[4] *J. Sauer & H. Krapf*, Tetrahedron Letters *1969*, 4279.

[5] *H. W. Krapf*, Dissertation Universität München, 1970.

[6] *N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank & D. J. Wallace*, J. Amer. chem. Soc. *71*, 3337 (1949); *N. J. Leonard & J. A. Adamcik*, J. Amer. chem. Soc. *81*, 595 (1959); *G. Opitz & E. Tempel*, Liebigs Ann. Chem. *699*, 68 (1966); *Z. Horii, K. Morikawa, Y. Tamura & J. Ninomiya*, Chem. pharm. Bull. *14*, 1399 (1966); *C. A. Grob & H. J. Wilkens*, Helv. *50*, 725 (1967); *N. Sygiyama, M. Yamamoto & C. Kashima*, Bull. chem. Soc. (Japan) *42*, 1357 (1969).

[7] *G. Pascual, J. Meier & W. Simon*, Helv. *49*, 165 (1966).

[8] *R. R. Fraser & R. B. Swingle*, Tetrahedron *25*, 3469 (1969); *R. Radeglia*, Z. Physikal. Chem. *235*, 335 (1967).

[9] *R. M. Silverstein & G. C. Bassler*, «Spectrometric Identification of Organic Compounds», J. Wiley & Sons, Inc. New York, Second Edition 1968.

[10] *W. E. Stewart & T. H. Sidall III*, Chem. Reviews *70*, 517 (1970).

[11] *A. Mannschreck & U. Koelle*, Tetrahedron Letters *1967*, 863.

[12] *H. W. Krapf, P. Riedl & J. Sauer*, unveröffentlichte Resultate.

[13] *L. J. Haynes & A. H. Stanners*, J. chem. Soc. *1956*, 4103.

[14] *E. Carstensen-Oeser*, unveröffentlichte Resultate.

---

170. Structure and spectra of murexide and of alkali purpurates: Crystal structure of lithium purpurate dihydrate

by **H. B. Bürgi, S. Djurić, M. Dobler** and **J. D. Dunitz**

Laboratorien für organische und anorganische Chemie der Eidg. Technischen Hochschule, 8006 Zürich

(5. V. 72)

Summary. Crystals of lithium purpurate dihydrate are triclinic, $a = 6.715$, $b = 6.822$, $c = 14.038$ Å, $\alpha = 96.85$, $\beta = 100.94$, $\gamma = 67.41°$, space group $P\bar{1}$, $Z = 2$. From the results of a detailed three-dimensional analysis the lithium ion is found to be bonded to three atoms (two oxygen plus central nitrogen) of one purpurate anion, and also to an oxygen atom of a second purpurate anion and to a water molecule to complete a roughly square-pyramidal 5-coordination. The purpurate anion is markedly nonplanar, the two six-membered rings being twisted by 22° around the central C—N bonds. A molecular mechanics calculation, based on reasonable interatomic potential functions, reproduces the observed geometry of the lithium complex and indicates that with larger cations the degree of out-of-plane twisting should increase. The observed dependence of the characteristic long-wave absorption of purpurate complexes on ionic radius is explained qualitatively on the basis of simple HMO-theory.

Murexide, the ammonium salt of purpuric (5,5′-nitrilo-dibarbituric) acid, has been used for many years as an indicator for complexometric titrations [1]. In weakly acid media (water or methanol) the purpurate anion **1** forms 1:1 complexes with mono-, di-, and trivalent metal cations. Complexation is accompanied by characteristic spectral changes, the long-wave absorption band at $\lambda_{max} = 522$ nm (aqueous solution of murexide) being displaced to shorter wavelength. The displacement and intensity of the band both become greater the smaller the radius of the complexed cation [2] [3], as shown in Table 1. From a comparison of the complexing abilities of compounds related to purpuric acid, *Gysling & Schwarzenbach* [4] concluded that the central N-atom is directly involved in coordination to the metal ion. Recently, *Winkler* [2]

has proposed that the spectral changes are connected with twisting of the two barbiturate ring systems relative to one another, brought about by complexation.

1
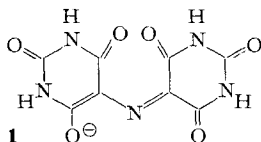
However, the information necessary for discussing the spectral changes in terms of the detailed structure of the complexes has not been available so far. To fill this gap, we have determined the crystal structure of lithium purpurate, which can be obtained as a dihydrate in suitable crystal form[1]). From the results of the crystal structure analysis we abstract a simple model that accounts qualitatively for the observed spectral changes in solution.
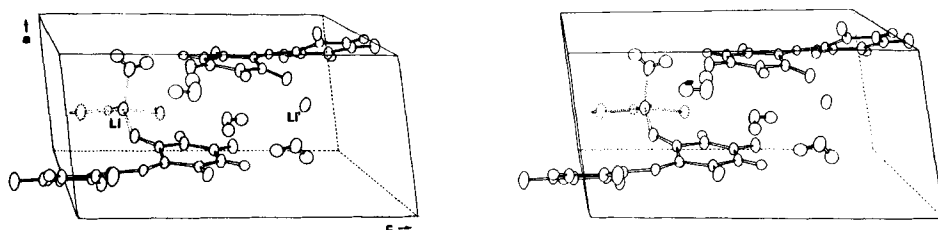

Fig. 1. *Stereographic view of crystal structure of lithium purpurate dihydrate*

The structure analysis of the crystalline di-aquo lithium complex was fairly straightforward (details are given in a later section). The main features of the crystal structure (Fig. 1 and 2) can be summarized as follows:

(a) The lithium ion is bonded to two carbonyl oxygen atoms and to the central nitrogen atom of one purpurate anion (Li...O, 2.01, 2.14 Å; Li...N, 2.13 Å). It is further bonded to a carbonyl oxygen atom of a second purpurate anion (Li...O, 1.95 Å) and to a water molecule (Li...O, 2.30 Å) to complete a roughly square-pyramidal 5-coordination with the water molecule as apex (Fig. 2).
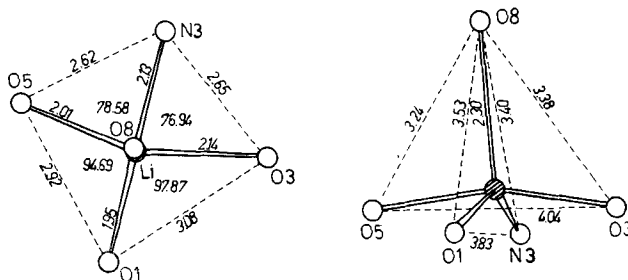

Fig. 2. *Coordination of lithium ion in lithium purpurate dihydrate*

(b) The purpurate anion deviates markedly from planarity. It has virtual (non-crystallographic) C_2 symmetry, with the two six-membered rings twisted by 22° (in

the same sense) out of the plane of the central three atoms. Some of the bond angles show large deviations from the standard value of 120° at trigonal atoms; in particular, the central C–N–C angle is increased to 135° and its two adjacent N–C–C angles to 128°.

The observed long-wave absorption of purpurate complexes is very intense and must be due to a $\pi \to \pi^*$ transition. It is reasonable to suppose that its wavelength depends on the dihedral angle between the two six-membered rings, which, in turn, should depend on the radius of the coordinated cation of given charge. The results of the structure analysis provide a model for discussing this dependence. A planar purpurate anion with standard bond distances and 120° bond angles would have an impossibly short O...O distance of ca. 0.5 Å. Moreover, it would not provide a suit-

Table 1. *Spectroscopic data*[a] *for some complexes of the purpurate anion with alkali- and ammonium-ions in methanolic solution*

cation	[purpurate] (Ml^{-1})	[cation] (Ml^{-1})	λ_{max} (nm)	$\varepsilon (\lambda_{max})$
Li+	$4 \cdot 10^{-6}$	$0 \cdot 1$	468 ± 2	$20\,500 \pm 1000$
Na+	$4 \cdot 10^{-6}$	$0 \cdot 1$	488	18 500
K+	$5 \cdot 10^{-6}$	$0 \cdot 1$	510	15 400
NH$_4$+	$5 \cdot 10^{-5}$	$0 \cdot 2$	516	15 400
Rb+	$5 \cdot 10^{-6}$	$0 \cdot 1$	517	14 100
Cs+	$5 \cdot 10^{-6}$	$0 \cdot 1$	520	13 400
N(C$_2$H$_5$)$_4$+	$5 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	530	13 100

[a]   Provided by *H. Hohl & K. Bornemann*.

able environment for efficient coordination of a small cation, e.g. lithium, since the base of the relevant O...N...O triangle would be too long – about 4.8 Å instead of the required 3.9–4.0 Å. Widening the central C–N–C angle simultaneously increases the too short O...O distance and decreases the too long one, whereas twisting the six-membered rings out of planarity increases both these O...O distances. The actual effect of varying the cation radius is not easily foreseen intuitively since it depends on a rather complicated interplay of attractive and repulsive forces. One might hope, however, that if a molecular mechanics calculation, based on a suitable choice of interatomic potential functions, can reproduce the observed geometry of the lithium complex it might also serve to derive approximate geometric parameters for the other alkali metal complexes.

We have made such calculations, using the procedure described by *Jacob, Thompson & Bartell* [5], as adapted by *Thompson*[2]) to include the effects of ring constraints. To reduce the number of variables we consider a model, consisting only of one purpurate anion with a metal ion coordinated to the atoms O(3), O(5), N(3) (i.e. we neglect the two additional ligand atoms); further, we assume the model to have exact C_2 symmetry and hold the bond lengths of the anion and the internal angles of the six-membered rings constant at their experimentally observed values (Fig. 3). Moreover, each six-membered ring, with its substituents, is constrained to be strictly

[2])   We thank Prof. *H. B. Thompson* for a copy of his program DIPSY VII.

Table 2. *Potential energy terms and constants used in energy minimization* [a])

---

a) Bond stretching [b])

$$V = \frac{q^2 c^2}{r} + \frac{B_0 c^2 (r_+ + r_-)^{(n_+ + n_- - 1)}}{r^{(n_+ + n_- - 1)}}$$
[6]

$q_O = -0.5$ $B_0 = 0.035$

$q_N = -0.1$ [c]) $r_- = 1.341$ Å [d])
[6]

$q_{M^+} = +1.0$ $n_- = 1.9$ [d])

	Li	Na	K	Rb	Cs	
r_+	0.607	0.958	1.331	1.484	1.656 Å	[6]
n_+	4.5	5.2	5.1	4.9	4.6	[6]

$(c^2/Å = 336.2 \text{ kcal/mol})$

b) Bond angle bending [e])

$V = 0.403 \cdot 10^{-1} \cdot (\theta - 120°)^2 \text{ kcal/mol}$
[7]

c) Torsional potential [f])

$V = 0.384 \cdot 10^{-2} \cdot \omega^2 \text{ kcal/mol}$ (ω in degrees)

d) Nonbonded potentials

$V = 2.993 \cdot 10^5 \cdot r^{-12} - 3.252 \cdot 10^2 \cdot r^{-6} \text{ kcal/mol}$ [g])
[8]

$$V = \frac{q_O{}^2 \cdot e^2}{r}$$ [h])

---

a)   To reduce the number of parameters, the model was constrained to have C_2 symmetry. Initial parameter values were taken to be appropriately averaged experimental values (Fig. 3).

b)   All bond lengths in the purpurate anion were held at fixed values (Fig. 3); the distance $O \cdots M^+$ and $N \cdots M^+$ were allowed to vary. For definitions of B_0, r_+, r_-, n_+, n_- see reference [6].

c)   The partial charge on the central nitrogen atom was chosen to approximately reproduce the observed $N \cdots Li^+$ distance.

d)   The values of r_- and n_- for O and N were assumed to be those of F^-.

e)   The internal ring angles were held at fixed values (Fig. 3). All other angles were allowed to vary under the constraint that the sum of the three angles at each ring atom is 360° (planarity). Energy changes arising from deformation of $Li^+ \cdots N–C$, $Li^+ \cdots O–C$, $O \cdots Li^+ \cdots O$, and $O \cdots Li^+ \cdots N$ angles were neglected. A single angle-bending force constant was taken for all other variable angles (numerical value from a valence force field [7]). Note that with these assumptions angle deformation at N(3) costs half as much in energy as at C(6), C(5) or C(7).

f)   This force constant was estimated from a HMO-calculation on the linear uncomplexed ligand system. The total π-electron energy E_π was calculated as a function of the torsion angle ω, assuming the standard values [9]: $h_N = 0.5$, $h_O = 1.0$, $k_{C-N} = 0.8$, $k_{C=O} = 1.0$, except for N(3) where $h_N = 1.0$, $k_{C-N} = \cos\omega$ or $\sin\omega$ (for the two orthogonal p-orbitals). The function $E_\pi(\omega)$ was found to be approximately quadratic over the whole range of ω.

g)   Since the angle-bending force constant was taken from a valence force field 1,3-interactions were omitted from our calculation. For simplicity only the following 1,4- and higher interactions were taken into account: $N(3) \cdots O(1)$, $N(3) \cdots O(3)$ and $O(1) \cdots O(4)$.

h)   This term represents the *Coulomb* repulsion between atoms O(5) and O(3).

planar, which is not the case in the actual structure. The energy can then be minimized with respect to five independent parameters. The interatomic potential functions assumed are given in Table 2, and the results of the calculations are summarized in Table 3.

For the lithium complex the calculated structural parameters agree well with the experimental ones. The Li...N distance is calculated about 4 percent too short, a discrepancy that could be removed by decreasing the assumed partial charge on the

Table 3. *Experimental and calculated structural parameters for alkali purpurate complexes*

	θ_1 (°)	θ_2 (°)	θ_3 (°)	θ_4 (°)	θ_5 (°)	θ_6 (°)	θ_7 (°)	d_1 (Å)	d_2 (Å)	d_3 (Å)	ω (°)
Li+	134	112	123	120	128	125	119	2.07	2.13	2.62	22[1])
Li+	133.4	110.2	120.5	122	129.8	124.7	119.8	2.08	2.05	2.59	23.0
Na+	129.4	113.3	120.8	121.7	126.7	124.2	120.3	2.42	2.29	2.62	27.8
K+	126.6	115.6	121.3	121.2	124.4	123.9	120.6	2.74	2.61	2.66	30.5
Rb+	125.7	116.3	121.5	121.0	123.7	123.8	120.7	2.87	2.74	2.68	31.2
Cs+	124.8	117.0	121.7	120.8	123.0	123.8	120.7	3.01	2.90	2.69	31.9

[1])   Averaged experimental values, see footnote [a]) Table 2.
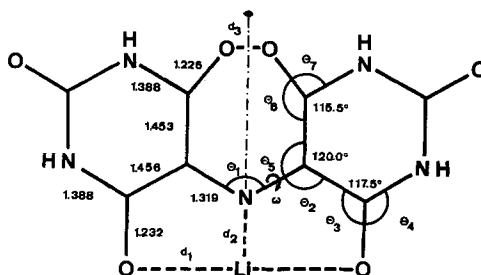
Fig. 3. *Parameters used for energy minimization calculation*

nitrogen atom. However, in view of the crudity of the model, this adjustment and others that could be introduced to reach perfect numerical agreement do not seem justified. The structural parameters of the other alkali metal complexes have been calculated with the same force field as for the lithium complex, changing only the repulsive part of the M^+...N and M^+...O potential functions to introduce differences in effective cation radii. With increasing cation radius the angles θ_1, θ_2 and θ_5 approach their reference value of 120° and the torsion angle increases from 22° for Li+ to 32° for Cs+, the largest cation considered. One encouraging feature of the calculation is that the predicted M^+...O distances are close to the M^+...F^- distances found in the corresponding alkali fluorides.

In order to correlate the calculated structural changes with the observed changes in the optical absorption spectra we make use of the simple *Hückel* molecular-orbital theory for two extreme conformations of the purpurate anion, both with linear C–N–C angle. One conformation is planar (symmetry D_{2h}), the other has the two rings mutually perpendicular (symmetry D_{7d}). For the D_{2h} conformation the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals are shown diagramatically in Fig. 4. The HOMO can be visualized as the antisymmetric combination of E_{1g}-type orbitals of the two six-membered rings with anti-bonding C–O character; this orbital has a node on the central N-atom. The LUMO is the symmetric combination of the same E_{1g}-type orbitals with anti-bonding behaviour between the central N-atom and the two rings. Twisting the rings out of the common plane gives intermediate con-formations of D_2 symmetry and leads finally to the perpendicular D_{2d} conformation, for which the HOMO and LUMO become degenerate, each being an anti-bonding

Table 4a. *Fractional coordinates* (estimated standard deviations $\times 10^4$ in parentheses)

	x	y	z
O(1)	.4513 (2)	.3251 (2)	.2384 (1)
O(2)	.5313 (2)	.2224 (2)	.5577 (1)
O(3)	− .1292 (2)	.3197 (2)	.3749 (1)
O(4)	.4074 (2)	.0255 (2)	.1117 (1)
O(5)	− .3471 (2)	.4086 (2)	.0889 (1)
O(6)	− .0132 (3)	.2304 (3)	− .1781 (1)
O(7)	.9794 (3)	.2359 (3)	.6133 (1)
O(8)	.4062 (3)	.2781 (3)	.7395 (1)
N(1)	.4927 (2)	.2565 (2)	.3962 (1)
N(2)	.2015 (2)	.2633 (2)	.4658 (1)
N(3)	.0221 (2)	.2831 (2)	.2098 (1)
N(4)	− .1794 (2)	.3319 (2)	− .0435 (1)
N(5)	.1964 (2)	.1478 (2)	− .0303 (1)
C(1)	.3766 (3)	.2818 (2)	.3025 (1)
C(2)	.4150 (3)	.2452 (3)	.4776 (1)
C(3)	.0659 (3)	.2867 (2)	.3777 (1)
C(4)	.1627 (2)	.2679 (2)	.2902 (1)
C(5)	.2292 (3)	.1402 (2)	.0700 (1)
C(6)	.0384 (2)	.2589 (2)	.1163 (1)
C(7)	− .1756 (3)	.3366 (3)	.0550 (1)
C(8)	.0011 (3)	.2374 (3)	− .0900 (1)
Li	.6911 (5)	.4168 (5)	.2348 (2)

Table 4b. *Anisotropic vibrational parameters*, expressed in the form
$$\exp\left(-2\pi^2\left(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl\right)\right)$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	.0220	.0525	.0203	− .0201	.0038	.0052
O(2)	.0217	.0510	.0181	− .0136	− .0013	.0038
O(3)	.0152	.0451	.0239	− .0129	.0051	.0046
O(4)	.0178	.0386	.0226	− .0016	.0040	.0038
O(5)	.0155	.0573	.0228	− .0069	.0039	.0083
O(6)	.0367	.0541	.0186	− .0085	.0057	.0040
O(7)	.0496	.0800	.0272	− .0370	.0065	.0055
O(8)	.0560	.0400	.0357	− .0081	.0179	.0064
N(1)	.0164	.0438	.0173	− .0151	.0012	.0042
N(2)	.0157	.0349	.0158	− .0095	.0029	.0030
N(3)	.0149	.0264	.0158	− .0083	.0028	.0021
N(4)	.0182	.0392	.0164	− .0073	.0016	.0043
N(5)	.0198	.0348	.0175	− .0050	.0069	.0010
C(1)	.0145	.0304	.0173	− .0097	.0032	.0007
C(2)	.0163	.0307	.0176	− .0083	.0025	.0020
C(3)	.0150	.0273	.0178	− .0090	.0038	.0011
C(4)	.0136	.0281	.0160	− .0085	.0035	.0007
C(5)	.0173	.0269	.0179	− .0071	.0043	.0009
C(6)	.0146	.0271	.0155	− .0077	.0027	.0014
C(7)	.0159	.0320	.0170	− .0074	.0024	.0037
C(8)	.0244	.0309	.0175	− .0087	.0046	.0026
Li	.0179	.0428	.0269	− .0108	.0057	.0049

Table 4c. *Calculated hydrogen atom fractional coordinates,*
B_{iso} [$Å^2$], N—H, 1.00 Å, N—H bisecting C—N—C angle.
Hydrogen atoms H(5) to H(8) were not included in the structure factor calculations

	x	y	z	B_{iso}
H(1)	.6484	.2458	.4047	1.8
H(2)	.1398	.2592	.5248	1.6
H(3)	− .3253	.4036	− .0848	1.8
H(4)	.3256	.0817	− .0624	1.5
H(5)	.4660	.1720	.7800	
H(6)	.4690	.2180	.6870	
H(7)	.0280	.2200	.6750	
H(8)	− .1300	.2000	.6000	

linear combination of an E_{1g}-type orbital with the appropriate p-orbital on the central N-atom. The orbital correlation diagram is shown schematically in Fig. 4.

According to this simple model, the long-wave absorption band of the purpurate anion should be polarized along the longest molecular dimension, and should decrease both in energy and in intensity with increasing torsion angle.
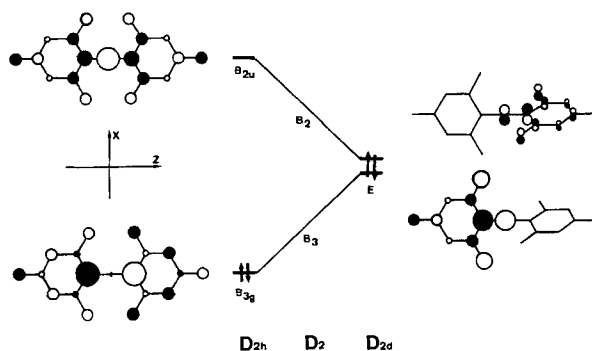

Fig. 4. *Orbital correlation diagram for HOMO and LUMO of hypothetical purpurate anion with linear arrangement at the central nitrogen atom*

Table 1 shows that as the cation becomes larger, i.e. as the torsion angle ω increases, the absorption moves to longer wavelength and becomes less intense, in accordance with the model.

We have also confirmed that crystals of lithium purpurate dihydrate have the expected dichroism. Maximum absorption occurs when the electric vector is polarized approximately parallel to the c axis; for this orientation of the electric vector the crystals appear deep red in transmitted light, whereas for other orientations they appear light yellow. The crystal structure analysis shows that the long dimension of the purpurate anion runs approximately in this direction (Fig. 1).

Although the *Hückel*-model correctly reproduces the observed trends in the experimental data, its quantitative aspects are not to be taken too seriously. Among other things configuration interaction has been neglected. The lowest excited configuration for the linear, planar model is of B_{1u} symmetry and its calculated energy is $0.60 \beta_0$

above the ground configuration (calculation based on *Hückel*-parameters given in Table 2, note f). Other excited configurations of the same symmetry are 0.92 and 1.69 β_0 above the ground configuration but are relatively insensitive to the molecular conformation. Configuration interaction should therefore be greatest for the planar conformation and hence the falloff in excitation energy should be somewhat less pronounced than as suggested by our crude calculation. A more important objection is that the purpurate anion is not linear at the central N atom. With a bent C–N–C angle the p_x and p_y orbitals of the central atom are not symmetry equivalent, and the degeneracy of the HOMO and LUMO orbitals in the perpendicular conformation is removed. However, even for a perpendicular conformation that is strongly bent at the central N atom, the energy difference between these orbitals is certainly smaller than for the corresponding planar conformation. We therefore believe that in spite of its shortcomings the simple model incorporates the essential features of a more complete theory.

Crystal Data: Lithium purpurate dihydrate, $C_8H_4N_5O_6Li \cdot 2H_2O$, deep red triclinic prisms (Fig. 5), $a = 6.715$, $b = 6.822$, $c = 14.038$ Å, $\alpha = 96.85$, $\beta = 100.94$, $\gamma = 67.41°$, $U = 582.2$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_x = 1.763$, $D_m = 1.75$, linear absorption coefficient $\mu(MoK\alpha) = 1.6$ cm^{-1}.
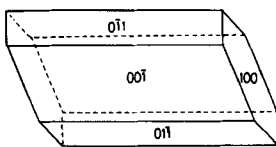

Fig. 5. *Lithium purpurate dihydrate: typical crystal form*

Intensity Measurements: Intensities of more than 4000 independent reflexions were measured with a computer-controlled 4-circle diffractometer (*Hilger and Watts* Y290) with MoKα radiation monochromatized by reflection from graphite. Intensities were converted to |F|- and |E|-values in the usual way, absorption corrections being neglected.

Structure Analysis and Refinement: The reflexion (020) is extremely strong (| E | = 3.26), and packing considerations suggest that the structure semi-invariant E(020) must be negative. The structure was solved directly by the symbolic addition method [10] applied to the 281 reflexions with | E | ≥ 1.8, assuming E(020) to be negative. The approximate positions of all 22 non-hydrogen atoms in the asymmetric unit could be recognized without difficulty in the resulting E-*Fourier* synthesis.

After 2 cycles of refinement by full-matrix least-squares analysis (isotropic thermal vibration parameters) a $(F_0 - F_c)$-*Fourier* synthesis showed peaks corresponding to all 8 hydrogen atoms in the asymmetric unit. The four H-atoms of the purpurate anion were included in the structure model with positional coordinates estimated from stereochemical assumptions (N–H, 1.00 Å, N–H bisecting C–N–C angle). The H-atoms associated with the water molecules were not included. Two further least-squares cycles (anisotropic thermal vibration parameters for nonhydrogen atoms, H-atoms not refined but included in F_c with isotropic vibration parameters) led to a final
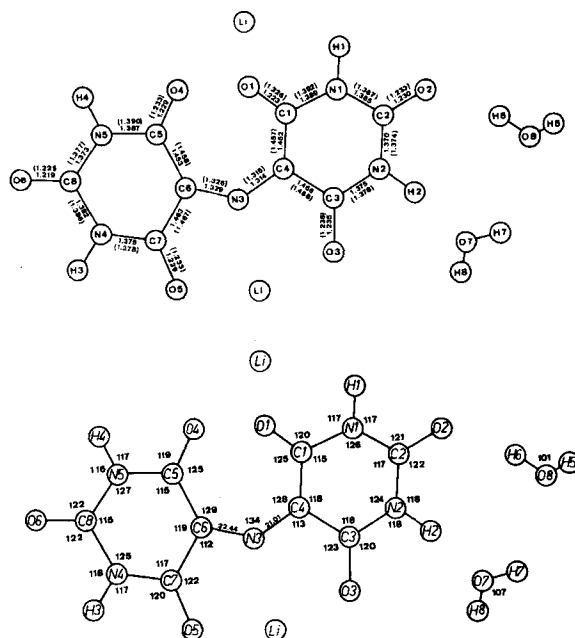
Fig. 6. *Molecular topography. Top: bond distances in Å (values in parentheses are corrected for thermal motion; the two rings were treated separately as rigid bodies). Bottom: bond angles and torsion angles (about central C—N bonds only)*

R-factor of 0.056 over 3175 significant reflexions included in the analysis with unit weight, as seemed justified by the uniform distribution of the quantity $\langle w^2 \Delta^2 \rangle$.

Positional coordinates and vibrational tensor components derived from the final least-squares cycle are listed in Table 4 along with their standard deviations obtained by inversion of the normal equations matrix. For convenience some of this information is given in Table 5 with respect to a Cartesian molecular coordinate system. Interatomic distances, bond angles and torsion angles of interest are given in Fig. 6.

Results of Crystal Analysis: The lithium ion is in roughly square-pyramidal 5-coordination (Fig. 2). The ligands in the basal plane are the oxygen atoms O(3) and O(5) and the central nitrogen atom N(3) of one purpurate anion, plus a carbonyl oxygen O(1) of a second purpurate anion related to the first by the *a* translation of the crystal. The apical ligand is a water molecule $H_2O(8)$. Thus there are chains schematically represented by:

$$\ldots N(3)-O(1)\ldots\, Li\ldots N(3)-O(1)\ldots\ldots\, Li\ldots$$
$$H_2O \qquad\qquad\qquad H_2O$$
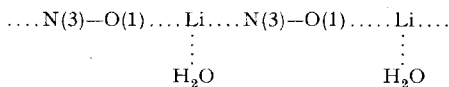
running along *a*. In addition to these bonds involving the lithium ion the purpurate anions and water molecules are further interconnected by a complex network of hydrogen bonds, in which all H-atoms in the crystal partake (Fig. 7; Table 6).

The vibration tensors of the atoms are listed in Table 4, where the components U_{ij} refer to unit vectors along the triclinic axes. It is apparent that the vibrational

Table 5. *Coordinates in Å units*, referred to an orthogonal coordinate system.
The transformation matrix from fractional to orthogonal coordinates is defined as follows:

$$
\begin{bmatrix} XO \\ YO \\ ZO \end{bmatrix} = \begin{bmatrix} 6.71490 & 2.62115 & -2.66519 \\ & 6.29890 & -0.70408 \\ & & 13.76499 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix}
$$

	XO	YO	ZO
O(1)	3.2472	1.8799	3.2816
O(2)	2.6642	1.0082	7.6767
O(3)	– 1.0288	1.7498	5.1605
O(4)	2.5048	.0820	1.5375
O(5)	– 1.4967	2.5111	1.2237
O(6)	.9899	1.5767	– 2.4515
O(7)	5.5603	1.0541	8.4421
O(8)	1.4856	1.2311	10.1792
N(1)	2.9248	1.3367	5.4537
N(2)	.8018	1.3305	6.4117
N(3)	.3313	1.6355	2.8879
N(4)	– .2188	2.1212	– .5988
N(5)	1.7870	.9523	– .4171
C(1)	2.4613	1.5620	4.1639
C(2)	2.1565	1.2082	6.5742
C(3)	.1874	1.5400	5.1990
C(4)	1.0213	1.4832	3.9946
C(5)	1.7200	.8338	.9635
C(6)	.6265	1.5489	1.6009
C(7)	– .4434	2.0815	.7571
C(8)	.8695	1.5587	– 1.2388
Li	5.1074	2.4601	3.2320
H(1)	3.9196	1.2633	5.5707
H(2)	.2195	1.2632	7.2239
H(3)	– .9005	2.6019	– 1.1673
H(4)	2.5668	.5586	– .8589
H(5)	1.5011	.5342	10.7367
H(6)	1.8897	.8895	9.4565
H(7)	– 1.0343	.9105	9.2914
H(8)	– 1.9478	.8373	8.2590
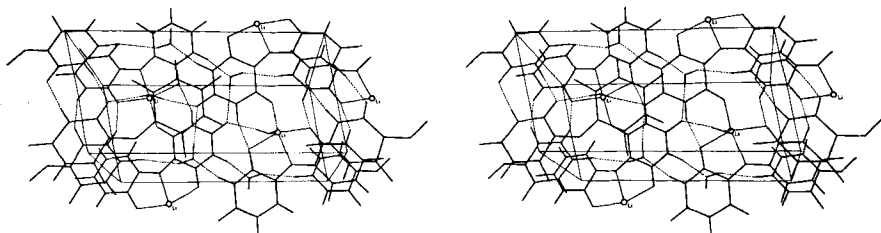
Fig. 7. *Stereographic view of the packing in the unit cell with hydrogen bond network*

amplitudes are in general largest in the *b* direction ($U_{22} > U_{11} \sim U_{33}$), particularly for the peripheral O-atoms of the purpurate anion and the O(7) water molecule, the one not bonded to lithium.

Table 6. *Hydrogen bonds*

N(1)—H(1)...O(3)	$[x+1, y, z]$	2.80 Å	O(8)—H(5)...O(4)	$[\bar{x}+1, \bar{y}, \bar{z}+1]$	2.87 Å
N(2)—H(2)...O(7)	$[x, y, z]$	2.83 Å	O(8)—H(6)...O(2)	$[x, y, z]$	2.78 Å
N(4)—H(3)...O(5)	$[\bar{x}-1, \bar{y}+1, \bar{z}]$	2.97 Å	O(7)—H(7)...O(6)	$[x, y, z+1]$	2.92 Å
N(5)—H(4)...O(4)	$[\bar{x}+1, \bar{y}, \bar{z}]$	2.86 Å	O(7)—H(8)...O(2)	$[x-1, y, z]$	3.00 Å

We have attempted to analyse the experimental vibration tensors in terms of the librational and translational motions of various structural units, regarded for this purpose as rigid bodies. We used the method of *Schomaker & Trueblood* [11], which requires the least-squares fitting of librational and translational tensors **L** and **T** and of an additional tensor **S** (to account for the average quadratic correlation of translation and vibration) to the individual vibration tensors **U**. It is questionable whether the purpurate anion as a whole can be regarded as a rigid body since internal motions involving rotation about the N(3)-C(6) and N(3)-C(4) bonds may not be negligible. When the entire anion is regarded as a rigid unit the *Schomaker-Trueblood* analysis yields a tensor **L** with eigenvalues 16.9, 3.1, 1.7 deg² and a tensor **T** with eigenvalues 0.023, 0.017, 0.011 Å²; the eigenvector corresponding to L_{11} (the largest eigenvalue of **L**) runs almost parallel to the long dimension of the purpurate anion. The tensor components U_{ij} of the individual atoms are reproduced reasonably well, the quantity $Q = \langle (U_{ij}(obs) - U_{ij}(calc))^2 \rangle^{1/2}$ being 0.0022 Å². When the two six-membered rings, each with their directly attached substituents, are treated separately as rigid bodies, the **L** tensors have eigenvalues 20.6, 7.9, 3.5 deg² for the ring containing C(6) and 15.7, 5.3, 2.9 deg² for the other ring. For both cases the eigenvector corresponding to L_{11} runs approximately parallel to the N(3)-C bond. The corresponding Q values are 0.0015 Å² and 0.0018 Å² for the two rings separately. The model with the two rings librating independently thus gives somewhat better agreement and seems to be physically reasonable in that it corresponds to torsional vibrations of considerable amplitude about the N(3)-C bonds.

Bond lengths and angles in the barbiturate rings are very similar to those found in barbituric acid [12] and in barbituric acid dihydrate [13]. In particular, the internal ring angles at the nitrogen atoms (124–128°) are markedly larger than those at the carbon atoms (115–119°). The bond lengths fall into the following ranges:
purpurate anion; C = O, 1.22–1.24 Å; C–N, 1.37–1.39 Å; C–C, 1.45–1.47 Å;
barbituric acid [13, 14]; C = O, 1.20–1.23 Å; C–N, 1.35–1.39 Å; C–C, 1.47–1.50 Å;
whereby it should be remembered that the conjugated π-electron system is cyclic in the former case but interrupted by the methylene group in the latter. In the anhydrous crystals of barbituric acid, the molecule is non-planar, with the methylene carbon atom about 0.20 Å out of the plane of the other five atoms of the ring and the two vicinal oxygen substituents displaced by 0.10 Å on the opposite side of this plane. In the crystalline dihydrate, the barbituric acid molecule appears to be planar, presumably as a result of disorder – 'the O atoms appear to have a systematically greater thermal motion normal to the layer plane than do the pyrimidine ring atoms' [13]. In the purpurate anion, the deviations of the pyrimidine rings and their substituents from planarity are larger than in barbituric acid and less regular, mainly because of overcrowding of the carbonyl oxygen atoms (O(1)...O(4), 2.62 Å) and the additional steric constraints from metal-ion coordination.

BIBLIOGRAPHY

[1] *G. Schwarzenbach, W. Biedermann* & *F. Bangerter*, Helv. *29*, 811 (1946); *G. Schwarzenbach* & *H. Gysling*, Helv. *32*, 1314 (1949); see also *F. Beilstein*, Liebigs Ann. Chem. *107*, 186 (1858).
[2] *R. Winkler*, Structure and Bonding *10*, 1 (1972).
[3] *G. Geier*, unpublished observations.
[4] *H. Gysling* & *G. Schwarzenbach*, Helv. *32*, 1484 (1949).
[5] *E. J. Jacob, H. B. Thompson* & *L. S. Bartell*, J. Chem. Physics *47*, 3736 (1967).
[6] *L. Pauling*, 'The Nature of the Chemical Bond', Cornell University Press 1960, p. 526–532.
[7] *S. Califano*, Pure Appl. Chem. *18*, 335 (1969).
[8] *L. S. Bartell*, J. Chem. Physics *32*, 827 (1960).
[9] *A. Streitwieser, Jr.*, 'Molecular orbital theory for organic chemists', John Wiley & Sons, New York and London 1961, p. 123.
[10] *J. Karle* & *I. L. Karle*, Acta crystallogr. *21*, 849 (1966).
[11] *V. Schomaker* & *K. N. Trueblood*, Acta crystallogr. *B24*, 63 (1968).
[12] *W. Bolton*, Acta crystallogr. *16*, 166 (1963).
[13] *G. A. Jeffrey, S. Ghose* & *J. D. Warwicker*, Acta crystallogr. *14*, 881 (1961).

171. Synthèse d'une série de spiropyrannes benzothiazoliniques photochromes substitués en position 3

par **André Samat[1]), Robert Guglielmetti[2]) et Jacques Metzger[1])**

Résumé. – La synthèse de spiropyrannes photochromes substitués en position 3 montre que la méthode de cyclisation classique est limitée dans certains cas, notamment pour les composés multifonctionnels ou lorsque les anhydrobases intermédiaires sont peu réactives; elle constitue en même temps une généralisation de la synthèse en série benzothiazolinique. Les nouveaux substrats obtenus sont intéressants pour étudier l'influence des paramètres structuraux sur le photochromisme (cinétiques de décoloration thermique, sensibilité spectrale). Nous donnons enfin les caractéristiques spectroscopiques des composés synthétisés.

Introduction. – La synthèse des spiropyrannes portant en position 3 un substituant X (**1**), fait intervenir des bases benzothiazoliques (**2**) possédant en position 2 un groupement –CH$_2$X; ces bases sont transformées en sels quaternaires (**3**) par exemple par l'iodure ou le tosylate de méthyle.

Le spiropyranne (**1**) est obtenu par cyclisation en milieu basique du sel quaternaire **3** avec un aldéhyde salicylique convenablement substitué tel que l'hydroxy-2-méthoxy-3 nitro-5-benzaldéhyde. Cet aldéhyde apporte à la partie benzopyrannique de (**1**) les substituants nitro en 6 et méthoxy en 8, considérés comme responsables d'excellentes propriétés photochromes pour des températures voisines de l'ambiante [1–8].

[1]) Laboratoire de Chimie Organique A, Université de Provence, St-Jérôme, Traverse de la Barasse, 13 Marseille (13°), France.
[2]) Laboratoire de Synthèse Organique, Université de Bretagne Occidentale, 6, avenue Victor Le Gorgeu, 29. N. Brest, France.