Configuration of the Ring A Methoxyl in Delphinine and Aconitine from the Crystal Structure of a Synthetic Intermediate, $C_{22}H_{30}O_5N \cdot C_2HO_4$*

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The synthetic acid oxalate, $C_{22}H_{30}O_5N \cdot C_2HO_4$, m.p. 189–192°C, crystallizes in the monoclinic space group $C2/c$, with eight molecules in a unit cell of dimensions $a = 23 \cdot 972$ (1), $b = 10 \cdot 346$ (2), $c = 18 \cdot 656$ (1) Å; $\beta = 93 \cdot 16$ (2)°. The densities are: $D_x = 1 \cdot 373$, $D_m = 1 \cdot 372$ g.cm^{-3}. The structure was determined by the symbolic addition method from data collected at room temperature on a four-circle diffractometer using the θ–2θ scan technique. It was refined by the block-diagonal least-squares method to $R = 4 \cdot 28\%$ for 3115 observed reflexions. Ring A occurs in the chair conformation, and the C(1)-methoxyl is in the equatorial position, *cis* to the nitrogen bridge. This finding makes it necessary to revise the configurations of the corresponding methoxyl groups in delphinine and aconitine. Pairs of cations are hydrogen-bonded to pairs of oxalate anions, a centre of symmetry being located between each pair. Each cation is linked to two anions by one normal and two bifurcated hydrogen bonds.

Introduction

As part of a projected total synthesis of the alkaloid delphinine, the two epimers (I) and (II) were prepared by Wiesner, Jay, Demerson, Kanno, Křepinský, Poon, Tsai, Vilím & Wu (1970). Wiesner, Jay & Poon-Jay (1971) showed that one of the two racemates could be resolved to yield a substance identical with an optically active degradation product of delphinine. However, the configuration at C(1) of the methoxyl group in ring A remained unknown. This X-ray analysis of the acid oxalate of the 'identical racemate' was carried out in order to determine this configuration as well as to ascertain the rest of the structure and its conformation. Since the configuration at C(1) in delphinine was correlated with that in aconitine (Wiesner, Simmons & Fowler, 1959), the results of this structure analysis would apply to both alkaloids. On the basis of a conformational argument, the C(1)-methoxyl of aconitine was assigned the configuration *trans* to the nitrogen bridge (Bachelor, Brown & Büchi, 1960), and a similar argument led to the same result for delphinine (Wiesner, Simmons & Wightman, 1960). The result of this X-ray analysis, which was reported in a preliminary communication (Birnbaum, Wiesner, Jay & Jay, 1971), showed that the structure of the free base is (I) and that the structure of delphinine has to be revised to (III).
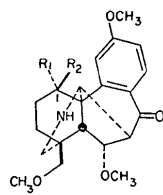
(I·R_1=OCH$_3$; R_2=H)
(II·R_1=H; R_2=OCH$_3$)
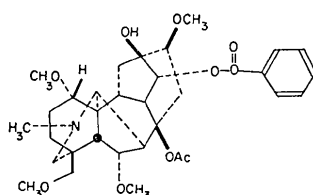
(III)

Crystal data

$C_{22}H_{30}O_5N \cdot C_2HO_4$, F.W. 477·52, m.p. 189–192°C. Monoclinic, $a = 23 \cdot 972(1)$, $b = 10 \cdot 346(2)$, $c = 18 \cdot 656(1)$ Å; $\beta = 93 \cdot 16(2)°$. $V = 4619 \cdot 9$Å^3 [Cu $K\alpha_1$ ($\lambda = 1 \cdot 54051$Å) and Cu $K\alpha_2$ ($\lambda = 1 \cdot 54433$Å) radiations were used]. $D_m = 1 \cdot 372$ g.cm^{-3} (by flotation in a mixture of dichloromethane and bromobenzene), $D_x = 1 \cdot 373$ g.cm^{-3}, $Z = 8$, $F(000) = 2032$, μ(Cu $K\alpha$) = 8·9 cm^{-1}. Systematic absences: hkl absent when $h + k$ is odd and $h0l$ absent when l is odd. Possible space groups Cc and $C2/c$. $C2/c$ was determined from the statistics of $|E|$'s.

Experimental

Transparent, diamond-shaped crystals, obtained from a methanol–ether solution, were kindly supplied by Professor Wiesner. One of them, cut to a size of $0 \cdot 29 \times 0 \cdot 50 \times 0 \cdot 57$ mm, was mounted along the b axis on an automated four-circle diffractometer (Picker), equipped with a scintillation counter and a pulse-height analyser. Ni filtered Cu $K\alpha$ radiation was employed. The cell dimensions are weighted averages obtained from measurements of axial reflexions and their e.s.d.'s were derived from r.m.s. deviations. The intensity data were collected by the moving-crystal moving-counter (θ–2θ) scan technique. A 2·0° scan was used for reflexions with $2\theta \le 100°$ and a 3·0° scan for those with $100° < 2\theta \le 130°$. The scans were symmetrical, and the background was measured for 20 sec on each side of the scan. When the count rate exceeded 20,000 c.p.s. the current was lowered and, when necessary, brass attenuation filters were used. A standard reflexion, 0,0,10, was measured at intervals of about 30 reflexions and was used to scale the data. There was no evidence of deterioration of the crystal during the collection of data. Of the 3921 independent reflexions with $2\theta \le 130°$, 3120 (79%) were observed above threshold value. The threshold was taken as a net count of 150 or 10% of the background, whichever was higher. The inten-

sities were corrected for Lorentz and polarization factors, but no absorption correction was applied, the minimum and maximum transmission coefficients $\exp(-\mu t)$ being 0·61 and 0·77 respectively.

Structure determination

The scale factor and overall isotropic temperature factor ($B = 3·82\text{Å}^2$) were derived from a Wilson plot and used to calculate the normalized structure factors ($|E|$'s). From the statistics of the $|E|$'s it could be seen that the distribution agrees with a centrosymmetric structure and consequently the space group is $C2/c$.

The structure was solved by the symbolic-addition procedure (Karle & Karle, 1966), using 382 terms with $|E| \geq 1·65$. Karle & Karle (1966) suggested that a phase should only be accepted if the probability, given by $P_+(\mathbf{h}) \simeq \frac{1}{2} + \frac{1}{2} \tanh \sigma_3\sigma_2^{-3/2}|E_\mathbf{h}|\sum_\mathbf{k}E_\mathbf{k}E_{\mathbf{h}-\mathbf{k}}$, is 97% or higher. However, since only nine $\sum_2$ triplets satisfy this condition, it had to be relaxed to $P(\mathbf{h}) \geq 95\%$. Further, in order to develop the phases, four reflexions were chosen in addition to the two origin-defining ones and the four to which the program assigned symbols. These

reflexions had $\sum_2$ triplets with high probabilities and all 16 possible combinations of their signs were tried. The set of signs used to solve the structure was the one which resulted in the largest number (379 out of 382) of signs deduced and in fewest contradictions in the determination of the symbols. Another indication that this set of signs was correct was the low value of $R(\text{Karle}) = \sum||E_o|-|E_c||/\sum|E_o| = 16·5\%$. An E map was calculated with these terms, and all 34 non-hydrogen atoms were located on it. A structure factor calculation based on these coordinates gave a value of $R = \sum||F_o|-|F_c||/\sum|F_o| = 35\%$.

Structure refinement

Coordinates, thermal parameters and the scale factor were refined by the block-diagonal approximation of the least-squares method, minimizing the expression $\sum w(|F_o|-|F_c|)^2$. The matrices used were 9×9 for coordinates and thermal parameters (4×4 for isotropic thermal motion) of each atom. The scale factor and the overall isotropic thermal parameter were refined by a 2×2 matrix. A shift factor of 0·8 was used throughout the refinement.

Table 1. *Final fractional coordinates and thermal parameters* (Å^2)

(a) Non hydrogen atoms

All coordinates are $\times 10^5$ and all U^{ij}'s are $\times 10^4$. The thermal-vibration expression used was:

$$\exp[-2\pi^2(U^{11}h^2a^{*2} + U^{22}k^2b^{*2} + U^{33}l^2c^{*2} + 2U^{23}klb^*c^* + 2U^{13}hla^*c^* + 2U^{12}hka^*b^*)].$$

	x	y	z	U^{11}	U^{22}	U^{33}	$2U^{23}$	$2U^{13}$	$2U^{12}$
C(1)	36901 (8)	1082 (19)	30604 (10)	334 (9)	435 (10)	415 (11)	−136 (17)	102 (16)	−63 (15)
C(2)	31669 (8)	4775 (22)	26047 (11)	342 (9)	556 (12)	494 (11)	−278 (20)	−9 (16)	−113 (18)
C(3)	32884 (8)	15478 (23)	20853 (11)	392 (9)	615 (13)	418 (11)	−137 (20)	−81 (16)	99 (19)
C(4)	35666 (8)	27438 (20)	24389 (10)	372 (9)	479 (11)	388 (9)	−73 (17)	43 (16)	135 (16)
C(5)	41421 (7)	23441 (18)	27904 (9)	351 (9)	408 (10)	336 (9)	−27 (16)	117 (14)	0 (15)
C(6)	44385 (8)	33844 (19)	32733 (10)	395 (9)	387 (10)	392 (10)	−31 (16)	120 (16)	−29 (16)
C(7)	42238 (8)	31362 (20)	40459 (10)	450 (12)	433 (10)	385 (9)	−197 (17)	183 (16)	−83 (16)
C(8)	46905 (9)	25859 (22)	45252 (10)	467 (12)	547 (12)	341 (9)	−99 (18)	77 (16)	−302 (19)
C(9)	49116 (8)	13720 (20)	42432 (10)	421 (9)	495 (11)	323 (9)	81 (17)	11 (16)	−199 (18)
C(10)	46222 (7)	7391 (18)	36627 (9)	360 (9)	426 (10)	304 (9)	97 (15)	90 (14)	−133 (15)
C(11)	40513 (7)	12459 (18)	33480 (9)	308 (9)	415 (10)	327 (9)	−69 (15)	72 (14)	−56 (15)
C(12)	48713 (8)	−3362 (19)	33781 (10)	366 (9)	441 (10)	355 (9)	89 (16)	41 (14)	−58 (16)
C(13)	53943 (8)	−7706 (20)	36386 (10)	406 (9)	476 (11)	413 (11)	282 (18)	84 (16)	21 (18)
C(14)	56734 (8)	−1532 (23)	42124 (12)	377 (9)	611 (13)	494 (11)	351 (21)	−108 (16)	−51 (19)
C(15)	54241 (9)	9020 (23)	45095 (11)	476 (12)	600 (13)	385 (11)	148 (19)	−165 (16)	−279 (20)
C(16)	61112 (11)	−23580 (29)	35589 (16)	612 (15)	724 (16)	795 (18)	378 (27)	27 (25)	538 (26)
C(17)	37939 (8)	20580 (19)	39361 (10)	383 (9)	470 (11)	332 (9)	−81 (16)	136 (16)	−64 (16)
C(18)	36077 (9)	37712 (22)	18511 (12)	508 (12)	546 (12)	466 (11)	84 (20)	50 (18)	310 (20)
C(19)	32081 (8)	33415 (22)	30121 (11)	401 (9)	568 (12)	480 (11)	−61 (20)	99 (16)	208 (19)
C(20)	38875 (14)	39631 (33)	6713 (15)	937 (20)	900 (20)	533 (14)	425 (27)	314 (27)	744 (33)
C(21)	47271 (12)	55543 (24)	33627 (16)	801 (17)	425 (12)	854 (18)	−180 (24)	79 (27)	−284 (24)
C(22)	34425 (15)	−19621 (27)	35140 (19)	1048 (23)	483 (14)	1013 (23)	29 (29)	402 (36)	−329 (29)
C(23)	25842 (11)	1934 (29)	52593 (14)	653 (15)	815 (18)	561 (14)	−163 (25)	147 (23)	425 (26)
C(24)	22651 (8)	10117 (22)	46970 (11)	340 (9)	592 (12)	445 (11)	−239 (19)	108 (16)	−188 (18)
N(1)	32366 (7)	26057 (18)	37048 (9)	386 (9)	551 (10)	424 (9)	−196 (15)	224 (14)	−1 (15)
O(1)	35650 (6)	−6514 (14)	36702 (8)	499 (9)	444 (8)	552 (9)	0 (13)	147 (14)	−199 (13)
O(2)	39719 (7)	33366 (17)	13342 (8)	624 (9)	717 (10)	508 (9)	344 (16)	269 (14)	518 (16)
O(3)	43417 (6)	46575 (14)	30284 (8)	566 (9)	402 (8)	563 (9)	−3 (13)	54 (14)	−64 (13)
O(4)	48706 (8)	31057 (18)	50722 (8)	778 (12)	778 (11)	454 (9)	−354 (16)	−131 (16)	−260 (18)
O(5)	55994 (6)	−17961 (16)	32800 (8)	496 (9)	571 (9)	584 (9)	158 (15)	−2 (14)	327 (14)
O(6)	30035 (9)	−4881 (24)	50153 (11)	845 (12)	1112 (16)	700 (11)	−60 (22)	208 (20)	940 (24)
O(7)	24233 (6)	8933 (17)	40712 (8)	505 (9)	768 (11)	473 (7)	−253 (15)	224 (14)	−187 (15)
O(8)	18918 (6)	16975 (18)	49154 (8)	482 (9)	797 (11)	457 (7)	−188 (15)	54 (11)	222 (15)
O(9)	24748 (12)	1698 (28)	58809 (11)	1355 (20)	1359 (21)	527 (11)	285 (23)	427 (23)	1464 (35)

Table 1 (cont.)

(b) Hydrogen atoms

All coordinates are $\times 10^4$ and U_{1so}'s are $\times 10^3$

	x	y	z	U_{1so}
H(11)	3923 (8)	−400 (19)	2765 (10)	30 (5)
H(21)	3042 (9)	−266 (21)	2333 (11)	40 (5)
H(22)	2860 (10)	721 (23)	2915 (12)	49 (6)
H(31)	3537 (10)	1238 (23)	1747 (13)	50 (6)
H(32)	2935 (10)	1807 (24)	1817 (13)	51 (6)
H(51)	4394 (9)	2039 (21)	2408 (11)	40 (5)
H(61)	4847 (7)	3245 (17)	3289 (9)	23 (4)
H(71)	4068 (9)	3919 (21)	4230 (11)	39 (5)
H(121)	4700 (9)	−802 (22)	2979 (11)	41 (5)
H(141)	6015 (10)	−413 (24)	4376 (13)	54 (6)
H(151)	5626 (10)	1330 (24)	4901 (13)	56 (7)
H(161)	6195 (14)	−3072 (34)	3257 (18)	91 (10)
H(162)	6407 (14)	−1710 (35)	3594 (19)	93 (10)
H(163)	6074 (13)	−2675 (31)	4054 (16)	78 (9)
H(171)	3738 (9)	1577 (22)	4365 (12)	44 (6)
H(181)	3215 (10)	3969 (23)	1655 (13)	50 (6)
H(182)	3709 (11)	4613 (26)	2050 (14)	60 (7)
H(191)	2802 (10)	3339 (22)	2850 (12)	47 (6)
H(192)	3342 (10)	4242 (25)	3122 (13)	56 (7)
H(201)	3492 (17)	3760 (40)	481 (22)	112 (12)
H(202)	4169 (15)	3688 (35)	349 (19)	93 (10)
H(203)	3878 (17)	4927 (41)	736 (22)	114 (12)
H(211)	5131 (14)	5245 (33)	3293 (18)	88 (9)
H(212)	4665 (15)	5648 (35)	3858 (19)	92 (10)
H(213)	4673 (13)	6369 (31)	3147 (17)	80 (9)
H(221)	3790 (29)	−2314 (71)	3379 (37)	194 (24)
H(222)	3337 (15)	−2417 (37)	3963 (19)	98 (11)
H(223)	3036 (27)	−2060 (62)	3282 (35)	183 (21)
H(N11)	2964 (11)	1950 (25)	3709 (14)	57 (7)
H(N12)	3151 (10)	3148 (24)	4058 (13)	52 (6)
H(O61)	2989 (19)	−442 (46)	4517 (25)	126 (14)

The hydrogen atoms were located on peaks varying in height from 0·29 to 0·63 e.Å^{-3} in a low-angle $(\sin \theta/\lambda \leq 0\cdot40\text{Å}^{-1})$ difference Fourier synthesis, and they were subsequently refined with isotropic thermal parameters. All other atoms were refined anisotropically. Anomalous scattering correction of $\Delta f'' = 0\cdot1$ (*International Tables for X-ray Crystallography*, 1962) was applied to the scattering curve of oxygen. Towards the end of the refinement the $|F_o|$'s of the eight strongest reflexions were corrected for extinction by 2–12% (Pinnock, Taylor & Lipson, 1956).

The following weighting scheme, chosen so as to reflect the trends in $|\Delta F|$'s, was used:

$$w = w_1 . w_2,$$

where

$$w_1 = 1 \qquad \text{when } |F_o| \leq p_1$$
$$w_1 = p_1/|F_o| \qquad \text{when } |F_o| > p_1$$

and

$$w_2 = \sin^2 \theta/p_2 \qquad \text{when } \sin^2 \theta \leq p_2$$
$$w_2 = 1 \qquad \text{when } \sin^2 \theta > p_2 .$$

The parameters were adjusted during the refinement in order to make $w(\Delta F)^2$ as linear as possible with respect to $|F_o|$ and to $\sin^2\theta$. The final values were $p_1 = 28\cdot0$ and $p_2 = 0\cdot328$.

The refinement converged to an R value of 4·28% and $R' = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2} = 5\cdot13\%$ for 3115 ob-
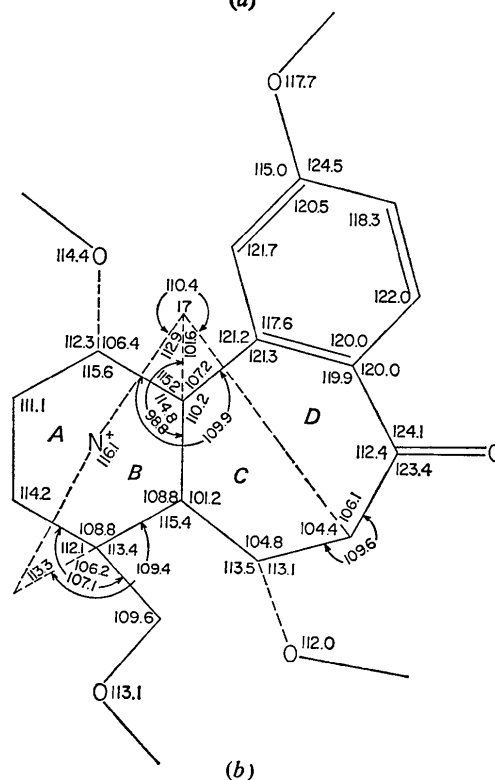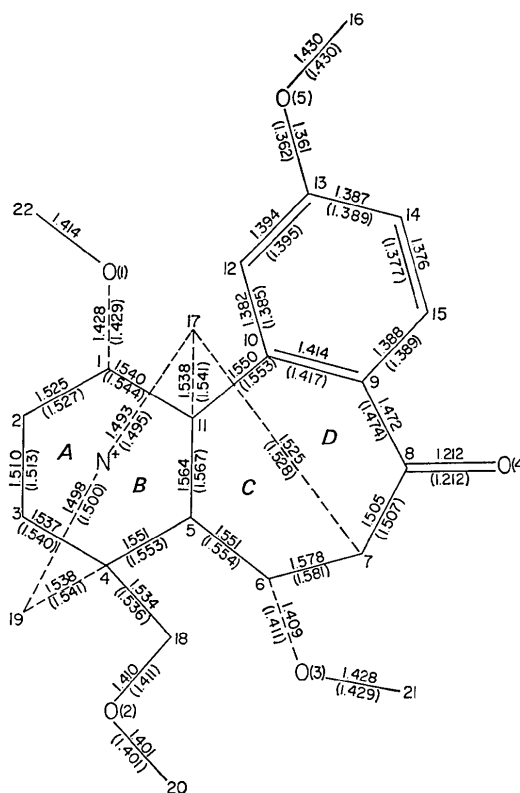

(a)

(b)

Fig. 1. (a) Bond lengths in the cation. The values given in parentheses are the corrected bond lengths. The e.s.d.'s are 0·003 Å. (b) Valency angles in the cation. The e.s.d.'s are 0·2°.

Table 2. *Observed and calculated structure factors*

All F values are $\times 10$. Unobserved reflexions are marked with an asterisk. The reflexions 023; 313; 3,1,11; 602 and $\bar{8}22$ were suspected to be double reflexions and were excluded from least-squares calculations.

Table 2 (cont.)

served reflexions. Five reflexions were excluded due to poor agreement between observed and calculated structure factors. All of them have $|F_o|$ values larger than $|F_c|$, and it is suspected that this is due to double reflexion. After the last cycle of refinement, most shifts in the parameters were less than $0\cdot1\sigma$ and no shift was greater than $0\cdot5\sigma$.

A final difference Fourier map showed no significant negative regions and only three significant peaks of $0\cdot20$–$0\cdot23$ e.Å^{-3}. Two of these could be attributed to lone-pair electrons of oxygen atoms and the third to anisotropic vibrations of H(181) and H(182).

The scattering factors of Hanson, Herman, Lea & Skillman (1964) were used throughout the analysis for carbon, nitrogen and oxygen atoms, and those for bonded hydrogen atoms were taken from Stewart, Davidson & Simpson (1965).

The final coordinates and thermal parameters are listed in Table 1. The listed e.s.d. values were obtained from the inverse of the least-squares matrix. Table 2

shows the observed and calculated structure factors. The unobserved reflexions are marked with an asterisk. They were given the threshold value but were excluded from the least-squares refinement. A summary of the agreement between $|F_o|$ and $|F_c|$ is given in Table 3.

Thermal vibration analysis

The thermal vibration of the cation and that of the anion were analysed separately in terms of the rigid-body tensors of translation (T), libration (L) and screw motion (S) (Schomaker & Trueblood, 1968). Atom C(22) showed additional vibration and was thus excluded from the calculations. The fit of the rigid-body model is better for the anion than for the cation, the values of $\sigma(U_{calc}) = [\sum(\Delta U^{ij})^2/(n-s)]^{1/2}$ being 0·0023 and 0·0031Å^2 and those of $\langle\sigma(U_{obs}^{ij})\rangle$ being 0·0011 and 0·0010Å^2 respectively. The results of the analysis are listed in Table 4. The positional parameters were corrected for the libration motion, and the resulting bond lengths are shown in parentheses in Figs. 1 & 2. The corrections to the valency angles were negligible and are not shown.

Description and discussion of the structure

The bond lengths and angles for non-hydrogen atoms are shown in Figs. 1 & 2. The bond lengths involving hydrogen atoms range from 0·90(2) to 1·05(6)Å. The

valency angles involving hydrogen atoms do not differ from usually observed values, and they are not listed. All the given e.s.d.'s were derived from the block-diagonal approximation of the least squares; correlations between the x and z coordinates and between atoms were not taken into account. The e.s.d.'s may therefore be somewhat underestimated.

Configuration and conformation of the cation

The structure of the cation has been determined to be the protonated form of the free base (I) and its enantiomer. It is illustrated better by the stereoscopic diagram (Fig. 3), which also shows the conformation. The portion of the skeleton involving rings A, B, C and D has also been found in the structures, all of them determined in this laboratory, of the following alkaloids: demethanolaconinone (Przybylska, 1961a); des-(oxymethylene)-lycoctonine (Przybylska, 1961b); delcosine (Marion, 1963); heteratisine (Przybylska, 1965); and lappaconine (Birnbaum, 1970a). Both A/C and B/D ring junctions are cis. Rings A and B are chair-shaped, the five-membered ring C occurs in the envelope conformation, and the six-membered ring D is a distorted half-chair. There are several bicyclic systems fused to each other, resulting in considerable strain in the molecule. Many of the rings are therefore distorted from ideal conformations.

In the present structure and consequently also in delphinine (III) and aconitine (see Introduction), the

Table 3. Agreement summary

3115 observed reflexions in the range $4·54 \leq F_o \leq 338·69$:

Category	Limits		Number
1	$|\Delta F|/|F_o| \leq 2R(0·086)$, or	$|\Delta F| \leq |F_{th}|$	3061
2	$2R < |\Delta F|/|F_o| \leq 3R(0·128)$, or	$|F_{th}| < |\Delta F| \leq 2|F_{th}|$	50
3	$3R < |\Delta F|/|F_o| \leq 4R(0·171)$, or	$2|F_{th}| < |\Delta F| \leq 3|F_{th}|$	4

801 unobserved reflexions:

1		$|F_c| \leq |F_{th}|$	752
2		$|F_{th}| < |F_c| \leq 1·5|F_{th}|$	49

$|F_{th}|$ is the threshold amplitude as defined in the experimental part of the text. Its range is $3·50 \leq |F_{th}| \leq 6·22$.
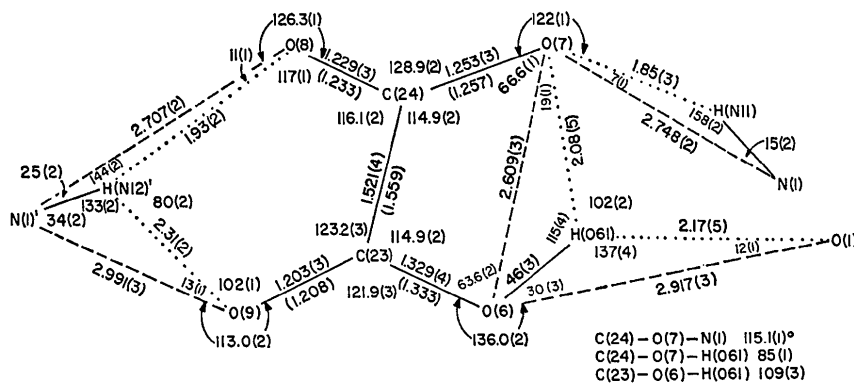
Fig. 2. Geometry of the acid oxalate anion and the hydrogen bonds. The values given in parentheses are the corrected bond lengths. N(1′) and H(N12′) are at $(\frac{1}{2}-x, \frac{1}{2}-y, 1-z)$.

equatorial methoxyl group at C(1) is *cis* to the nitrogen bridge. The same configuration was found in the salts of delcosine, heteratisine and lappaconine, but in those structures ring A is a flattened boat, due to the formation of an intramolecular hydrogen bond between N(1) and O(1). These atoms are involved in hydrogen bonds to the oxalate anion in the present structure. In des-(oxymethylene)-lycoctonine the C(1)-methoxyl is epimeric; thus an intramolecular hydrogen bond is impossible and ring A occurs in the chair conformation.

The conformation of the azabicyclo[3,3,1]nonane system is very similar to that observed for simple bicyclo-[3,3,1]nonane compounds (Tamura & Sim, 1968). It adopts a twin-chair conformation, flattened in order to decrease the strain caused by non-bonded interaction of the two hydrogen atoms, H(22) and H(N11). The H(22)$\cdots$H(N11) and C(2)$\cdots$N(1) distances are 1·96(3) and 3·008(3)Å respectively, as compared with 0·75 and 2·52Å if there were no flattening. However, there is also some increased puckering due to fusion of the azabicyclo[3,3,1]nonane system to rings C and D. These distortions are manifested by deviations of the valency angles from tetrahedral values and deviations of the torsional angles (Fig. 4) from the ideal values of $\pm 55\cdot8°$ calculated for a cyclohexane chair (Bucourt & Hainaut, 1965).

Ring C does not have an ideal envelope conformation since C(5), C(6), C(7) and C(17) are not coplanar

Table 4. *Rigid-body thermal parameters*

The direction cosines are given with respect to the orthogonal axes **a**, **b**, **c***.

Principal axes of L

| | | Cation | | | | Anion | | |
	Eigenvalues	Direction cosines ($\times 10^4$)			Eigenvalues	Direction cosines ($\times 10^4$)		
L1	$10\cdot9(°)^2$	7161	-6295	3017	$193\cdot4(°)^2$	5985	-4087	-6891
L2	6·5	3748	-168	-9270	13·3	6495	7511	1186
L3	5·1	5891	7767	2230	(0)†	4690	-5186	7149

Principal axes of reduced T†

T1	$0\cdot0364$ Å^2	-4723	8359	-2796	$0\cdot0632$ Å^2	2940	-7946	5312
T2	0·0320	-5461	-5260	-6517	0·0387	5379	-3219	-7791
T3	0·0259	-6920	-1562	7051	0·0238	7900	5148	3330

† Since the eigenvalue of L3 was negative, the reduced T for the anion is the one after origin shift to make S symmetric rather than the one according to equation (20) of Schomaker & Trueblood (1968).

Table 5. *Least-squares planes*

Plane 1 (ring C)		Plane 2 (ring D)		Plane 3 (aromatic ring)		Plane 4 (anion)	
	Δ		Δ		Δ		Δ
C(5)	$-0\cdot013$ Å	C(8)	$0\cdot012$ Å	C(9)	$0\cdot007$ Å	C(23)	$0\cdot011$ Å
C(6)	0·025	C(9)	$-0\cdot021$	C(10)	0·002	C(24)	0·003
C(7)	$-0\cdot026$	C(10)	0·016	C(12)	$-0\cdot011$	O(6)	$-0\cdot035$
C(17)	0·017	C(11)	$-0\cdot007$	C(13)	0·009	O(7)	0·014
C(11)*	$-0\cdot788$	C(7)*	0·354	C(14)	0·001	O(8)	$-0\cdot017$
$\chi^2 = 485$		C(17)*	$-0\cdot638$	C(15)	$-0\cdot012$	O(9)	0·037
		O(4)*	$-0\cdot181$	C(8)*	0·142	H(O61)*	0·08
Plane 5		$\chi^2 = 266$		C(11)*	0·037	O(1)*	$-0\cdot420$
(carbonyl group)				O(5)*	0·066	H(N11)*	$-1\cdot54$
	Δ			C(16)*	$-0\cdot026$	N(1)*	$-2\cdot464$
C(7)	$0\cdot002$ Å			H(121)*	0·00	H(N12')*	$-0\cdot33$
C(8)	$-0\cdot009$			H(141)*	0·04	N(1')*	$-0\cdot715$
C(9)	0·002			H(151)*	0·00	$\chi^2 = 593$	
O(4)	0·002			$\chi^2 = 112$			
$\chi^2 = 25$							

* Atoms excluded from the calculation of the plane. N(1') and H(N12') are at ($\frac{1}{2}-x, \frac{1}{2}-y, 1-z$).

Equations of the planes (X', Y, Z' are orthogonal coordinates in Å, *i.e.* $X' = X - Z \cos \beta^*$, $Z' = Z \sin \beta^*$).

1: $-0\cdot721X' + 0\cdot659Y - 0\cdot216Z' = -6\cdot457$ Å
2: $0\cdot520X' + 0\cdot536Y - 0\cdot665Z' = +1\cdot427$
3: $0\cdot488X' + 0\cdot593Y - 0\cdot641Z' = +1\cdot303$
4: $-0\cdot636X' - 0\cdot753Y - 0\cdot172Z' = -5\cdot441$
5: $0\cdot689X' + 0\cdot512Y - 0\cdot513Z' = +4\cdot490$

Some dihedral angles between the planes:

$\angle 1,2$	$\angle 2,3$	$\angle 2,5$	$\angle 3,5$
83·0°	4·0°	13·1°	14·5°

($\chi^2 = 485$) and the displacement of C(11) (0·788Å from plane 1 of Table 5) is larger than the calculated value of 0·58Å (Sim, 1965), based on the mean bond angle of 104·4° in the ring.

It can be seen from plane 2 of Table 5 that C(7) and C(17) are displaced by unequal amounts from the mean plane through the other four atoms of ring D which can therefore be described as a distorted half-chair. Its conformation is close to that of the cyclohexene ring in the energetically most favourable Δ^2-cis-octaline, which has torsional angles of -21, 0, -11, 43, -65 and 52° (Bucourt & Hainaut, 1965). The increased puckering in ring D is presumably due to the fact that it is fused not only to ring B but also to ring C.

The aromatic ring is not quite planar (Table 5); a similar phenomenon has been observed in the past (Birnbaum, 1970b). All three hydrogen atoms, H(121), H(141) and H(151), lie in the aromatic mean plane, while C(8), C(11) and the methoxyl group do not. In 5-methoxy-(N,N)-dimethyltryptamine hydrochloride (Falkenberg & Carlström, 1971), the methoxyl group was also displaced significantly from the aromatic plane.

The side chain attached to C(4) is not a fully extended chain, since C(20) is displaced by 0·465Å from the plane through the other three atoms and the torsional angle C(4)–C(18)–O(2)–C(20) is $+158·8°$. The orientations of all the side chains can be seen from the torsional angles (Fig. 4).

Bond lengths of the cation

Most bond lengths agree with usually observed values, but some of them require comment. There are several C–C bonds which are longer than normal. However, all these bonds are between highly substituted carbon atoms and lengthening of such bonds is common. For instance, in delnudine hydrochloride (Birnbaum,

1971) C_{sp3}–C_{sp3} bonds up to 1·580(4)Å were observed. There is one short bond, C(2)–C(3) (1·513Å), in ring A. It is remarkable that the very same bond is the shortest of the C_{sp3}–C_{sp3} bonds observed in three other structures with similar ring systems, viz. 1·507(5)Å in delnudine (Birnbaum, 1971), 1·472(16)Å in lappaconine (Birnbaum, 1970a) and 1·515(8)Å in denudatine (Brisse, 1971). Thus it seems that this bond really is shorter than normal in this type of compound.

The C(13)–O(5) bond (1·362Å) is very close to the observed values: 1·363(4)Å in 5-methoxy-(N,N)-dimethyltryptamine hydrochloride (Falkenberg & Carlström, 1971) and 1·358(4)Å in salicylic acid (Sundaralingam & Jensen, 1965). Since in these compounds the C_{ar}–O bond has some double-bond character, it is likely that the resonance form (a) contributes to the present structure. This is consistent with deviations from normal values in two of the bond lengths in the aromatic ring.

(a)
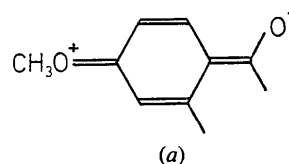
The thermal vibration analysis revealed additional motion of some of the side chains. This may be the reason for three of the C_{sp3}–O bonds being shorter than the mean value of $1·426 \pm 0·005$Å given by Sutton (1965).

Oxalate anion

The acid oxalate anion is close to being planar; the angle of twist about the central C–C bond is only 3·0°. This is comparable to the twist of 6·1° observed in the
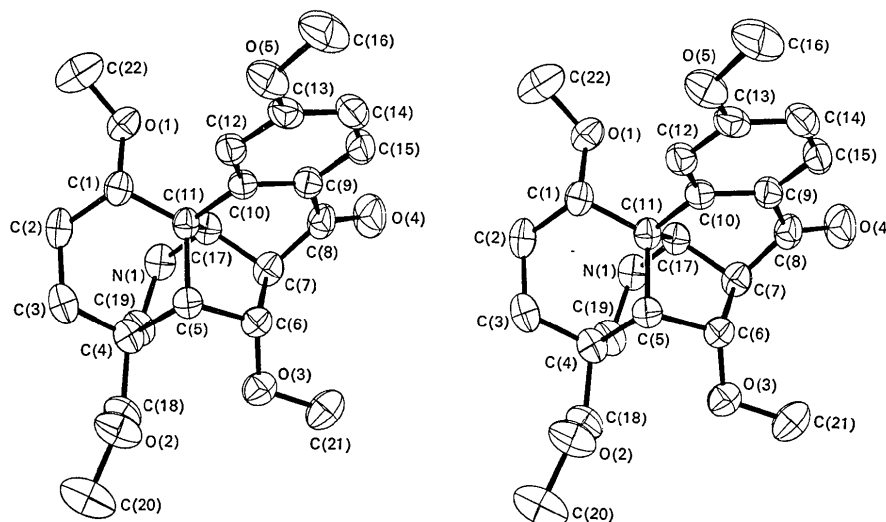
Fig. 3. Stereoscopic view of the cation. The thermal ellipsoids enclose 50% probability.

acid oxalate group of potassium tetraoxalate (Haas, 1964). All the corrected bond lengths (Fig. 2) agree with those in the latter structure except the C(23)–O(6) bond which is $3\cdot6\sigma$ longer here. There is also a reason-
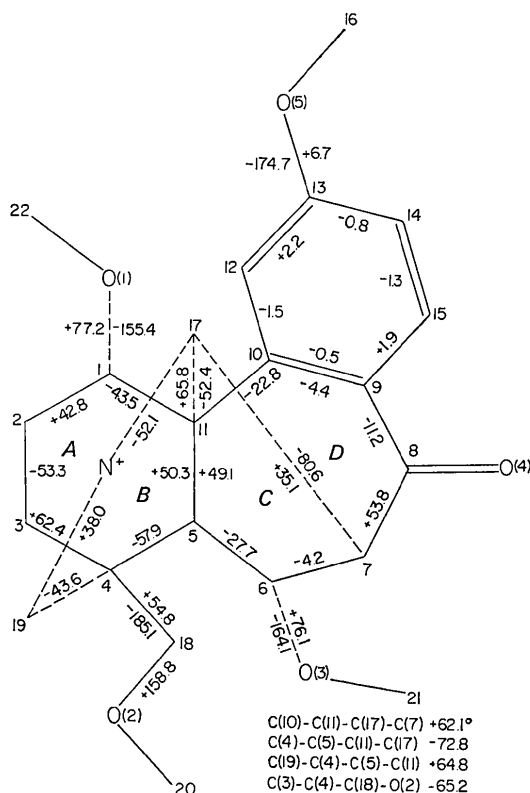
able agreement between the bond angles; the largest difference ($5\cdot0\sigma$) occurs in the O(6)–C(23)–O(9) angle. The central C–C bond length is equal, within experimental error, to that found in fully ionized oxalates [*e.g.* $1\cdot569(8)$Å in ammonium oxalate; Robertson, 1965], but significantly longer than $1\cdot536(3)$Å, which was observed in α-oxalic acid (Sabine, Cox & Craven, 1969). The C(24)==O(8) bond is significantly shorter [by $0\cdot024(4)$Å] than C(24)==O(7). This is probably due to hydrogen bonding: O(8) accepts one proton, while O(7) accepts two (*vide infra*). In potassium tetraoxalate, where the difference is $0\cdot039(8)$Å, each oxygen atom accepts one proton but one of the hydrogen bonds is much stronger than the other. In potassium oxalate monohydrate (Hodgson & Ibers, 1969), only one of the oxygen atoms is involved in a hydrogen bond and the difference is $0\cdot012(2)$Å.

Hydrogen bonding and packing

The structure includes a normal and two bifurcated hydrogen bonds (Fig. 2). All H$\cdots$O distances are $0\cdot3$ to $0\cdot7$Å shorter than $2\cdot6$Å, the sum of the van der Waals radii. The C=O$\cdots$H angles are close to 120°, except the intra-ionic angle C(24)–O(7)$\cdots$H(O61), which is 85(1)°. H(O61) lies in the mean plane of the anion, while H(N11) and H(N12') are displaced from it by $1\cdot54$ and $0\cdot33$Å, respectively. Both bifurcated hydrogen bonds are asymmetric. Neither H(O61) nor H(N12) lies in the planes defined by donor and acceptor atoms, but the deviations are small: $0\cdot23$ and $0\cdot13$Å respectively.

The hydrogen bonds are also marked on the packing diagram (Fig. 5). It can be seen that two cations, related by a centre of symmetry, are linked together *via* hydrogen bonds to two equally related anions, thus forming pairs of $C_{22}H_{30}O_5N.C_2HO_4$.

C(10)–C(11)–C(17)–C(7) +62.1°
C(4)–C(5)–C(11)–C(17) −72.8
C(19)–C(4)–C(5)–C(11) +64.8
C(3)–C(4)–C(18)–O(2) −65.2

Fig.4. Torsional angles (Klyne & Prelog, 1960). The e.s.d.'s (Huber, 1961) are $0\cdot2$–$0\cdot3$°.

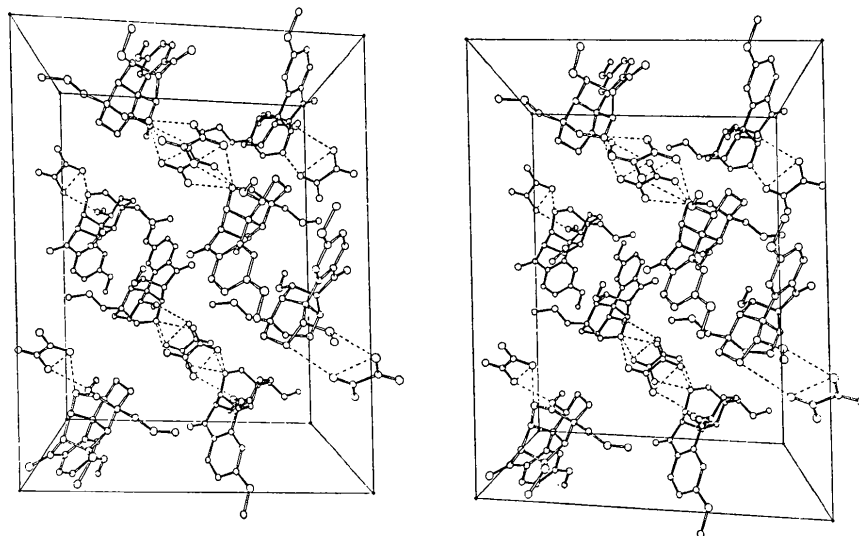

Fig.5. Stereoscopic packing diagram. The hydrogen bonds are marked with broken lines. The origin is at the rear, lower-left corner. The directions of the axes are a↑, c→.

Apart from the hydrogen bonds, there are no inter-molecular distances shorter than van der Waals contacts.

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The Crystal Structure of Tris-Sarcosine Calcium Chloride

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The structure of the room-temperature phase of tris-sarcosine calcium chloride, $CaCl_2.3(CH_3NH_2^+CH_2COO^-)$, has been studied. The crystal is ferroelectric below the Curie point, 127°K [Makita, Y. *J. Phys. Soc. Japan* (1965), 20, 2073].It is orthorhombic with $a = 9.156$, $b = 17.460$, $c = 10.265$ Å, space group *Pnma* and $Z = 4$. The structure was determined by use of the data obtained on a four-circle diffractometer, and the final R was 0.059. Out of two kinds of sarcosine, both having a zwitterion form, one is in the mirror plane perpendicular to the b axis; the other in the general position is also not far from being planar, and is roughly perpendicular to the bc plane. There are only three hydrogen bonds in the crystal, of the kind $N-H\cdots Cl$. The Ca ion is located in a mirror plane, and is coordinated by 6 oxygen atoms arranged in an octahedron. The crystal has a pseudo-hexagonal symmetry if viewed down the b axis, and the complex around the Ca ion and the hydrogen bonds play an important role together in making up the crystal.

Introduction

Tris-sarcosine calcium chloride, $CaCl_2.3(CH_3NH_2^+CH_2COO^-)$, was found to exhibit ferroelectric behaviuor below the Curie point, 127°K (Pepinsky & Makita, 1962). Since then a detailed study of the physical properties of the crystal has been made by Makita (1965), who deduced an order–dis-