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Theoretical Structures of Pyridazino[4,5-*d*]pyridazine and 1,4,5,8-Tetramethoxypyridazino-[4,5-*d*]pyridazine

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Lattice-energy computations employing semi-empirical potentials and the atom–atom approach were carried out to justify the crystal structures of pyridazino[4,5-*d*]pyridazine and 1,4,5,8-tetramethoxypyridazino[4,5-*d*]pyridazine. Results confirm the general validity of the method. In the case of pyridazino-[4,5-*d*]pyridazine better agreement between experimental and theoretical structures was obtained by considering also the contribution of electrostatic terms arising from the dipole–dipole interactions of the lone pairs on nitrogen atoms to the total energy. This shows that these effects, though small in absolute value, may sometimes be important in determining crystal structures.

Introduction

Lattice energies and their relationships to crystal structures have been investigated for a number of organic molecules. Semi-empirical potential functions, to account for the van der Waals interactions between non-bonded atom pairs, have been used. The eventual presence of hydrogen bonds and electrostatic forces has also been considered. The interest in finding the potential energy surface is that it allows: (*a*) crystal-structure interpretation with reference to molecular packing, (*b*) the solution of the phase problem for the determination of unknown crystal structures, (*c*) an approach to the study of the dynamics of molecular crystals and hence the calculation of other properties depending on atomic vibrations.

Success in packing analysis, within the limits of the approximate nature of the atom–atom approach and of the other approximations of the method,* is essentially dependent on the validity of the potential functions used in computing the packing energy. In the case of hydrocarbons, such functions have been tested with largely satisfying results (Kitaigorodskii, 1973; Williams, 1970); fairly good results have also been obtained with potentials involving atomic species other than carbon and hydrogen (Giglio, Liquori & Mazzarella, 1968; Giglio, 1969, 1970; Di Nola and Giglio, 1970; Ramachandran, Sarathy & Kolaskar, 1973).

To test the reliability of potential functions involving nitrogen, the present study on pyridazino[4,5-*d*]-pyridazine and 1,4,5,8-tetramethoxypyridazino[4,5-*d*]-pyridazine (hereinafter PP and TMPP respectively) was undertaken. Experimental structures of these substances are known (PP: Sabelli, Tangocci & Zanazzi, 1969; TMPP: Fanfani, Zanazzi & Sabelli, 1972). The following considerations form the basis of our choice: (*a*) the simplicity of the molecular structure and its high symmetry; (*b*) in the crystal, molecules lie on the inversion centres and therefore the degrees of freedom are reduced to three rotational variables, with consequent ease and rapidity in computation; (*c*) these molecules represent a good test for potentials involving nitrogen because their partial contribution to the resulting lattice energy would be relevant; furthermore, especially in PP, nitrogen atoms are 'unscreened' by atoms of other species.

Crystal data of PP and TMPP

The unit cell of PP has the following parameters: $a=3{\cdot}748$, $b=7{\cdot}464$, $c=10{\cdot}392$ Å, $\beta=95{\cdot}62°$; space group $P2_1/c$, $Z=2$. The molecular configuration, atomic numbering and axial system are shown in Fig. 1: the molecule was assumed to be perfectly planar with symmetry *mmm* and bond distances and angles were approximated to the values listed in Table 1.

Table 1. *Bond lengths* (Å) *and bond angles* (°) *assumed for the model of the* PP *molecule*

Bond		Angle	
a	1·42 Å	*ab*	123°
b	1·31	*bc*	120
c	1·38	*ad*	117
d	1·39	*ae*	119
e	1·05	*eb*	118

The cell constants of TMPP are: $a=4{\cdot}312$, $b=16{\cdot}826$, $c=7{\cdot}727$ Å, $\beta=101{\cdot}01°$; space group $P2_1/n$, $Z=2$. Apart from the rotation of methyl groups, the molecule presents four internal rotational degrees of freedom around C(1)–O(1), C(2)–O(2) and the centrosymmetrically related bonds. On the basis of the X-ray structure determination, the molecule was assumed to be rigid and planar with symmetry *mmm*. Its configuration is shown in Fig. 2 and bond distances and bond

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* For a general discussion of non-bonded energy see, for example, Hirschfelder, Curtiss & Bird (1954) and Mason (1970).

Table 2. *Bond lengths* (Å) *and bond angles* (°) *assumed for the model of the* TMPP *molecule*

Bond		Angle	
a	1·44 Å	*ab*	123°
b	1·30	*bc*	120
c	1·37	*ad*	117
d	1·38	*ae*	119
e	1·35	*eb*	118
f	1·44	*ef*	117

angles used in building the molecular model are listed in Table 2.

Method of lattice-energy calculation

Since both molecules lie with their centres on a crystallographic centre of symmetry, the translational degrees of freedom are lost and only three rotational parameters are needed. These are three Eulerian angles ψ_1,ψ_2 and ψ_3 as defined by Goldstein (1951). The orthogonal *XYZ* axes around which the rotations are performed, are defined in the following way, with respect to the monoclinic crystal axes: *Z* coincides with the *c* axis, *X* lies in the plane defined by **a** and **c** and *Y* coincides with **b***.

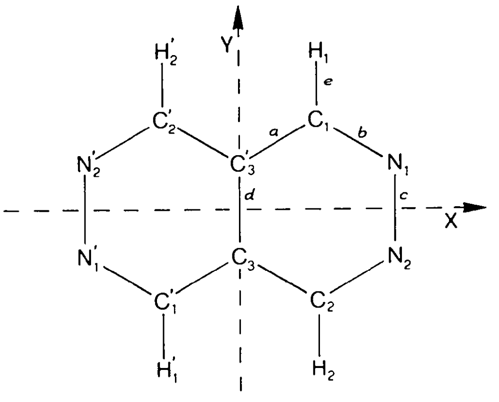

Fig. 1. The molecular model of pyridazino[4,5-*d*]pyridazine.

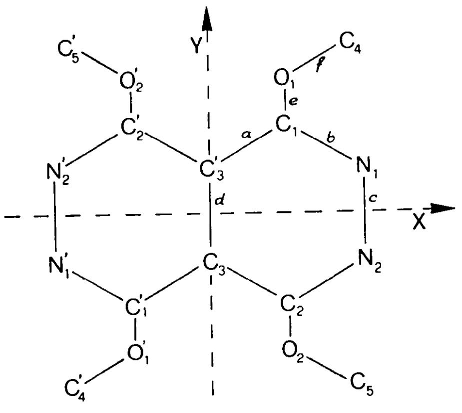

Fig. 2. The molecular model of 1,4,5,8-tetramethoxypyridazino[4,5-*d*]pyridazine.

It is assumed that the intermolecular interactions are pairwise-additive and that they can be described as non-bonded interactions between the constituent atoms; this is the characteristic feature of the atom–atom approach. The non-bonded interatomic potentials φ_{ij} were expressed in the generalized form:

$$\varphi_{ij}=-A/r_{ij}+B\exp\left(-Cr_{ij}\right)/r_{ij}^{D}$$

where r_{ij} is the non-bonded interatomic distance between atoms *i* and *j* of different molecules and *A*, *B*, *C*, *D*, are parameters dependent on the atoms considered. The crystal potential energy is expressed as:

$$\phi=\tfrac{1}{2}\sum_{i}\sum_{j}\varphi_{ij}$$

where the summation involves all distances between atoms of one molecule and all the atoms of surrounding molecules. At 0 K and neglecting zero-point energy, this quantity must be a minimum for the equilibrium structure of a perfect crystal. The parameters of the atom–atom potential functions used in this work are those of Williams (1972) for the C···C, C···H and H···H interactions. These parameters were selected because their reliability has been assessed by a number of investigations (Williams, 1972; Taddei, Bonadeo, Marzocchi & Califano, 1973). For the O···O interactions, potential parameters proposed for Ne–Ne interactions by Mason & Rice (1954). were used. For

Table 3. *Coefficients of the potential functions*

The energy is in kcal mole^{-1} if the interatomic distance is in Å.

Atom pair	Reference	*A*	*B*	*C*	*D*
H·····H	1	24·39	2171	3·74	0
C·····H	1	111·82	8503	3·67	0
C·····C	1	512·69	71782	3·60	0
N·····H	2	132·00	52100	2·04	6
N·····C	2	340·00	340000	0	12
N·····N	2	354·00	387000	0	12
N·····H	3	128·00	42000	4·25	0
N·····C	3	305·00	42000	3·69	0
N·····N	3	259·00	42000	3·78	0
N·····H	4	99·10	11802	3·69	0
N·····C	4	454·40	67863	3·62	0
N·····N	4	402·70	64155	3·64	0
N·····N	5	1557·00	439600	4·01	0
N·····C	6	572·00	337000	0	12
N·····N	6	547·00	243000	0	12
N·····C	7	366·00	216000	0	12
N·····N	7	363·00	161000	0	12
N·····C	8	363·00	483000	0	12
N·····N	8	354·00	387000	0	12
O·····O	5	200·00	186400	4·55	0
CH_3···CH_3	9	2943·80	273900	3·33	0
CH_3···O	10	606·70	115000	3·97	0
CH_3···N	10	606·70	115000	3·97	0
CH_3···C	10	936·00	290600	3·83	0
O·····C	10	244·00	212100	4·44	0
O·····N	10	200·00	186400	4·55	0

(1) Williams (1972). (2) Coiro, Giacomello & Giglio (1971). (3) Ahmed & Kitaigorodskii (1972). (4) Shmueli & Goldberg (1973). (5) Mason & Rice (1954). (6) Brant, Miller & Flory (1967). (7) Scott & Scheraga (1966). (8) Parsonage & Pemberton (1967). (9) Mason & Kreevoy (1955). (10) Dentini, De Santis, Morosetti & Piantanida (1972).

methyl–methyl interactions, parameters were taken from the paper of Mason & Kreevoy (1955). For mixed interactions involving CH_3, groups and O atoms, relevant parameters were taken from Dentini, De Santis, Morosetti & Piantanida (1972). Finally, for the N···N and mixed interactions involving nitrogen, several parameters were tried in order to verify their validity. All parameters used are listed in Table 3.

Lattice-energy maps were obtained by systematically varying the orientation of the molecules, *i.e.* by assigning discrete values to the three Eulerian angles ψ_1, ψ_2 and ψ_3 and by computing the sum of the atom–atom interactions for each orientation. The grid-point interval was initially set equal to 10°; subsequently this value of the angular increment was gradually reduced in the regions where relative energy minima were found. The most promising minima were scanned at angular intervals of 2°. The extension of the Eulerian space to be scanned was reduced, because of the crystallographic and molecular symmetry, according to Tollin, Main & Rossmann (1966), Thus the range of ψ_1 was from 0° to 90°, that of ψ_2 from 0° to 90° and that of ψ_3 from 0° to 360° for both crystals studied.

The lattice energy was computed by summing the atom–atom interactions between one molecule and the 249 nearest neighbours. Some attempts made with a larger sphere of interactions showed that the variation in the total energy is negligible and without influence on the location of energy minima.

Results of packing analysis for PP

Following the techniques described above, in an initial run with the set of parameters No. 1,3 in Table 3, two minima were found deeper than the rest. On repeating the energy calculations at closer intervals in these regions, one of the two minima at angles of 38°, 68° and 85° was discarded because it gave a higher energy value. The values of the Eulerian angles found for the retained minimum are: $\psi_1=34°$, $\psi_2=62°$, $\psi_3=260°$, which compare with the experimental values: $\psi_1=41°$, $\psi_2=61°$ and $\psi_3=270°$. Although the observed structure falls in a region of low energy, the agreement between experimental and theoretical values is not as good as has been obtained in other investigations, mainly involving C and H atoms. This was ascribed to the presence of nitrogen atoms in the molecule. Several computations were then carried out in the region of the minimum, employing different parameter sets for interactions involving N atoms (see Table 3). Absolute energy values are significantly affected by the use of different parameters, but this is not significant with regard to the molecular arrangement; ψ_1, ψ_2 and ψ_3 approximately maintain the same values. Results are listed in Table 4. No effort was made to adjust the parameters of the N potential function to fit our experimental data, because we were interested in checking the general applicability of the existing parameters.

Table 4. *Values of Eulerian angles at the minimum of the potential energy of the* PP *molecule for different sets of coefficients of potential functions involving nitrogen*

Reference numbers are those of Table 3; they refer to N···H, N···C and N···N interactions respectively and were used always in connexion with the parameters of reference (1) for C···C, H···H and C···H interactions.

	Eulerian angles		
Parameter set	1	2	3
3,3,3	34°	62°	260°
2,2,2	34	62	260
4,4,5	38	60	256
4,6,6	34	60	258
4,7,7	32	60	260
4,4,4	36	60	258
4,8,8	34	60	258

To improve the agreement between experimental and theoretical structure, electrostatic interactions due to asymmetry in the electronic charge distribution in the molecule were taken into account. Partial charges on each atom have been calculated using the CNDO/2 method; results are summarized in Fig. 3. The Coulomb energy is given by:

$$\phi_{\rm el}=\tfrac{1}{2}\sum_{ij} q_iq_j/r_{ij}$$

where q_i and q_j are partial charges on atoms i and j of different molecules and r_{ij} is the interatomic distance. The electrostatic forces are long-range and problems involving the convergence of the above sum may arise. Convergence-acceleration techniques are available (Williams, 1971), but in the present case trials made with an increasing number of neighbouring molecules have shown that this is unnecessary. Thus for the electrostatic interactions the same summation limit employed in the evaluation of the van der Waals energy was maintained.

The inclusion of this electrostatic term in the total potential energy has negligible effect on the position of the minimum. Also, the energy itself was slightly af-

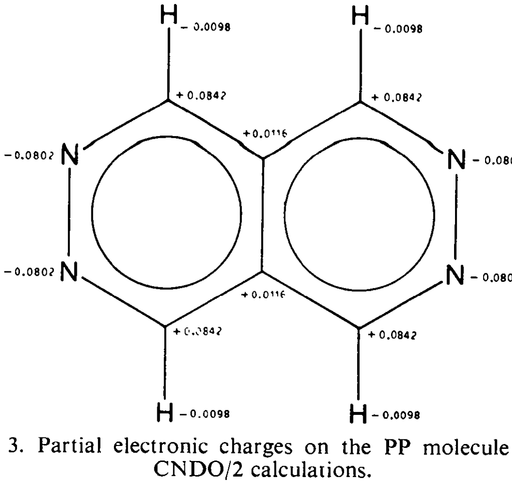

Fig. 3. Partial electronic charges on the PP molecule from CNDO/2 calculations.

fected, the Coulomb energy values being about 0·2 kcal mole^{-1} and slowly varying with the orientation of the molecules. Hence, it may be concluded that Coulombic interactions are not relevant in the molecular packing of PP, as has been found, for example, in the case of *s*-triazine (Mason, 1970).

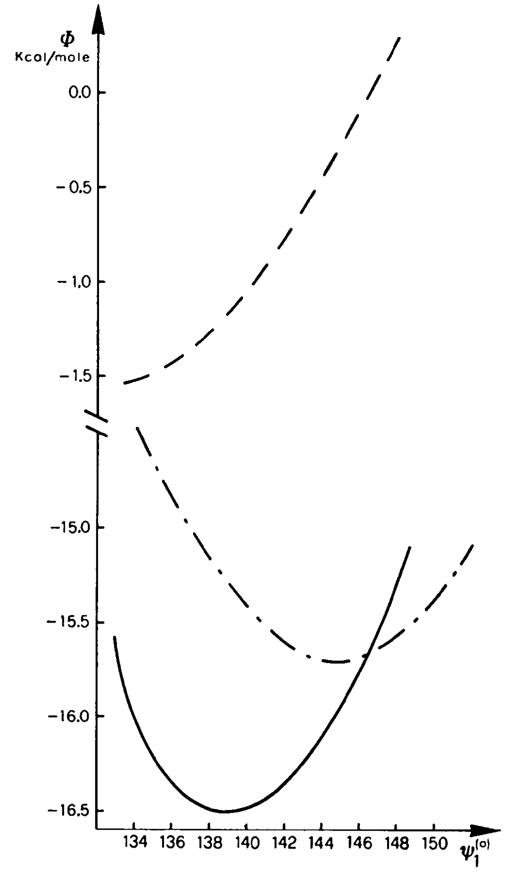

Fig. 4. The behaviour of the potential energy against ψ_1 angle for the PP molecule. Full line: total energy; dashed line: dipole–dipole term; dot-dashed line: van der Waals term.

Another possible cause of the discrepancy between theoretical and experimental packing could be the presence of lone pairs on nitrogen atoms. According to Coulson (in Mason, 1970), it is possible to attribute to the lone pair a dipole moment of 1·7 D; a rough value of 2·2 D was attributed to the same quantity by Lucken (1961) from n.q.r. measurements on pyridine. Assuming for the lone-pair dipole the former value, computations were carried out to evaluate the contribution of dipole–dipole interactions to the total energy. The single dipole–dipole contribution was computed with the formula:

$$\phi_{\mathrm{dip}} = 1/r^3_{ij}[(\boldsymbol{\mu}_i\,.\,\boldsymbol{\mu}_j) - 3(\boldsymbol{\mu}_i\,.\,\mathbf{r}_{ij})\,(\boldsymbol{\mu}_j\,.\,\mathbf{r}_{ij})/r^2_{ij}]$$

where $\boldsymbol{\mu}_i$ and $\boldsymbol{\mu}_j$ are point dipoles centred on nitrogen atoms of different molecules, at distance r_{ij}. The formula, obtained for ideal dipoles, is a good approximation (Hirschfelder, Curtiss & Bird, 1954) when $r_{ij}/l > 2$, where l is the length of the dipole. In this case it is applicable with a fair approximation on the assumption that the distance between two nearest dipoles is larger than twice the length of the dipole. Concerning the cut-off distance, the same value used for the other interactions was maintained because there is evidence of a good convergence.

Although the values of the dipole–dipole interactions are relatively low, with respect to the van der Waals energy (about 1 kcal mole^{-1} in the minimum region), the non-centrality of these forces caused the angle ψ_1 to increase from 34° to about 41°, which is very close to the experimental value. The ψ_2 and ψ_3 angles were largely unaltered (60° and 258° respectively). The predictions of Kitaigorodskii (1965, 1973) that the contribution of small electrostatic effects in zones

Table 5. *Atomic fractional coordinates of* PP (*for non-hydrogen atoms only*)

	Experimental			Theoretical [exp (−6) term only]				Theoretical [exp (−6) term plus dipole–dipole]			
	x/*a*	*y*/*b*	*z*/*c*	*x*/*a*	*y*/*b*	*z*/*c*	*Δ* (Å)	*x*/*a*	*y*/*b*	*z*/*c*	*Δ* (Å)
N(1)	0·1453	0·3036	0·0917	−0·0161	0·3184	0·0634	0·65	0·0065	0·3077	0·0873	0·52
N(2)	0·2805	0·1818	0·1834	0·1617	0·2290	0·1669	0·58	0·1894	0·2031	0·1814	0·37
C(1)	−0·0196	0·2453	−0·0170	−0·1310	0·2321	−0·0373	0·46	−0·1224	0·2369	−0·0180	0·39
C(2)	0·2410	0·0102	0·1624	0·2090	0·0612	0·1607	0·40	0·2274	0·0368	0·1620	0·20
C(3)	0·0675	−0·0609	0·0463	0·0889	−0·0447	0·0517	0·15	0·0914	−0·0523	0·0471	0·11

Table 6. *Fractional atomic coordinates of* TMPP

	Experimental			Theoretical			
	x/*a*	*y*/*b*	*z*/*c*	*x*/*a*	*y*/*b*	*z*/*c*	*Δ* (Å)
O(1)	0·2835	0·0321	−0·3187	0·2803	0·0260	−0·3182	0·10
O(2)	−0·3231	0·1162	0·1998	−0·3126	0·1146	0·2041	0·06
N(1)	0·0428	0·1240	−0·1722	0·0455	0·1212	0·1745	0·05
N(2)	−0·1078	0·1461	−0·0389	−0·1065	0·1439	−0·0407	0·04
C(1)	0·1317	0·0506	−0·1860	0·1292	0·0486	−0·1851	0·04
C(2)	−0·1672	0·0937	0·0725	−0·1615	0·0920	0·0709	0·04
C(3)	−0·0763	0·0108	0·0670	−0·0760	0·0114	0·0670	0·01
C(4)	0·3170	0·0946	−0·4409	0·3356	0·0858	−0·4385	0·17
C(5)	−0·3805	0·2001	0·2138	−0·4004	0·1957	0·2099	0·11

of broad energy minima may significantly shift the absolute minimum are thus confirmed in this case. The behaviour of the van der Waals and dipole–dipole contributions to the total energy can be appreciated in Fig. 4. In Table 5 are listed the fractional crystallographic coordinates of atoms from the X-ray structure determination, those obtained from van der Waals and from van der Waals plus dipole–dipole calculations, and deviations (in Å) of atoms from their experimental positions in both cases. The projections on the *bc* plane of the molecular model are compared in Fig. 5.

As is shown, the inclusion of the dipole–dipole interactions gave a fair improvement over the results previously obtained with only the van der Waals forces.

Results of packing analysis for TMPP

The lattice-energy map obtained with the techniques described above revealed only one deep minimum at angles $\psi_1=22°$, $\psi_2=65°$ and $\psi_3=77°$, very near to the experimental values $\psi_1=21{\cdot}7°$, $\psi_2=64{\cdot}4°$ and $\psi_3=76{\cdot}6°$. Sections of the energy surface through the minimum are shown in Fig. 6. Fractional atomic coordinates from the X-ray analysis and energy calculations are compared in Table 6. Since electrostatic effects are expected to be small, they were not considered in this case. The agreement between the theoretical and experimental structures is satisfactory with the contribution of the van der Waals energy alone.

Conclusions

This work presents further evidence to show that the atom–atom approach, employing semi-empirical potentials to evaluate the single interatomic contribution to the total lattice energy, is a simple and powerful method with which to interpret the packing of molecules and crystal structures of organic compounds. As has been shown in the literature, the method is also reasonably valid for substances containing atoms other than C and H, especially when these atoms are partially screened by C and H. In the case of TMPP there is no problem because the N atoms are screened by the large methyl groups which essentially control the packing of the molecules in the crystal. The use of the atom–atom approach is wholly justified in this case, as is confirmed by the results obtained.

When this is not the case, as in the PP molecule, this study has shown that neglect of some contributions, such as the lone pair dipole–dipole interactions for nitrogen-containing compounds, could give a poorer agreement between experimental and theoretical structures.

This explanation still represents a rough approximation to the actual situation and further studies are necessary to obtain more reliable models for the interactions involving N atoms.

Authors are indebted to Dr R. Cambi who carried out the CNDO/2 computations on PP molecule.

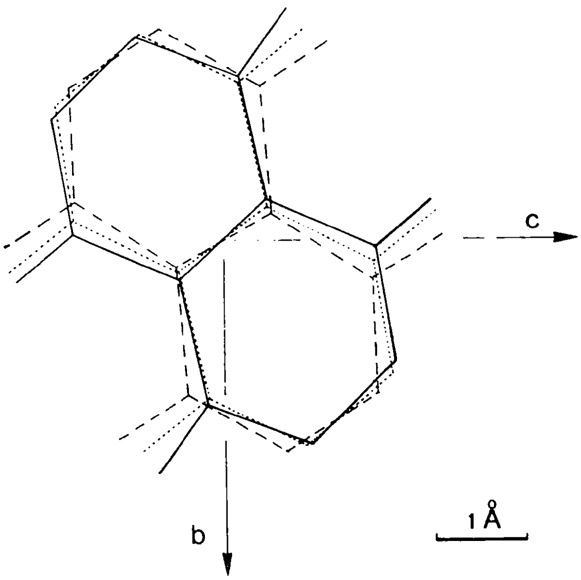

Fig. 5. Projection of the PP molecule on the *bc* plane. Full line: experimental structure; dashed line: structure obtained from van der Waals energy calculations; dotted line: structure obtained after the inclusion of the dipole–dipole contribution.

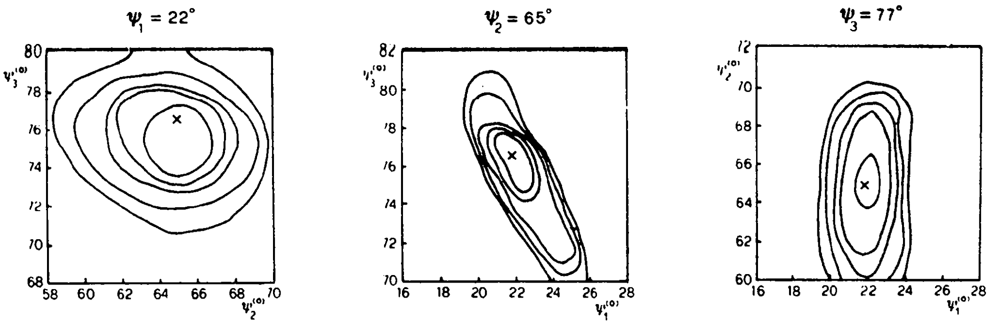

Fig. 6. Sections through the potential energy surface of TMPP at the Eulerian angles corresponding to the minimum. Contour lines at arbitrary intervals. Crosses mark the position of the experimental structure.

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2,4-Pentandionato-Lithium (Li-acac) – ein neuer Strukturtyp von Metall-β-Diketonato-Komplexen[*]

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Dem Gedenken an E. Funck gewidmet

2,4-Pentanedionatolithium, $LiO_2C_5H_7$, orthorhombic, *Ccca* (No. 68), $a_o = 16{\cdot}793$, $b_o = 15{\cdot}184$, $c_o = 13{\cdot}970$ Å, $Z = 24$, $D_{pyc} = 1{\cdot}181$, $D_x = 1{\cdot}187$ g cm^{-3}. The structure consists of endless strings of pseudo Li(acac)$_2$ groups, connected by Li atoms, and is a basic new type of 2,4-pentanedionato-metal complex. It should be described as an 'oxygen-chelated-metal bridged complex' of the metal-β-diketonato series of compounds.

Funck, Jungermann, Kaiser & Schröder (1971) untersuchten kürzlich das IR-spektroskopische Verhalten von 2,4-Pentandionato-Lithium-(Li-acac)-Einkristallen und bestimmten deren Raumgruppe. Da trotz der dadurch erhaltenen Ergebnisse noch keine erschöpfenden Aussagen über die Struktur der Verbindung möglich waren, haben wir eine dreidimensionale Röntgenstrukturanalyse durchgeführt.

Experimentelles

Eine Überprüfung der experimentellen Dichte ergab das Vorliegen eines Messfehlers. Sorgfältige Messungen mit verschiedenen Methoden lieferten den Wert $d_4^{20} = 1{,}180_8$ g cm^{-3}. Somit stellt sich die Geometrie

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