M.Liquori et A.Ripamonti (J.of Polymer Science, 1963,A,1,1383-1404). Pour chaque cycle n, les rapports $\partial W/\partial \alpha i$ et $\partial W/\partial y$ ont été déterminés pour des accroissements $\partial \alpha i$=0°.2 et ∂y=0.02Å. Les vitesses étaient obtenues par récurrence :

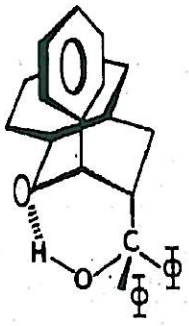
$$\alpha'_{i,n} = \alpha'_{i,n-1} + (\alpha''_{i,n} + \alpha''_{i,n-1})\tau/2 \quad ,$$

$$y'_n = y'_{n-1} + (y''_n + y''_{n-1})\tau/2 \quad .$$

Un coefficient d'amortissement f a été appliqué en supposant des forces de frottement proportionnelles à la surface du maître couple S et à la vitesse de balayage v de chaque élément mobile : f = kSv.

The structure has been found by direct methods using the Multan program and refined by full matrix least squares with anisotropic thermal parameters for the carbon and oxygen atoms.
The IR and NMR results have been fully confirmed by the X-ray diffraction study, which shows only a slight distortion from the perfectly transdiaxial position of the two substituents. This unusual conformation for vicinally trans disubstituted ring (where anomeric or polar effects are absent) can be explained by reduction of the synaxial interactions as compared to cyclohexane derivatives and by destabilisation of the alternate diequatorial conformation owing to steric overcrowding of bulky substituents.
Furthermore the crystallographic study ascertains the nature of the intramolecular hydrogen bond occuring in the trans isomer 1;despite its low IR $\Delta\nu_{OH}$ value (34 cm^{-1}) it is an OH...O bond which involves the heterocyclic ether oxygen atom and the alcohol hydrogen, and not an OH...π bond which could arise from interaction of the hydroxyl with one of the phenyl groups.
Nevertheless stabilizing effect of intramolecular hydrogen bonding in the above conformation does not seem determinant, since in the cis isomer 2 the axial position of the 3-substituent is no more maintained ; it occupies the normally expected equatorial position, whereas the 2-phenyl group is axial. The intramolecular hydrogen bond observed in the cis isomer occurs between the hydroxyl and the 2-phenyl group and is of OH...π nature, although it is characterized by a larger IR $\Delta\nu_{OH}$ value (50 cm^{-1}) than in the above case.

12.4- 2 UNUSUAL CONFORMATION OF A DIHYDROPYRAN SHOWING ABNORMALLY WEAK INTRAMOLECULAR HYDROGEN BONDING : CIS AND TRANS 2-PHENYL-3-HYDROXY DIPHENYL METHYL CHROMAN.
F. Baert, R. Fouret, Laboratoire de Physique du solide (ERA N° 465); M. Sliwa, H. Sliwa, Laboratoire de Chimie Organique II ; Université des Sciences et Techniques de LILLE. B.P. 36 - 59650 Villeneuve d'Ascq, France.



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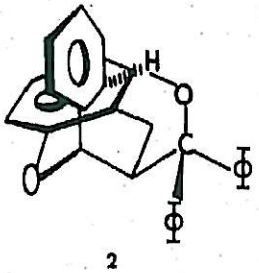

2

X-Ray analysis of the two isomeric flavan-3-yl diphenyl carbinols ($C_{28}H_{24}O_2$) 1 and 2 has been performed in order to compare with previous studies in solution by IR and NMR spectroscopy, which led to the assumption that the trans isomer 1 should exist exclusively in a diaxially substituted half chair conformation of its dihydropyran ring. The trans and cis compounds crystallize respectively in space group Pbca and $P2_1/c$ with :

trans			cis		
a =	9.99 Å		a =	10.77	Å
b =	18.76 "		b =	16.20	"
c =	22.44 "		c =	12.04	"
V =	4203.9 Å^3		β =	91°3	
Z =	8		V =	2099.8	Å^3
			Z =	4	

12.4- 3 TEMPERATURE DEPENDENCE OF PACKING AND CRYSTAL SITE SYMMETRY OF A HIGHLY SYMMETRIC TETRAAZASTANNANE.
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A full structure determination at 193 K shows that the compound 1,3,5,7-Tetrakis(tert.-butyl)-2,2,6,6-tetramethyl-1,3,5,7-tetraaza-2,6-disila-4-stannospiro[3,3]heptane crystallizes in the monoclinic space group C 2/c with 4 molecules per unit cell. The crystal dimensions are quite remarkable, in that two celledges are equal: a = c = 1860.4(1.0), b = 899.3(5) pm, β = 111.6(1)°, V = 2894.7 · 10^6 pm^3. The molecules occupy a 2(C_2) site symmetry, but the inherent symmetry of the molecule deviates not much from $\bar{4}2m$ (D_{2d}). The above centered pseudorhombic cell changes into a truly orthorhombic cell when the temperature is raised: According to powder patterns the low temperature phase α changes via an intermediate phase β into a high temperature phase γ at about 370 K. The γ-phase crystallizes in Fddd with 8 molecules per unit cell (a = 2047(2), b = 965.4(7), c = 3106(5) pm, V = 6137 · 10^6 pm^3; single crystal data), the molecules attaining the site symmetry 222(D_2). As can be derived from atomic coordinates the molecules only have to shift by ca 110 pm with respect to the b-axis of α-phase, whereas x and z coordinates remain practically unchanged. Following the priciples of Kitaigorodskii the spiro compound thus suffers a loss of symmetry by packing ($\bar{4}2m \rightarrow 2$), but retains a memory of its higher symmetry when heated in the solid ($2 \rightarrow 222$). The space groups along the path of transformation are not directly related by space-group-subgroup-relationships, as one might have expected.

12.4- 4 THE CMCA SPACE GROUP OF DICHLORINE.
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The reason why $C\ell_2$ (also Br_2 and I_2) crystallizes in orthorhombic Cmca rather than in the more closely packed hexagonal P6m2 or cubic Pa3 structures has never been satisfactorily explained despite the considerable attention the problem has received.

It has been suggested[C. A. English and J. A. Venables, Proc.Roy.Soc.Lond.,A340,57(1974)] that quadrupole-quadrupole Θ_{zz}-Θ_{zz} interactions are responsible. We have shown that the (point) Θ_{zz}-Θ_{zz} interaction is a very poor approximation to the electrostatic potential calculated from the difference density $\Delta\rho$ (obtained from the best available SCF wavefunction) by numerical integration. Not only is Θ_{zz}-Θ_{zz} different in magnitude from $\Delta\rho$-$\Delta\rho$ for a wide range of molecular orientations it is even, in many cases, of the wrong sign.

The calculations show clearly that of all three space groups, Cmca is in fact most stabilized by the electrostatic $\Delta\rho$-$\Delta\rho$ interaction. However this in itself is insufficient to make Cmca the most stable structure. Using a 6:12 potential for dispersion repulsion and imposing the stringent condition of no net compressive or expansive force on the crystal as a whole it can be shown that the remaining effect comes from anisotropy of the dispersion-repulsion field. This is cylindrically symmetric about the internuclear axis but not spherical about each atom. This field closely resembles in form those obtained theoretically for isolated homopolar diatomics by other workers. The effect is to 'flatten' the atoms at their poles thus giving them shorter van der Waals radii in this direction than at the equator.

12.4- 5 DETERMINATION OF CRYSTAL AND MOLECULAR STRUCTURE OF N-METHYLACRIDONE BY MOLECULAR PACKING ANALYSIS AND X-RAY DIFFRACTION.
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As a part of study of N-substituted acridone derivatives the crystal and molecular structure of N-methylacridone was determined. Crystals are orthorombic, a=5.109(2), b=14.56(1), c=13.59(1)Å, Z=4, space group $P2_12_12_1$. The intensities were measured on Syntex PI diffractometer. Because of small size of crystal and insufficient quantity of intensity data the application of direct methods was not successful. So the structure was solved by the minimization of crystal lattice energy E as a function of three translational and three rotational degrees of freedom of the molecule, which was treated as a rigid body. Two types of atom-atom potential functions were used for calculation of E: Williams's repulsive quadratic functions and Kitaigorodskii's '6-exp' functions of 'universal curve'. The grid of trial models was generated in the reduced 'Cheshire cell' which was obtained assuming mmm idealised symmetry of the molecule. The initial optimization of trial models was performed using quadratic functions only; '6-exp' functions were used for the additional refinement of localized minima. As a result of energy minimization two lowest minima with E=-23.8 (model I) and -22.8 kcal/mole (model II) were found. Further least squares refinement based on diffraction data starting with model I non-hydrogen atomic coordinates [illegible] determination of the [illegible]

12.4- 6 STRUCTURE AND LATTICE ENERGY OF THE FERROCENE $Fe(C_5H_5)_2$ DISORDERED PHASE.
J.F. Bérar, G. Calvérin, and G. Clec'h. Laboratoire de chimie-physique du solide, Ecole Centrale des Arts et Manufactures, 92290 Chatenay Malabry, France.

The crystalline structure of ferrocene $Fe(C_5H_5)_2$ is known to be disordered at room temperature. In analysing neutron diffraction data, B.T.M. Willis indicates that the disorder is due to the staggered molecules (D_{5d} symmetry) which assume two different orientations in the 2/1 proportion. We have computed the intermolecular distances H...H with this model. Some distances are very much shorter than the usual Van der Waals contacts, so that the existence probability of one orientation should be quasi zero. Our energetic calculations confirm this result; moreover they suggest possible existence of eclipsed molecules (D_{5h} symmetry) in the disordered phase.

Consequently, we have redetermined the structure of ferrocene by X-ray diffraction at 295 K. We have refined several disorder models with a simply-statistic spatial group symmetry. We have computed from semi-empirical atom-atom potential functions the occupancy rates of the different molecules with each refined disorder model. The results agree with the structural ones for only one model: that one with one kind of staggered molecules (A) and two kinds of eclipsed ones (P_1 and P_2). The latter are related by an inversion center and they are slightly shifted (orientation and position) with regard to the staggered molecules. Therefore the reorientation process among A, P_1 and P_2 implies a movement of both rings (C_5H_5). With this disorder model there are still some very short intermolecular distances indicating short range order. We have made energy calculations based upon the Monte Carlo method. They confirm the former results and allow the determination of the correlated directions.

12.4- 7 INTERMOLECULAR POTENTIALS FOR CARBOXYLIC ACIDS.
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Intermolecular force fields for carboxylic acids have been derived in two ways:

a. by means of a least-squares fit of the parameters of non-bonded atom-atom potentials and a hydrogen-bond potential to experimental data. The latter include heats of dimerization and dimer structures of formic, acetic and propionic acid, and heats of sublimation and crystal structures of acetic, α and β-oxalic, α and β-fumaric and isophtalic acid. It was found that (exp-6-1) atom-atom potentials and the Lippincott-Schroeder potential for the hydrogen bonds reproduce fairly well the experimental energies as well as the structures. The transferability of the potentials was studied with respect to the crystal structure of allene dicarboxylic acid and to the crystal structure and the lattice energy of formic acid, and was found to be good. A comparison is made with the results of other authors.

b. by making a least-squares fit to interaction energies, calculated by the *ab initio* MO-SCF method. Energies for 12 configurations of the formic acid dimer and 16 configurations of the methanol/formaldehyde complex were included in the process. Using (exp-6-1) atom-centred potentials, augmented with attractive exponential functions centred on the hydroxyl hydrogen and carbonyl oxygen atoms, a satisfactory fit was obtained (i.e. correspondence within 0.8 kcal/mol), especially for the hydrogen-bonded configurations of the formic acid pair. The resulting potential set was applied to the calculation of the structures and energies of the formic acid