Configuration of the Ring A Methoxyl in Delphinine and Aconitine from the Crystal Structure of a Synthetic Intermediate, C₂₂H₃₀O₅N.C₂HO₄*

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The synthetic acid oxalate, $C_{22}H_{30}O_5N$. 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 = 23.972 (1), b = 10.346 (2), c = 18.656 (1) Å; $\beta = 93.16$ (2)°. The densities are: $D_x = 1.373$, $D_m = 1.372$ 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 $\theta - 2\theta$ scan technique. It was refined by the block-diagonal least-squares method to R = 4.28% 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 hydrogenbonded 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).



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Crystal data

C₂₂H₃₀O₅N.C₂HO₄, F.W. 477·52, m.p. 189–192°C. Monoclinic, a=23.972(1), b=10.346(2), c=18.656(1)Å; $\beta=93.16(2)^{\circ}$. V=4619.9Å³ [Cu $K\alpha_1$ ($\lambda=1.54051$ Å) and Cu $K\alpha_2$ ($\lambda=1.54433$ Å) radiations were used]. $D_m=$ 1.372 g.cm⁻³ (by flotation in a mixture of dichloromethane and bromobenzene), $D_x=1.373$ 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 $0.29 \times 0.50 \times 0.57$ 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 Ka 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 $(\theta - 2\theta)$ scan technique. A $2 \cdot 0^{\circ}$ scan was used for reflexions with $2\theta \le 100^\circ$ and a 3.0° scan for those with $100^{\circ} < 2\theta \le 130^{\circ}$. 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 $2\theta \leq$ 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 intensities 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 $(B=3\cdot82\text{Å}^2)$ 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 $|E| \ge 1.65$. Karle & Karle (1966) suggested that a phase should only be accepted if the probability, given by $P_{+}(\mathbf{h}) \simeq \frac{1}{2} + \frac{1}{2} \tanh \sigma_{3} \sigma_{2}^{-3/2} |E_{\mathbf{h}}| \sum E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}$, is 97% or

higher. However, since only nine \sum_2 triplets satisfy this condition, it had to be relaxed to $P(\mathbf{h}) \ge 95\%$. 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:

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

	x	у	z	U^{11}	U^{22}	U33	$2U^{23}$	$2 U^{13}$	$2U^{12}$
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)	2 6047 (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 (14)	-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) F	Iydrogen	1 atoms
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All coordinates are $\times 10^4$ and $U_{\rm iso}$'s are $\times 10^3$

	x	У	z	$U_{ m iso}$
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 $(\sin \theta/\lambda \le 0.40$ Å⁻¹) difference Fourier synthesis, and they were subsequently refined with isotropic thermal parameters. All other atoms were refined anisotropically. Anomalous scattering correction of $\Delta f''=0.1$ (*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:

when $|F_o| \leq p_1$

when $|F_o| > p_1$

 $w = w_1 \cdot w_2,$

 $w_1 = 1$ $w_1 = p_1 / |F_o|$

where

and

 $w_2 = \sin^2 \theta / p_2$ when $\sin^2 \theta \le p_2$ $w_2 = 1$ when $\sin^2 \theta \ge p_2$. The parameters were adjusted during the refinement in order to make $w(\Delta F)^2$ as linear as possible with respect to $|F_{\theta}|$ and to $\sin^2 \theta$. The final values were $p_1 =$

28.0 and $p_2 = 0.328$. The refinement converged to an R value of 4.28% and $R' = [\sum w(\Delta F)^2 / \sum wF_o^2]^{1/2} = 5.13\%$ for 3115 ob-



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 $\overline{8}22$ were suspected to be double reflexions and were excluded from least-squares calculations.

x [ro] rc 2 240 238 4 364 363 6 233 244 8 296 -413 10 150 -167	x rc rc 7 164 -158 9 347 -540 11 564 -12 He -1. Le 3 L 66L 611	x kol rc 1 147 140 7 160 -101 5 211 233 7 117 117	K HCI FC 10 75* -48 H= -2, L* 0 2 A01 -753 6 248 -273 0 63 -52	K (FOL FC 1 156 5 3 530 504 5 199 205 7 76 - 29 9 62- 29 11 105 - 156	K FC FC 5 61+ 62 7 53+ 48 NH -3, 1+ 16 1 86 -31 3 431 483	x Foj F(2 142 117 4 411 404 6 457 -400 8 85 53 10 53* 28	K [FD] FC 11 Sav (*) He -5, L* 3 1 9+7 82+ 3 202 241 5 151 11#	K FO FC 7 1.77 187 F= 5, L= 17 1 FD F1 3 225 -274 1 100 -94	x rg FC = 272 2+1 = 56 57 10 56 -44 	x kc FC 11 120 -127 km =7, Lm 4 1 269 238 3 55 4 5 254 -245	x bel rc 1 p1 p1 3 p7 75 3 500 25 1 7, 10 15 1 10 - 100	x [Fo] F(0 758 557 2 153 -173 4 61* 55 6 177 -175 7 66* 61	x Fel Fe 3 242 343 7 222 226 8 80 - 33 He -0, L 6 1 422 - 546	s (ro) e; s (ro) -483 # 171 -154 10 121 -154 ***-17, 5* 1 2 22* -225	x 3rd rc 6 218 274 8 127 172 0-17, t+ 15 2 3r4 - 171 4 183 - 174
12 84 89 14 64 - 207 4 649 - 207 6 740 713 8 305 219 10 79 - 76 12 111 97	3 710 - 24c 5 154 -113 7 354 -330 9 04 -53 11 56* -31 w 1, L* 4 1 454 626 3 1571 - 123	He 1, 1 11 1 176 -170 3 62 11 7 190 190 He -1, 1 11 1 76 -64	He 2, Le 10 0 1310 -1235 2 342 -320 4 176 -172 6 636 623 8 624 -34	N= -3, (a) 1 2431 2591 3 830 866 5 82 -43 7 53- 14 9 104 109 11 507 -34	7 510 - 14 1 620 - 15 1 620 - 15 1 102 - 15 1 102 - 15 1 105 - 15 7 147 15 1 15	0 405 448 3 238 -244 4 365 -344 6 185 -183 1 75 -151 10 155 -151 H= -4, 1 = 10	9 0 0 00 11 137 -148 Me 5, to 4 1 219 149 3 1639 -1678 5 168 173 7 113 118 9 71 - 100	1 33 -44 1 151 144 2 208 201 3 217 211 7 499 -37 4- 5, t+ 18	2 103 -612 4 120 -705 6 +61 476 8 184 105 10 51* 27 H* 6, [* 11 2 476 452 4 +73 +75	4 141 141 11 524 -19 He 7, Le 5 1 962 1967 3 311 769 5 714 -37 7 398 398	1 177 -177 1 218 - 221 1 218 - 221 1 218 - 185 1 218 - 11 1 218 - 125 1 218 -	He - R. (- 12 2 142 152 4 000 15 0 431 - 441 8 202 240 He - B. (- 13	2 761 -743 5 162 164 7 645 -658 9 614 - 6 11 55 54 9 614 - 5 1 61 - 5 3 225 -720	102 - 102 10 - 1 - 102 10 - 1 - 102 10 - 10	6 56 44 H-10. (+ 15 2 381 374 4 360 186 4 71 -51 H+ 10. (+ 18 0 61+ 24
He 0, Le 2 0 210 -313 2 446 403 4 550 -443 6 152 -146 7 590 4 10 300 301 12 68 70	7 408 -478 9 169 -174 11 60 58 He -1: Le 4 1 1101 1075 3 491 939 5 508 709	5 161 154 7 51+ 42 4- 1, 1+ 18 1 184 180 3 80+ -29 4 55+ -8	H= -2, L= 10 0 8+4 -831 2 291 -283 4 800 547 6 277 -218 6 82* -11 10 69 62	1 555 611 3 1010 988 5 480 441 7 199 190 9 353 -369 11 58 -31 m -3, 1+ 4	1 248 - 261 3 144 147 4 548 30 7 180 159 H= 3, 1= 18 1 191 192 3 321 - 321	2 197 -169 4 519 -12 6 609 -17 8 629 -38 10 139 131 10 139 131 10 4. (-11 2 97 4.	11 18" 176 11 18" 176 1 595 -587 3 983 -644 3 489 -642 7 241 243 9 62" 11	3 211 -201 3 55 31 He	# af+ 15 10 208 -208 ************************************	1 41 78 H7, L - 1 1 374 360 3 750 370 5 77 345 7 162 -213 4 307 320	m7, (. 20 1 1 3 5126 m7, (. 21 1 4042	4 105 270 4 610 -27 4 112 113 He -6, (- 13 2 495 -454 4 770 260 - 114 115	4 114 -123 4 14 -123 4 -0, (4 7 1 246 -107 3 757 -167 4 14 -138 4 171 -271	a 124 -123 10 574 +3 ma-10, 14 2 C 520 +00 2 177 164 4 474 -19 4 474 -19	6 51 - 32
H 0, (= ? 2 177 -124 4 57 -22 e 523 497 8 243 234 10 418 -3 12 408 -10	4 271 271 11 559 -31 44 1, 1, 4 5 1 1183 1139 3 379 -7 5 540 526 7 212 210	1 122 -114 3 170 173 5 137 -174 H 1, t 19 1 59 -12 3 217 -214	+** 2, 1* 11 2 410 405 4 101 -125 5 92 -53 8 47 51 10 78 -70 1** -2, 1* 11 1 10 -11	3 434 440 3 613 -541 7 48- 14 7 71 224 11 55- 31 	m -3, [+ 18 1 61* -20 3 165 -173 3 118 126 m 3, [- 1* 1 176 173	e 128 120 8 167 -94 10 404 28 He -4, L- 11 2 175 -108 4 58 -62 6 93 90	H. C. L. S 1 2×0 2×0 3 42 -00 3 508 -507 7 476 360 4 1.6 360 11 104 101	1 247 -264 2 231 -230 1 155 -155 mm -5, 1+ 10 1 77 -63 1 769 -379 5 105 -91	H+ 6, 1+ 12 0 304 316 2 256 -257 4 323 316 6 150 74 5 e2 -52	He 7, Le 6 1 302 -303 1 17 -724 2 524 -47 3 604 -2 4 44 -105 11 494 49	0 67 -107 2 555 566 4 101 95 8 357 355 10 280 263 H+ 8, (+ 1	H. H. L. J. 0 112 - 401 4 93 - 74 4 00 - 40 6 500 - 41 10 10	He 4, 14 4 1 61 -71 3 842 941 4 107 110 7 62 31 9 233 -236	10 57* -40 He 10, Le 1 2 1702 1128 4 101 178 1 185 189 1 71 -132 10 Po -72	H: 10. (+ 17 2 454 -16 4 211 -222 H:-10. (+ 17 2 174 -173 4 104 -118 4 201 -205
0 1745 -1715 2 104 187 4 283 271 8 245 281 8 245 281 10 214 -34	11 Ca -92 m -1, L+ 5 1 1556 1500 3 255 245 5 1259 1271 7 403 -191 9 80 -94	-1, to 19 1 136 -120 3 136 127 5 62 55 	4 414 421 6 776 -376 8 179 -184 10 101 -1 	5 234 274 7 104 -95 9 354 349 11 549 -30 He -3, 14 3 1 89 -41 3 194 -165	1 165 -161 163 -161 1 243 -225 3 174 101 5 138 -139 1. 14 20	10 125 122 H= 4, L+ 17 0 53+ 42 2 55 - 28 4 214 218 6 2-6 234 8 89 - 72	He -5, 10 5 1 647 -676 3 146 1192 5 46 65 7 312 312 9 824 -6 11 537 -30	No -1, L+ 20 1 147 144 2 70* -10 No -1, L+ 20 1 148 -118 3 222 -270	0 730 -111 2 219 240 4 142 -130 5 624 22 8 78 -66 78 -66	-7, L. 6 L. 423 427 3 447 -611 5 417 -303 7 600 - 40 4 620 -3L 11 77 72	4 444 -24 6 41 117 8 174 -116 10 172 165 H4 -7, L4 1 2 556 -542 4 1003	6 473 -438 2 417 244 4 218 -328 6 124 44 8 192 -207 4 8, L 15 2 624 37	1 442 444 1 501 -401 1 510 -211 7 201 210 8 213 -204 No. 0, 10 0 1 213 -211	H-10, L- 3 2 3e0 - 167 4 118 124 8 100 - 104 10 47 12 H- 10, L- 4	He 10, Le 14 0 390 396 2 112 120 4 247 230 He-17, Le 18 0 366 350 2 352 351
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4 342 341 6 137 -121 8 231 240 10 510 -23 H= C, L+ 12 C 391 597 2 213 190 4 159 -154	7 116 113 9 226 229 11 499 42 10 1, to 4 1 51 44 1 545 -506 5 139 147 1 7 29 -261	He -2. te 2 0 345 255 2 1646 -1675 4 547 523 8 247 -235 8 151 -144 10 619 -15	2 81 -83 4 199 196 8 255 -289 8 100 -101 H= 2, 1+ 16 0 320 374 2 624 37 2 624 32	1 480 453 3 317 -332 3 424 11 7 210 -208 4 614 -24 11 404 -25 4 3, Le 6 1 6 -31	He -e, (e 2 0 2874 2416 2 235 246 4 232 -207 6 300 -11 2 335 334 10 610 -47	He 4, to 16 0 270 -200 2 535 -536 4 82* 34 6 57* 23 8 40* 27 He -4, to 18	11 -44 - 8 1 5-1 -521 3 4-5 -450 3 1122 1117 1 142 -208 9 87 -80	2 778 762 4 1404 1451 6 272 277 8 776 -315 10 435 -429 8 -6. L - 3 2 1106 -1112	6 167 -14C 8 55 40 H= 6, L= 17 2 614 -06 4 77 -61 6 124 -22 H= -0, 14 17	3 74+ -18 5 249 -25e 1 62+ -67 9 131 -110 H+ -7, 14 10 1 453 -440 7 85 -9 1 14 -14	6 245 -217 8 510 542 10 116 94 He P, Le S 2 510 677 4 571 -574 6 567 -11	100 -4. (- 10 2 127 -120 4 61 62 H+ 8. 1- 72 0 167 17 2 176 -175 N4 48. 1- 20	He - C, (- 12 - 35 - 14) 1 - 44 - 50 2 - 44 - 50 2 - 14 - 10 2 - 14 - 10 2 - 14 - 24 10 10 14 10 	2 114 -116 4 245 246 6 60* -11 8 125 128 10 52 35 m-10, 1* 7 2 855 -827	11 75 -66 11 75 -66 1 4.4 -77 1 4.4 -77 1 7.6 -77 3 7.6 -77 3 7.6 -77 4 61 -50 4 61 -50
6 483 497 8 81 -91 10 48* 44 k= C, L= 13 2 319 -360 4 213 -205 6 22* -6 8 217 205	4 80 -82 11 47* -21 H= -1. L. 4 1 949 -953 3 155 -168 5 54* -74 1 7 212 -202 1 9 61* 40	** 2, 1* 1 2 977 859 4 955 -559 4 357 -559 4 397 -466 10 61* 42 12 63 6*	a 72 a5 8 47* a 14* -2. (* 16 0 61* -23 2 364 380 4 134 -101 a 90 -46 8 45 -58	3 444 404 5 195 175 7 510 -32 9 215 -217 P* -3, 1* 9 1 518 525 3 468 419 5 500 -545	4 940 -417 4 940 -417 4 241 -108 8 303 -200 10 61* -41 He -4, [4 3 2 2423 -2418	0 675 -611 2 222 -228 4 126 -126 6 64 -39 8 214 -221 9 4 124 -17 2 231 -241 4 151 140	Ha - 5, (. 4 1 106 111 3 c15 - 591 5 271 271 7 105 - 105 9 80 77 He 5, (. 10 1 517 507	4 267 -233 8 256 259 10 256 254 10 256 254 10 1076 2011 2 300 10 10 211 -201 2 300 10 10 256 256 10 256 256 1	2 374 -379 4 60 -12 8 54 -12 M 6, 1 18 0 60 -46 2 275 372 4 320 320 6 187 164	7 67* -*2 9 12* -*2 9 12* -*1 1 293 -276 3 120 -116 3 120 -464 7 62* -*3	10 41 -41 He -f, Le 9 2 60 44 4 174 176 6 3(2 301 8 624 36 10 584 21	0 103 -:01 2 84 -A1 4 203 212 44 -8, L+ 21 2 141 141 14 0, L+ 0 1 457 490	1 71 -71 3 624 38 5 181 -147 2 63 -72 44 -9, Le 13 1 156 154 3 547 -156 5 120 176	6 364 373 8 326 -248 10 68 46 H= 10, t+ 8 0 571 568 2 161 -187 4 60 -42	He 11, 10 1 1 3 49 137 3 144 149 5 253 -240 7 163 211 6 167 164 11 44* 12
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2 221 -224 4 91 -01 4 55 64 He 0, L+ 19 2 103 -96 4 197 158 6 144 -132	9 236 220 N= 1, t= 12 1 130 -118 3 293 -105 5 519 -117 7 171 -172 9 122 117	e co o 10 103 -103 w -2, c 4 2 co -5, 4 455 702 6 107 -103 8 456 -400	2 223 -235 4 24 -83 6 40* 2 1.4 20 0 74 -86 2 104 116 4 177 105	5 277 254 7 440 -442 9 55* 21 Her 3, 1+ 12 1 185 -181 3 103 101 5 62* 4	He -4, [+ 5 2 210 706 4 1230 -1158 6 212 237 8 113 115 10 314 -311 He 4, [+ 6	0 747 - 741 2 510 - 43 4 470 - 70 10 - 4, (* 20 0 173 177 2 544 - 15 4 51 - 41	3 401 -391 3 337 -319 7 44 -41 9 111 -99 1147 145 7 761 -264	2 354 356 4 474 427 c 267 264 8 107 -105 10 254 274 0 1247 145C 2 568 110	He 7. Le 0 1 591 -557 3 284 -12 5 54 -28 7 148 -161 9 101 101 11 89 -66 He 7. Le 1	9 181 -149 He -7, Le 17 L 321 215 3 88 -90 5 487 487 7 158 -158 9 76 61	8 356 -4C1 10 514 -33 He P, Le E 0 P41 -822 2 139 -140 4 341 -352 8 251 235 8 167 -186	4 114 116 11 117 116 H= -9, L= 2 1 214 -209 3 511 -24 5 253 -26 9 702 216	1 263 256 3 107 01 5 56* -39 7 112 -113 H -9, 1* 16 1 210 -105 3 46 -94	2 380 - 184 6 413 446 6 82 - 82 8 184 - 160 9 284 - 252 2 510 - 501 4 438 - 434	7 62* -13 9 5** eD 1***13, 1* 5 1 746 -714 3 453 4** 5 3** 7*0 7 253 2*1 9 258 23*
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1 1231 -1390 3 1045 -1153 5 443 421 7 230 244 9 102 -161 11 51+ -14 Me 1, L+ 1 1 3317 9402	3 00 37 5 286 -291 7 106 -40 9 52* -47 We -1, Le 13 1 289 -277 1 3 58* -15 5 41* 12	H 2: L - 6 0 5 6 707 2 750 715 4 064 632 6 362 -355 8 44 - 66 8 200 - 207 H 2: L - 7	2 90 -82 He 3, Le 9 I 208 251 3 944 1065 5 818 852 7 247 -101 9 225 -276 11 76 -69	Max 7. L= 13 1 4.9 6.1 3 125 -10.9 5 570 -570 7 232 -223 8 66 Mm -3. L= 11 1 22.0 -222	+ 1108 1038 8 207 -101 8 104 -107 10 210 -20- H= 4, 10 7 2 861 -517 8 366 -355	1 223 343 1 129 -124 9 315 310 11 514 43 He 9, L- 1 1 1140 1226 3 455 407 1 160 170	He -5, Le 13 1 640 -650 3 196 212 5 620 24 7 610 14 4 120 110 He 5, Le 14	10 138 137 H0, L+ 7 2 415 397 4 804 798 6 154 -165 4 105 -165 10 82 -85	3 80 54 7 341 -343 9 624 -7 11 283 275 Me 7, Le 2 1 516 -643 3 21(5) 275	7 127 -129 H+ 7, 1+ 15 1 276 203 3 544 535 3 544 535 7 544 -58 7 544 -15 H= -7, 1+ 15	He 8, L 4 2 573 577 4 219 -246 6 500 498 8 200 273 10 500 -273 He -8, L 9 2 1100 1340	H0, L+ 1 1 540 -564 3 434 -50 5 575 -565 7 238 235 4 126 -123 1 504 -24 H- 0, L+ 4	5 461 451 5 96 -08 He 9, 1-14 1 85 -88 5 54 5 5 48 10 He -0, 1-18	He-10, L+ 11 2 303 317 4 337 -145 4 179 -143 8 80 82 He 10, L+ 12 0 418 454 2 377 485	3 541 -526 5 318 332 7 275 -255 9 70 49 He 11. to 7 1 500 43 3 99 -13
5 493 -426 7 177 -171 9 3C4 326 11 67 61 11 395 358 3 316 260 5 116 -753	4 91 -44 1 280 -281 1 3 443 -356 1 3 423 -41 1 3 423 -113 1 7 106 -113 1 9 409 1 1	4 45 -26 6 42 - 14 0 173 174 He -2, 14 7 2 55 21 4 755 -706	He 3, Le 1 1 1060 -1107 3 1377 -1031 5 114 136 7 45 126 9 127 -125 11 50* -29 He -3, 10 1	5 295 -240 7 192 192 9 65 61 105 -At 3 333 3** 5 91 65	10 107 113 Na -4, 14 7 2 1145 1127 4 849 858 6 829 810 8 76 83 10 79 -70	4 117 -121 11 193 -197 He -5, Le 1 1 1867 -1763 3 1825 -168 5 368 -36* 7 309 -290 9 33* 38	1 210 233 1 62 -64 7 160 -164 He -4, 14 14 1 376 -340 3 140 -144 5 401 600 2 409 31	0 1112 1135 2 348 277 4 91 120 4 129 -115 8 242 -257 10 160 145 He -0, L+ 8	4 174 -172 11 53* 23 H= -7, 1* 2 1 15% 1762 3 216 -176 5 26 92 7 53* 27 9 10 -170	3 62* 17 5 125 -115 7 188 151 ** 7, 1* 16 1 152 157 3 559 -372 5 55* 55	• 725 144 • 175 161 10 52* 17 • • • • • 10 0 107 - 378 2 66 102 • 172 165	5 252 -765 5 259 -247 7 187 -193 4 140 149 11 137 -130 #9, 1-4 1 207 199	3 510 - 16 5 102 100 1 101 101 3 51 - 100 40 - 0, Le 10	4 121 -125 4 73 -83 H+-10. L+ 12 6 224 230 2 213 196 4 739 -234	9 211 -239 H=-11.12 7 1 541 -559 3 414 -425 3 414 -450 7 72 -76 9 58 62
7 157 -167 9 246 265 11 578 -15 10 1. (* 2 1 617 580 7 1667 -1421 5 283 -274 7 507 -487	n=-1. (= 14 1 1% - 1.6 3 214 5 274 7 163 6 4% - 12 m= 1.6 1 526 256 -520	* 235 256 0 504 -55 ** 2, 1, 8 0 451 -472 7 710 -602 * 125 -137 8 147 -188	1 1908 - 1943 3 998 1023 1 144 1023 7 447 - 435 9 268 - 208 11 58 - 15 H+ 2, 1+ 2 1 819 - 819	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 71 78 2 50 38 4 324 -335 5 119 129 8 624 -26 10 226 212 10 -5, La B	11 143 -178 He 5, 1 2 1 1413 -2020 3 476 -520 5 470 -444 7 56 37 4 62 37 11 55 -41	 122 -116 370 -380 374 386 45 42 67 65 86 -5, Le 16 	2 440 18 4 640 998 4 152 -143 8 77 -14 10 111 -118 4 6. (4 9 2 290 234 4 472 -447	11 10 ⁴ 91 1 251 276 3 256 -296 5 61 -16 7 186 -180 0 192 351 11 151 145	He -7, 1e 14 1 62+ 37 3 62+ -54 3 60+ -53 7 52+ -11 He 7, 1e 13 1 373 374	8	5 +54 +51 7 177 105 • 182 187 11 70 -57 +• 0, (+ 3 1 956 -965 3 710 -710 5 283 285	3 241 240 5 110 -104 44 0. L 20 1 120 -131 44 -9. L 20 1 52 -131 44 -9. L 20 1 52 -131 52 - 153	10. L+ 13 2 275 - 265 4 331 351 6 247 243 8 65 60 44-10, L+ 13 2 454 - 468	H- 11, L- # 1 103 105 3 80 -10- 5 301 -320 7 75 62 9 111 -210 H11, L- # 1 225 621
• 140 154 11 122 112 10 -1, 1 • 2 1 040 -001 3 253 -244 5 1224 118 7 120 125 9 020 -53	5 307 -401 1 5 210 -202 7 58* -34 4* -1, (* 15 1 100 -100 3 420 433 5 210 -226 7 38* 4 1	U 181 194 He -2, L 4 0 1724 -3845 2 757 274 4 455 -465 6 104 -08 8 66 -51 0 46 120	3 45 -58 3 476 460 7 113 -114 9 240 260 11 132 -119 He -3, Le 2 1 900 -594 3 216 -194	Her 3. Le 15 1 145 -145 3 327 328 5 374 328 7 378 -47 Her -3. Le 15 1 402 408 3 440 -455 440 -455	0 441 -487 2 1346 1311 4 453 -436 8 236 231 4 226 231 10 73 40 H+ 4, (* 9 2 433 -431	He -5, 1. 2 1.2252 227- 3.178 -215 5.1307 1270 7.127 -115 9.274 -274 11.120 119	1 619 7 3 240 -255 5 460 -102 7 100 -03 	e 516 525 8 62 51 10 53 52 10 53 52 10 53 66 10 67 68 6 672 60 6 145 -135 6 62 -16	M+ -7, 1+ 3 1 17: -207 3 C+5 C+2 1 25# 24 7 57# 24 • 52 83 11 55 -64	7 40* -7 5 55* -72 ** -7, L* 17 1 110 -103 3 61* -23 5 57* -85 7 10* -81	10 223 228 He 8. 1= 11 2 233 -234 4 39 -35 6 176 -356 8 159 148 He -9, 1= 11	7 61* -44 6 191 188 11 47* -8 8* -6, 1* 5 1 132 268 1 32 106 5 52* 28 2 332 -329	He - 4, t = 21 1 46* - 23 H= 10, t = 0 0 f 38 - 613 2 968 - 1033 4 162 - 163 6 133 327	4 314 372 6 212 -222 8 257 -222 m 10, L+ 14 0 521 522 2 385 -395 4 628 -395 6 438 1	3 450 -456 5 540 3 7 101 -103 9 120 -110 40 11, 40 61 3 707 363 5 610 19
1 485 444 7 767 254 1 100 -1220	He 1, 1 = 16 1 = 0? - +3 3 3C3 = 304 5 = 61 = 17 7 344 = 45	2, 1 - 5 2, 51, 535 4, 105 - 41 4, 006 - 401 8, 240 - 240	7 535 -555 9 624 -63 11 68 92 Ma 3, 14 2	· · · · · · · · · · · · · · · · · · ·	8 401 8 42 94 10 56 54 Hr -4, [. 9	1 1432 - 1430 3 1668 - 1644 5 872 840 7 854 - 644 9 514 536		10 190 18 10 6. 1. 10 0 76 85 2 215 -213 4 592 -593	1 1501 1446 1 707 - CVL 5 CC2 1209 7 470 9 218 - 225	He -7, Le 18 He -7, Le 18 He -7, Le 18	4 174 262 4 18 -411 4 201 -213 9 76 74 10 61 -15	- 200 117 11 03	8 172 171 10 150 -138 He 10.14 1 2 1500 -1055 4 550 540	+ 112 40 H=-10, 1= 1= 1= 0 1=2 1= 2 211 -231 4 74 -73	7 108 210 9 334 -36 He-11, Le 9 1 301 -291 3 270 264

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Table 2 (cont.)

n tral ne	s feel re	× ⊯el ≠c	n hol re	x irol er	s irol re	* (Fo) FC	a feol ac	* Ircl - rc	* *c1 *c	K Hel re	k ∦el re	ik kal ika	- lect re	+ 14 mi + c 1	- lect ec
5 492 492	6 100 -170	6 46* -14	9 46+ 31	6 231 -246 6 52 -88	3. 3726	1 238 260	4 159 154 6 272 -276		2 827 835	3 140 -143	6 216 273 6 96 91	1 424 42	6 73 44	1 165 161	1 15
9 165 159	- 12, 1	0 971 -978 2 110 -1-1	1 513 557	10 474 -24	H+ 15. L+ 1 1 +00 -00	7 50+ -19	H+ 16+ L+ 10	3 172 144	• •• -71	- 14, 14, 1		5 6C* 31	2 32 33		···/·. L· ·
1 242 -265 2 246 -216	2 449 -474	• 100 -101 • 78 78	5 258 200 7 600 41	2 52 30	3 64 55 5 594 -14 7 152 -158	1 04 -97	2 52* -33	7 134 -124	0 576 -546 2 137 160	3 604 712	2 447 488	#* 21. L* *	• 11• 117	3 119 154	1 320 313
5 355 351 7 61	6 322 -302	2 51 27	** 13: 1* 11	8 111 -112	• 50• 8	5 103 90	6 584 -28 8 4643	1 242 -262	4 722 -723 6 237 -244	· · · · ·	6 178 104 8 82 -60	3 e2* =3 5 e1 =51	2 12 11	He 23. 1. 9	
H 11. L- 10	84-12. 1. 4	H-12. L. 17	3 372 -414	No 14, Lo 6	1 13 13	1 130 -120	0 912 948	3 309 -471	** 18, 14 5	1 72 22	2 348			1 12 13	144 - 154
1 276 272	2 176 169 4 110 323	2 157 -153	7 121 116 He-12, Le 11	2 696 149	5 502 591 7 107 102 9 50* 14	7 216 -234	2 150 140 4 85 -79 6 93 87	·····	2 610 -30	3 157 151	214 - 215 104 - 215	3 161 176	2 144 -136	······································	1 7 6
7 189 202	• 137 -1•1 • 47• -3•	- 12, 1- 11	1 10 -73 3 244 -245	6 92 101 8 129 -150	Pre 15, 10 2	1 2 17	8 50+ 20	1 355 371	8 111 108	1 .72 .80		7 52 - 21	6 173 -97	5 64 14	5 484 -39
** 11, 1* 11 1 129 -120	H= 12. L= 3	2 51 20	7 169 163 9 162 100	He-14, L+ 6 0 84 75	201 202	5 61 50	2 139 -141	4 60 14	2 439 -434	* *** *1 7 56* 27	· 248 281	1 12 -15	2 13 15	3 25	3 11 -10
3 438 -444 5 208 -210 7 103 -108	2 765 800	He-12, Le 18 0 138 -133 2 564 30	#* 13. L* 12	2 179 -175	9 112 -113	1 41 64	0 105 148		• 13• -12- • 191 -102		8 105 98 He 20, L+ 4	7 102 -115	:		······································
9 48+ 37	10 234 -226	4 70 77 Hest7, 14 10	3 100 -108 5 176 187 7 223 -217	10 .7. 10	1 812 -833	5 104 111 He 13, (* 16	2 62 37	3	0 11 141	2 105 110 5 117 57	2 674 16	1 14	2 14 2 14 2		3 20 -1-5
3 217 229	M12, L+ 5 2 882 -509	2 200 -201	H12, L+ 12	He 14. 14 7 2 59 -65	5 125 136 7 620 -50	1 5 65	8 33 39	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	* 15* 210 * 50* -20	++ 14. 14 5		3 135 -115	• 150 - 124 • • • •	1 287 218	He 2". Le e 1 139 -1+3
7 112 104 9 51* 3	6 274 -276 8 62* -60	0 175 -174	3 30 310	6 67 7 8 58 6	H+ 15, L+ 3	1 590 -30	0 677 665	3 120 -117 5 276 -291 7 560 -35	B 520 -5		No. 20. Lo 4	1 21. LA 1	2 141 152		3 00 81 Ma-15. La L
** 11. t* 17 1 194 -197	10 87 84 H= 12, L= 6	1 17. 1 0	7. 44 48 H= 13. L= 13	He-14, 14 7	1 613 632 3 22# 226 5 6C# -17	3 56* 20	• 177 -160 • 59 -33		2 60 48	7 554 -23	2 174 - 147 4 201 194	3 64 -118 5 111 12*	÷ 117 104	·····	3 159 -1-1
3 211 -244	0 1081 -1113	1 33 - 33	1 213 273 3 62* -33	6 368 -374	7 143 133 9 110 -40	He 15, Le 17	He-18, (* 12 0 365 359 2 161 175	1 13 15	\$ 13° -15	3 326 -320	8 490 -43 He 24, 14 4	H 21 . L- 5	2	2 52 61	HF 25, (* 7 1 51 16
****11, 1* 12	17. 17.5	- 11. 1- 1	7 51 - 32	H- 14, L- 8	He-15, Le 3 1 7:4 -749	H15. (= 17	6 52 CD	H-17. L- 9	7 365 34	5 134 -129	2 220 2-6		6 57 -55	1 1+9 50	
3 139 -112	H-12, L+ +	3 198 -200	1 62* 6 3 121 -140	2 248 -263	\$ 118 -582 151 -135	3 520 -24	H- 16. L- 13 2 244 250	3 105 99			**- **	- 21	s 🗰 👯	2 45 -244	1 51
9 47 37	2 542 -554	• 17• 10•	7 544 -27	8 67 56	W- 15, 1- 4	1 59 72	6 122 -92	** 17, 1* 10	HA-18, LA 7	3 544 -14		3 275 -101	*****	e 100 -105	1 76
N= 11, L= 13 L 202 -204	6 60 27 8 62• 2	He-13, L+ 1 1 561 -556 3 697 -678	He 13, 1 14 1 135 134	H14, L- 8 0 158 -143 2 89 -93	3 241 254	H15, L- 14	4 - 1 - 13 2 97 - 95 4 44 -110	1 62+ 26 3 117 115 5 189 195	4 216 -275 6 215 282 8 116 162	1 1-1 -141	* 31* -115 H* X. L* 6	7 48 50	0 355 20-	2 243 -255	1 52 22
3 513	** 14. 1• J	5 245 -248	1 3: 3	• 124 -129 • 211 -227	7 97 119 9 71 51	- 16. L. 0	6 71 -75	1 150 -116	He 14, 14 4	\$ 201 192 7 201 155	2 200 -200	1 62 66	6 219 -146 Ha 19, 14 - 0	6 470 T	
H11, 1- 13 1 370 -201	4 356 374 c 9 85	W- 13, L- 2	H13. L- 14 1 453 -459	He 14. Le 9	Ma-15, La 4 1 395 410	2 274 243	0 59		2 278 -210	P+ 14, 14 7	\$ 215 2'5	7 24 70	2 20 - 27	2 265	3 52 53
245 213	10 48 37	1 252 222 3 570 -577 5 144 -159	7 73 -13	4 110 116 6 93 -101	5 470 487 7 624 -21	8 74 -63	4 340 -18 He-16, 10 14	7 64 62	6 18 60 H19, L= 9	3 162 -169 3 50 64 7 52• 38	0 271 24	1 12 -12		6 217 -2"1	1 237 234
K- 11. L- 14	2 121 02	9 110 -103	** 13. 1* 13	8 340 -40 He-14, 18 9	•	2 443 442	0 61 -73 2 61* -82 6 58* -31	H- 17, L- 11 1 215 349	2 62 3	MA-14, LA 7	• 101 -076 • 102 - 95	9 192 -142 He-21, 14 7	: : : :	2 55 - 1	1 65 67
1 164 -141 194 -21	6 107 -104 8 76 -52	1 344 -320	3 149 -145 5 57 -45	2 224 -222	1 209 207	8 452 447 8 179 141	o 17 -62	5 57• 41 7 120 112	a 225 227	2 284 246 3 610 - 16	20. 1. 7	1 185 185	22, 1- 10	6 674 -35	······································
M-11, L+ 14	H= 12, L = 8	5 141 -139 7 320 -313	He-13, Le 15 1 102 106	8 57+ 21	7 118 -170 9 53+ -61	H-16, L+ 1 2 99 80	1 1 1 1 1 1	He-17, 1+ 11 1 62+ -20	2 10 10	H- 19. L- 4	e 1re -1e5	1 1	4 104 9:	2 121 122	1
1 125 -110	2 513 -514	* 11 10*	117 -146	0 664 672	1 1'0 174	415 -407 67 57	Her-16, L+ 15 2 212 -218	5 216 -765 5 216 -97 7 520 -11	0 07 ·01	3 108 115	2 154 -100	1 67 41	0 414 -419	· ··· ···	2 83 -75
7 168 -194	A 108 108	1 221 -167	H= 13. 1- 16 1 - 18* - 62	6 107 -101 5 22 31	3 215 254 5 549 -171 7 321 337	10 145 124 He 16, Le 2	: 13 -12	H- 17, 1- 17	2 181 -172	7 126 -113 Her19, Le 8	* ** -**	5 187 170 He-21, Le B	* \$7* - 37	2 5802	No-2/. Lo 1
1 403 400	He-12, Le B 0 146 -121	7 831 834 9 59• 19	3 242 229	H14. L. 10	9 540 50	0 688 -314 2 369 -394	He 16. 1. 16 0 52 20	2 148 -136 549 -137	6 126 128	1 116 -109		1 40 -17 3 403 -47	2 112 115		1 10+ -37 ma 14- 14- 7
7 50 -19	241 233	1 1045 - 1055	1 144 150	2 59	1 317 345 3 470 -436	a 150 153 a 224 234		1 127 -111	N= 19. L= 10 0 P3 -61	3 534 -14		i ii iz	2 78 73	A 100 -178	9 117 277
1 169 171	10 40 42	5 344 -343	5 61 58	8 15+ 10	7 172 176	0 872 859	2 106 -94 4 69 -67	; 105 -111 ; 131 -112			0 270 284	1 19 11	······································	· · · · · · · · · · · · · · · · · · ·	Me - 26: 1 + 2
7 294 -299	2 196 198	N= 17. 1= 4	1 144 136	2 62	***-15, L* 6 1 40 #0	100 -113	He-16, Le 17 2 2/8 -230	1*************************************	Me-18. 10 10 0 100 -102	7 190 100	211 219	5 51 IA . H21, LA A .	······································	4 145 134	2 108 -47
1 420 472	8 38 -	1 248 287 3 319 119 5 269 -281	Ma-11, La 17	8 104 -91 8 109 -112	5 212 -213 5 212 -213	8 116 -119 He 10, 10 3	4 470 -11 HT-10, 10 10	3 116 -107 5 03 -60	2 274 -211 4 44 47 6 181 -260	He-10, Le 9 1 620 31 3 60 48	2 20. 1. 4	1 731 340	2 170 -161	0 244 -255	······································
5 53+ -ii	#*-12, L* * 2 55* -10	7 62 37	5 98 -105	H+-1+, L+ 11 Z A1+ 33	• 45 75	3 500 -20	0 31 9 - 31 6 2 - 15	He-17, Le 13	* 11. 1- 11	5 389 -306 7 123 116	· · · · ·	··· 21. L. 10	····27. L+ 13	4 90 -90 6 47• 37	4 -6+ -16
	6 152 -125 8 68 -99	1 300 200	1 1021	6 102 -275 5 115 116	1 647 -694 3 210 219	A 146 143	1 312 119	5 136 142		1 10, 10, 10	2 365 302	· · · · · ·	H	7 15 1.5	· · · · · · · · · · · · · · · · · · ·
7 124 -130	H+ 12. L+ 10 0 874 406	5 24C 271 7 46 51		He 14. Le 12 0 459 874	7 140 143	2 217 -239	5 400 -414 140 -13	1 57• 26 3 34• -14	2 274 -215	5 12 65	o 53+ -20	He-21, Le 10 1 274 272	2 75 -76		0 30 32
1 11 11 11 11 1 200 -10 2 10 00	2 144 -161 4 363 -390 6 92 101	• 128 -105 H• 13. L• 5	1 199 -197	2 343 -354 • 100 101 • 57• 2	H15, (- 7	6 174 102 8 87 -97	• 52• -45 +• 17, 1• 1	5 146 152 He-17, L+ 14	: ::: ::	He-10, Le 10 1 161 -171 3 226 226	0 1-6 -137 7 10 20	5 513 -321	1 226 -242	- 110 100	2 85 -43
5 11+ 141 H+-11, L+ 17	6 199 -179 He-12, Le 10	1 127 % 3 585 -617 5 399 -396	1 90 100	H14, 1- 12	3 305 296 5 3-1 3-6 7 61* -17	H 16.1. 4 0 55 60 2 556 51	1 474 418 3 167 161 5 263 -246	1 186 188	He 14, Le 12 0 600 -21 2 534 27	5 1C1 13 7 129 -110	• 241 -232	H 21. (* 11 1 55* 27 3 52* 45	5 157 142	0 10 11 11 11 11 11 11 11 11 11 11 11 11	2 55 54
1 400 -10	2 123 -114	7 174 174 9 91 -79	5 14 14	2 526 -516 4 100 -101 6 106 99	4 116 126 He 11, 1e 8	6 413 400 6 256 262 8 207 -196	7 576 540 9 79 -60	* 13: ** 13	6 126 -124	10. (* 11 1 74 70	He-26, L+ 10 0 408 -472 2 159 155	······································	1 1º1 3º3 3 60° 6º 5 190 -193	4 140 151 Herze, 14 6	
Nº 11, 1º 18	6 376 -401 8 58• 35	1 10 72	2 100 173	8 490 -43	1 407 471		H-17. L- 1 1 108 -500	2 50+ -24	0 110 -12	5 52+ 24	6 11 - 38	3 104 -109		2 21 - 202	Her 20. 1. 5
3 142 -155	* !; !•,!;	351 359	10 113 97	2 111 110	· · · · · · · · · · · · · · · · · · ·	2 343 346	31 301	1 167 -157	110 17	1 151 -160	2 2 2 2 2 2	1 21 12	3 00° 112		: :: .:
3 39 21	6 130 130 8 104 105	N= 13. L= 8	** 14. 1* 1 2 077 015	He-14, 1+ 13		8 186 -181	He 17, 14 2	5 64 E8	·····	5 68 62 He 14. L+ 12	H-20. L- 11	·····	** 23. 1. 2	1 22 23	0 184 -174 2 674 11
5 400 -14 No 11, 10 10	H12, L-11 2 240 -219	1.1	a 347 341 a 142 -166	6 310 - 34A 6 57+ -19		2 517 -170	3 394 41 3 322 -134	1 444 -31	Ne-18- Le 12	1 130 -140 3 135 112 5 77 67		3 107 11	2 241 256		0 220 -219
1 79 74		9 139 135	10 514 H14, L- 1	0 111 L. 14	• 57• 33 •• 15. 1• •	\$ \$?	· · · · · · ·	1 102 101		H10, L-12	5 4		He-21, 10 2	7 3	****}** E* 7
1 12 - 15	H- 12. L- 12	1 30+ -13	2 4/8 405	2 123 117 4 75 56 6 195 -198	3 740 -100	2 14+ -+ 4 152 -141	1 540 40	He-17. [+ 17 1 207 208		3 1ce -156	1 2 22		1 26+ 2+1	2 10 61	2 122 -121
1 454 12	2 314 323	5 276 -208 7 665 681	6 379 327 10 51* 40	He-14, L+ 14	7 166 154 Herit, 18 9	8 108 -97	5 1N 77 7 110 5 9 74 77	H17. L- 18	1 13 13	1 550 -12	0 627 675	3 126 127	1 119 111		2 16t 177
12. L. O	8 54 - 32	·	He 14, 14 2	2 210 214	1 214 -204 AC 40	n 155 - 128	1. 12. 1. 3	÷ 11. L. 2	0 101 -310	Me-16. 1 • 13	4 140 35	1 121 -124	5 241 237	··· /·· · ·	1 11 11
	0 464 479 2 121 124	3 174 202 5 146 204	• • • • • • • • • • • • • • • • • • •	W- 14. L- 14	7 236 -241 6 66 -103	f1 33		2 176 - 140			2 11 - 29	····21, 1. 1.	1 130 -1-7		
10 115 -156	6 117 -261 8 86 -17	1 34+ -7	10 10 -124	6 56 -42	He 15, 14 12	H	· ; ;	5	1.1.1.1	1 11, 1 · 14	2	** ??; **, ?	23. (- 4	1.16 1.15	\$ 5. 5
2 520 -510	······································	1 79 -90	0 40° -28 2 55 -103	2	3 61 - 44 7 157 -160	2 173 -174		2 22 12	2 10 -0.0	3 63 61 60-10, L+ 14		2 CF -41 4 71C -3C1 6 20C -274	3 31	C 21 125	1 03 -02
e 376 378	4 110 -134 8 305 310 8 69 83	5 150 -150 7 1+3 1+7 9 56+ -17	4 271 -246 6 60 43 8 133 -135	6 101 107	H15. L- 10	6 177 176	* *** *** * *** ***	8 80 82	· · · · ·	1 112 - 112	2 94 51 HP-27. 19 14	2 42 10		2 105 -140	H= 17. (+ 2 1 +9 +3
H12. L- 1	Me-12, Le 13	Me 13, Le 4	10 47 -78	M. 14, 1. 16 0 132 12- 2 147 142	3 341 -379 4 264 223	H- 16. L. 7 2 1201 1219	"· 17. (• 4	2 133 -120		He 19, 1- 19	2 75 75	• • • •:	2 248 239 5 11: -20h	Ma-24, 1+ 11	He-27. 14 2
10. 11	6 6C -23	3 107 145	2 215 -276	4 52 17	** 12 12.11	120 140 74 70	3 403 -415	6 210 121 8 102 41	2 148 -154	H	Ma-27. 1. 15	2 122 -121	1.61.2		,
10 145 -122	H+ 12. L+ 14	9 68 -40	4 68 -111 10 175 -169	0 73 -71 2 90 94	3 142 196	He-16, Le 7 2 7 -72	4 44 -44	5	2 4 92	3 54 TC	H 20. L+ 16	6 247 -247	1 12 IV	++ 25. 1+ 2	า "ก" อ่
X* 12, 1* 2 C 556 -513 2 101 304	0 128 -133 2 727 -739 4 6C* 26	1 134 131	He-14. Le 3 2 120 124	· · · · · ·	7 43 52 Herits, Le 11	a 147 -144 A 560 -4	1 57 - 46	2 116 227	H 10. [0 0	He-10, 10 16 1 716 224 3 79 68	0 410 10 He 21, 10 C	2 44 -257	1	1 153 -110	· · · · · · · · · · · · · · · · · · ·
4 207 221 6 324 342 8 219 -206	0 126 119 H=-12, L= 16	5 263 -275 7 384 -393 9 141 137	+ 1*9 175 + 378 391 8 cl+ -30	2 245 -237	1 818 37 3 318 324 5 42 420	H- 16. 1. #	7 177 177	e 120 125	;	- 2C. L. C	3 349 -155	6 76 - C	5 540 -31	m 25, 14, 3	1 17. LA
1C 160 149	0 342 564 2 110 117	He 13: 1- 4	10 225 -213 He 14, 14 4	He-14, L-17 2 564 -22 4 151 147	7 560 14	2 540 -*60 4 169 -154 6 F1 -85	H- 12 1- 3	0 136 140			• 120 111 ++ 21, 1+ •	C 536 -527	1 1 1	3 2. 2.	····
2 203 206	e e9 10e e e1 92	3 232 -24 3 1 ¹¹ 136	0 614 655 2 510 -555	H. 14, 1. 1.	3 142 -161	6 120 Te	1	: 13 -15	1 11 - 12	1 1 1				140 -110	1
	H+ 12. 1+ 15 2 01+ -34	\$ 65 -45	6 018 -091 8 64 -47	2??	1 10 14	0 254 -20 2 6C 11	• •• •	7 14 14 3	1 152 -1-4	2 62 40	, " <u>;</u> , ",	·····		5 156 155	1 110 11
10 130 127 No 12, Lo 3	€ 64 -48	1 362 -162 3 247 -250	10 123 113 H(+, L- 6	2 37 -13	1 279 -270	6 221 -230 8 544 31	1 211 - 253	* 313 -316 * 61 -51 * 124 -107	3 322 302 5 100 -100 7 101 -05	6 215 210 8 116 125	1 220 211	• 53• -310 • 53• -11	12:00	17 (d. 17)	1 62 64
2 780 790	He-12. Le 15 2 122 -227 4 140 154	5 279 -246 7 326 -336 9 520 44	0 147 174 2 222 -241 4 141 202	4 90 -91 He-14, Le 19	3 193 203 3 111 -149	7 16. 10 9	1 410 -11 1 410 -11 1 53 10		1 12	He-70. Le 1 2 257 247 4 218 -207	; 1/1 10t ; 1/0 -1/1	2	3 120 -11:	4 147 120 He-74, 14 2	1 00 -12
10 34+ -40	a ist hi	P* 13. L* 10	117 171	2 474 -16	1 341 377	6 141 -136	H- 17. 1. 4		1 149 150	6 101 102 8 104 114	1 2	e 264 256 10 22 1	1 67 -50	214 -204	č 31: **212
#**-12, 1* 3 2 406 -424	2 242 -234	3 176 190	· · · · · · · · · · · · · · · · · · ·	3 209 -201	5 101 -98	He-16, Le 0	3 363 -390	He 14, 14 A	H-15. L- 2	0 201 10 2 0 202 201	\$ 11 - 113	0 253 242	1 6 64 65	H= 25, 1= 3	0 47+ 25
- 342 -346	4 12 16		a 241 +337	1 3 436 -120		• • • • • • • • • • • •	1	· · · · · · · · · · · · · · · · · · ·		- 471 16°		- 100 124		. ,	

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 0.1σ and no shift was greater than 0.5σ .

A final difference Fourier map showed no significant negative regions and only three significant peaks of 0.20-0.23 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 rigidbody 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 0.0031Å² and those of $\langle \sigma(U_{obs}^{ij}) \rangle$ being 0.0011 and 0.0010Å² 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 chairshaped, 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 $4.54 \le F_0 \le 338.69$:

Category	Limits	Number
1	$ \Delta F / F_o \leq 2R(0.086)$, or $ \Delta F \leq F_{\rm th} $	3061
2	$2R < \Delta F / F_o \le 3R(0.128)$, or $ F_{th} < \Delta F \le 2 F_{th} $	50
3	$3R < \Delta F / F_o \le 4R(0.171)$, or $2 F_{\text{th}} < \Delta F \le 3 F_{\text{th}} $	4
801 unobsei	eved reflexions:	
1	$ F_c \leq F_{\rm th} $	752
2	$ F_{\rm th} < F_c \leq 1.5 F_{\rm th} $	49

 $|F_{\text{th}}|$ is the threshold amplitude as defined in the experimental part of the text. Its range is $3.50 \le |F_{\text{th}}| \le 6.22$.



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 55.8° 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*.

Princip	bal axes of L							
		Cation				An	ion	
	Eigenvalues	Direc	tion cosines	(×104)	Eigenvalues	Direct	ion cosines	s (×104)
L1	10·9(°) ²	7161	- 6295	3017	193·4(°) 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
Princip	oal axes of redu	iced T†						
T 1	0∙0364 Ų	-4723	8359	- 2796	0·0632 Ų	2940	- 7946	5312
T2	0.0320	- 5461	- 5260	- 6517	0.0387	5379	- 3219	- 7791
T3	0.0259	- 6920	-156 2	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-sauares L	lanes
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Plane 1 (ring C)Plane 2 (ring D)Plane 3 (aromatic ring)Plane 4 (anion) Δ Δ Δ Δ C(5) -0.013 Å C(6)C(8) 0.012 Å C(9)C(9) 0.007 Å C(10)C(23) 0.0111 Å C(23)C(6) 0.025 C(9)C(9) -0.021 C(10)C(10) 0.002 C(24) 0.003 C(24) 0.003 C(17)C(7) -0.026 C(10)C(10) 0.016 C(12)C(12) -0.011 $0.(6)$ C(6) -0.035 C(17)C(17) -0.17 C(11) -0.007 C(13) 0.009 O(7) $0.(7)$ O(10) 0.014 C(14)C(11)* -0.788 O(4)* $C(7)*$ O(4)* 0.354 C(17)* $C(14)$ O(37) 0.037 O(1)*Plane 5 (carbonyl group) $\chi^2 = 266$ C(11)* $C(11)*$ O(00) 0.037 O(1)* -0.420 O(5)*C(7) 0.002 Å H(121)* 0.00 H(141)* 0.00 V(1)* -2.464 H(151)*C(8) (C4) -0.002 H(151)* 0.00 V2=53 $\chi^2 = 593$						
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Plane 1 (ring C)	Plane 2 (ring D)	Plane 3 (aromatic ring)	Plane 4 (anion)		
	$\begin{array}{c} & \measuredangle \\ C(5) & -0.013 \text{ Å} \\ C(6) & 0.025 \\ C(7) & -0.026 \\ C(17) & 0.017 \\ C(11)^* & -0.788 \\ \chi^2 = 485 \end{array}$ $\begin{array}{c} Plane \ 5 \\ (carbonyl group) \\ & \measuredangle \\ C(7) & 0.002 \text{ Å} \\ C(8) & -0.009 \\ C(9) & 0.002 \\ O(4) & 0.002 \\ \chi^2 = 25 \end{array}$	$\begin{array}{c} & \Delta \\ C(8) & 0.012 \text{ \AA} \\ C(9) & -0.021 \\ C(10) & 0.016 \\ C(11) & -0.007 \\ C(7)^* & 0.354 \\ C(17)^* & -0.638 \\ O(4)^* & -0.181 \\ \chi^2 = 266 \end{array}$	$\begin{array}{c} & \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	$\begin{array}{cccc} & & & & & \\ C(23) & 0.011 & \text{\AA} \\ C(24) & 0.003 \\ O(6) & -0.035 \\ O(7) & 0.014 \\ O(8) & -0.017 \\ O(9) & 0.037 \\ H(O61)^* & 0.08 \\ O(1)^* & -0.420 \\ H(N11)^* & -1.54 \\ N(1)^* & -2.464 \\ H(N12')^* & -0.33 \\ N(1')^* & -0.715 \\ \chi^2 = 593 \end{array}$		

* 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: -0.721X' + 0.659Y - 0.216Z' = -6.457 Å 2: 0.520X' + 0.536Y - 0.665Z' = +1.4273: 0.488X' + 0.593Y - 0.641Z' = +1.3034: -0.636X' - 0.753Y - 0.172Z' = -5.4415: 0.689X' + 0.512Y - 0.513Z' = +4.490

Some dihedral angles between the planes:

∠1,2	∠2,3	∠2,5	∠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 $+158.8^{\circ}$. 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.



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 ± 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 3.6σ longer here. There is also a reason-



Fig.4. Torsional angles (Klyne & Prelog, 1960). The e.s.d.'s (Huber, 1961) are 0.2-0.3°.

able agreement between the bond angles: the largest difference (5.0σ) 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. 1.569(8)Å in ammonium oxalate; Robertson, 1965], but significantly longer than 1.536(3)Å, which was observed in α -oxalic acid (Sabine, Cox & Craven, 1969). The C(24)=-O(8) bond is significantly shorter [by 0.024(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 0.039(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 0.012(2)Å.

Hydrogen bonding and packing

The structure includes a normal and two bifurcated hydrogen bonds (Fig. 2). All $H \cdots O$ distances are 0.3 to 0.7Å shorter than 2.6Å, the sum of the van der Waals radii. The C=O...H angles are close to 120°, except the intra-ionic angle C(24)–O(7)…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 1.54 and 0.33Å, 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: 0.23 and 0.13Å 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 $C_{22}H_{30}O_5N.C_2HO_4$.



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 $a\uparrow$, $c\rightarrow$.

Apart from the hydrogen bonds, there are no intermolecular 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···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-