

precession photographs available to them. All computations have been carried out with the IBM 360 system using a compatible set of programs written for that computer in FORTRAN IV by Ahmed, Hall, Pippy & Huber (1966). Grateful acknowledgement is made to Mrs M. E. Pippy of this laboratory for assistance with the computations, and to the staff of the NRC Computation Centre for their cooperation.

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The Crystal Structure of Cryptopine, C₂₁H₂₃O₅N

BY S. R. HALL* AND F. R. AHMED

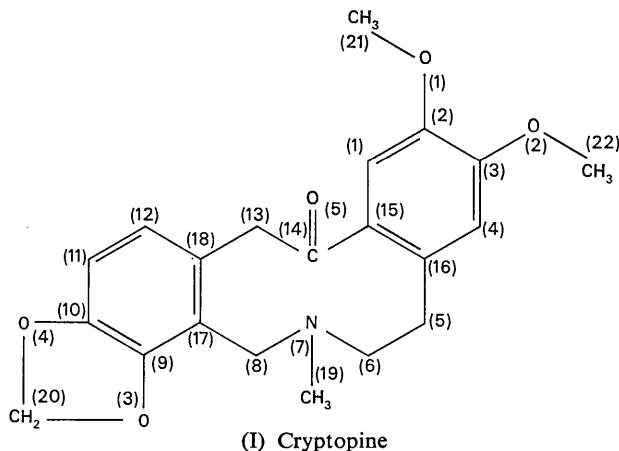
Pure Physics Division, National Research Council of Canada, Ottawa 7, Canada

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The structure of cryptopine, C₂₁H₂₃O₅N, has been determined by the symbolic addition procedure, and has been refined by least squares to an *R* index of 0.042 for 1948 observed reflexions measured with a scintillation counter. The space group is *P2₁/n* and the cell dimensions are *a* = 14.438, *b* = 8.702, *c* = 14.369 Å, *β* = 91°22'. The presence of two methoxyl groups in the cryptopine molecule in place of one of the five-membered rings of the protopine molecule has resulted in significant differences in the angles at the two oxygen atoms and at four carbon atoms of the benzene ring in that part of the two molecules. The short distance between the C atom of the carbonyl group and the nitrogen atom across the ten-membered ring is 2.581 Å in cryptopine as compared with 2.555 Å in protopine. In both structures, the nitrogen atom is well buried in the molecule and has the three C-N bonds and the short C...N distance across the ten-membered ring tetrahedrally arranged around it. The carbon-oxygen double bond has ketonic character and is well off the planes of the aromatic rings.

Introduction

Cryptopine, C₂₁H₂₃O₅N, is the dimethyl analogue of protopine, C₂₀H₁₉O₅N, whose X-ray crystal structure analysis has been reported by Hall & Ahmed (1968). Reference should be made to the introduction of that paper where the purpose of the X-ray analysis of these two compounds has been discussed. The schematic formula of cryptopine is shown in (I), and the numbering of the atoms is basically the same as that adopted for protopine for ease of comparison of the two molecules.



* National Research Council Postdoctorate Fellow. Present address: Department of Physics, The University of Western Australia, Nedlands, Western Australia.

The compound cryptocavine, $C_{21}H_{23}O_5N$, has been described in the literature (*e.g.* Manske & Holmes, 1954, p.155) to be different from but isomeric with and closely related to cryptopine. Since then, it has been proven by Thomas, Marion & Manske (1955) that cryptocavine is identical with cryptopine and it has been suggested that the designation cryptocavine should be deleted from the literature.

Crystal data

Crystals of cryptopine, $C_{21}H_{23}O_5N$, are monoclinic, space group $P2_1/n$, with unit-cell constants $a=14.438$ ($\sigma=0.004$), $b=8.702$ ($\sigma=0.005$), $c=14.369$ Å ($\sigma=0.004$), $\beta=91^\circ 22'$ ($\sigma=3'$); $U=1804.8$ Å³, mol. wt. 369.42, $D_c=1.359$ g.cm⁻³; D_m (by flotation at 20°C)=1.350 g.cm⁻³ (Barnes, 1967); $\mu(\text{Cu})=8.09$ cm⁻¹, $F(000)=784$. The space-group absences are $h0l$ with $h+l=2n+1$, and $0k0$ when k is odd.

Experimental

For this X-ray analysis, a small prismatic crystal of dimensions 0.07 mm × 0.13 mm in cross section and 0.20 mm in length was mounted with its length (the a axis) along the direction of a glass fibre. Precession photographs were taken for the preliminary examination of the crystal and the space group, but the cell dimensions and intensity data were measured on the General Electric XRD 5 diffractometer using Cu radiation ($\lambda K\alpha_1=1.54050$ Å, $K\alpha_2=1.54434$ Å). Take-off angles of 1° and 2°, and slits of 0.02° and 0.05° were employed during measurements of the 2θ -values of the axial reflexions from which the unit-cell constants were calculated. The β -angle was deduced from the χ -settings of the $h00$ and $00l$ reflexions after they had been centred with the top/bottom device. The intensity data were collected with the goniostat set at a 3° take-off angle, and with Ni filters inserted just before the open counter window. Each lattice site was scanned with the moving-crystal moving-counter method and the background was measured at the beginning and at the end of each scan. The 2θ scan was varied from 3° for the low-angle reflexions to 5° for the high-angle reflexions. All reflexions were first measured with the same tube-current setting, then the exceedingly strong reflexions were remeasured with a lower current setting. Also, most of the very weak reflexions were remeasured prior to the final stages of refinement. The intensity of the 004 reflexion was recorded at short intervals of time during the data collection and was employed for scaling of the data. The net counts of the observed reflexions were reduced to the same relative scale, and the corresponding 1/Lp corrections were applied to them. Errors due to absorption were considered to be negligible.

The number of non-equivalent lattice sites within the range of the instrument was 3914, but only 1948 reflexions were observed above threshold.

Structure determination by symbolic addition

The crystal structure of cryptopine was determined by the symbolic addition procedure for phase determination of centrosymmetric structures, using the same computer programs and the same scattering factor curves as for the protopine structure (Hall & Ahmed, 1968). All the necessary operations were carried out by the program, and without any adjustments by the authors. The statistics of the normalized structure factor amplitudes $|E|$ for cryptopine and those calculated by Karle, Hauptman, Karle & Wing (1958), given in parentheses, were as follows: $\langle |E| \rangle = 0.798$ (0.798); $\langle |E^2| \rangle = 0.963$ (1.000); $\langle |E^2 - 1| \rangle = 0.962$ (0.968); reflexions with $|E| > 3$ were 0.49% (0.3%); reflexions with $|E| > 2$ were 4.27% (5%); and reflexions with $|E| > 1$ were 30.35% (32%).

The procedure of sign determination was confined to the 458 reflexions with $|E| > 1.500$. For each of these reflexions a separate list was assembled containing all the pairs of reflexions with $|E| > 2.0$ which if combined with the original reflexion would satisfy the Σ_2 relationship. The three reflexions 11,1,1; 458; 12,2,1 which were selected by the program as the origin-defining reflexions, had the largest $|E|$ values in the data. The 12,1,3 reflexion, which had the fourth largest $|E|$ value, was also selected by the program for defining the symbol A , and it was not necessary to assume any other symbol. The first stage of sign determination was performed on the 167 reflexions with $|E| > 2.0$, and this operation was successful in fixing the signs of 163 of these reflexions. All these signs were found later to be correct. Correlation of the symbol A with corresponding positive and negative signs for each of these reflexions showed 283 coincidences in favour of A being a negative value, as compared with only 40 coincidences against. The symbol A was therefore taken as negative, and the signs of the remaining reflexions with $|E| > 1.500$ were determined directly from the Σ_2 relationship. Altogether, the signs were fixed for 449 out of the 458 reflexions, and only two of these reflexions were found later to be incorrectly signed.

The E map which was computed with the 449 reflexions gave the complete structure (with the exception of the hydrogen atoms). A composite drawing of the cryptopine molecule as deduced from the E map is shown in Fig. 1. The peak heights for the atoms, on a relative scale, varied between 3.5 and 9.3, and the highest spurious peak was only 2.5. The atomic positions for the trial model were taken from the E map, and their isotropic temperature factors were assumed between 2.9 and 4.6 Å² depending on their peak heights. The R index corresponding to these starting parameters was 0.24.

Refinement

The assumed structure was refined by successive cycles of block-diagonal least-squares. The R index was reduced to 0.15 after the first two cycles of refinement

with isotropic temperature factors, and it was reduced to 0.09 after four cycles with anisotropic thermal parameters. A difference map was computed at this stage and positions of all the hydrogen atoms were derived from it. The peak heights for the hydrogen atoms were between 0.35 and 0.60 e.Å⁻³, and the residual electron density elsewhere was within ± 0.20 e.Å⁻³. One more cycle of refinement was carried out with the hydrogen atoms included, assuming isotropic temperature factors for them. Consequently, the *R* index was reduced to 0.053. The refinement was interrupted at this stage until most of the weak reflexions were remeasured in order to improve on their counting statistics. The final three cycles of this refinement were carried out with the modified data, assuming the thermal vibration to be anisotropic for the C, N, and O atoms and isotropic for the hydrogen atoms. The *R* index was reduced very slowly to 0.045. A final difference map which was evaluated with all the atoms subtracted showed a residual electron density within ± 0.15 e.Å⁻³.

Throughout this refinement, the weights were calculated by the expression

$$w = 1/\sigma^2(|F_o|), \quad \text{or} \\ w = 4\{(\text{net count})^2/[|F_o|^2 \cdot \sigma^2(\text{net count})]\}, \quad (1)$$

where $\sigma^2(\text{net count}) = (\text{total count} + \text{background count})$. These weights were based on the counting statistics of the intensity data, and the expression was derived assuming the time spent in measuring the total count to be the same as that spent in measuring the background. However, in order to examine the effect of this weighting scheme on the final parameters, the last three cycles of refinement were repeated, starting with the same parameters of that stage, but this time the weights were calculated by the expression

$$w = 1/\{1 + [(|F_o| - 60)/40]^2\} \quad (2)$$

which had been employed in the refinement of the protopine structure. The *R* index this time was reduced to 0.042.

The average shifts in the final cycles of both refinements were about 0.2 of the e.s.d.'s, and the maximum shifts were within 0.7 of the e.s.d.'s.

Results

The final parameters as derived from the least-squares refinement with weighting scheme (2) are given in Table 1 for the C, N, and O atoms and in Table 2 for the H atoms. The e.s.d.'s for these parameters were calculated from expression 6.4.3(6) of *International Tables for X-ray Crystallography* (1959, p. 330) and increased by 50% in order to allow for the omission of the unobserved reflexions. The observed structure amplitudes and the structure factors calculated with the parameters in Tables 1 and 2 are listed in Table 3. Each of the 1948 observed reflexions has $|\Delta F|/|F_o| \leq 0.10$ or $|\Delta F| \leq |F_{th}|$. The $|F_o|$ values for the unobserved reflexions are $\leq |F_{th}|$ for 1846 reflexions, $1.5|F_{th}| \geq$

$|F_o| > |F_{th}|$ for 119 reflexions, and $|F_o| > 2|F_{th}|$ for only one reflexion, namely the 15,4,9, for which $|F_o| = 6.0$ and $|F_{th}| = 2.7$. The observed structure amplitudes are within the range $3.2 \leq |F_o| \leq 161.5$, and the threshold amplitudes are between 2.0 and 8.8.

The bond lengths and their e.s.d.'s (Ahmed & Cruickshank, 1953), and the bond angles and their e.s.d.'s (*International Tables for X-ray Crystallography*, 1959, p. 331) are presented in Fig. 2. All values in Fig. 2 do not include the correction for thermal vibration. The following angles have been excluded from this figure for simplicity: C(16)–C(5)–H(4), 110.0° (2.3); C(6)–C(5)–H(3), 109.6° (2.2); N(7)–C(6)–H(5), 108.7° (2.5); C(5)–C(6)–H(6), 109.7° (2.0); N(7)–C(8)–H(8), 107.8° (2.1); C(17)–C(8)–H(7), 113.1° (2.3); C(18)–C(13)–H(12), 109.5° (2.2); C(14)–C(13)–H(11), 105.4° (2.1); N(7)–C(19)–H(14), 112.2° (2.3); H(13)–C(19)–H(15), 102.9° (3.6); O(3)–C(20)–H(17), 109.7° (2.5); O(4)–C(20)–H(16), 112.8° (2.8); O(1)–C(21)–H(19), 111.5° (2.7); H(18)–C(21)–H(20), 105.2° (3.5); O(2)–C(22)–H(22), 107.7° (2.5); H(21)–C(22)–H(23), 117.3° (3.5).

The distance N(7)···C(14) across the ten-membered ring is 2.581 Å, and it makes angles of 108.6, 108.6, and 102.7° with the bonds N(7)–C(6), N(7)–C(8), and

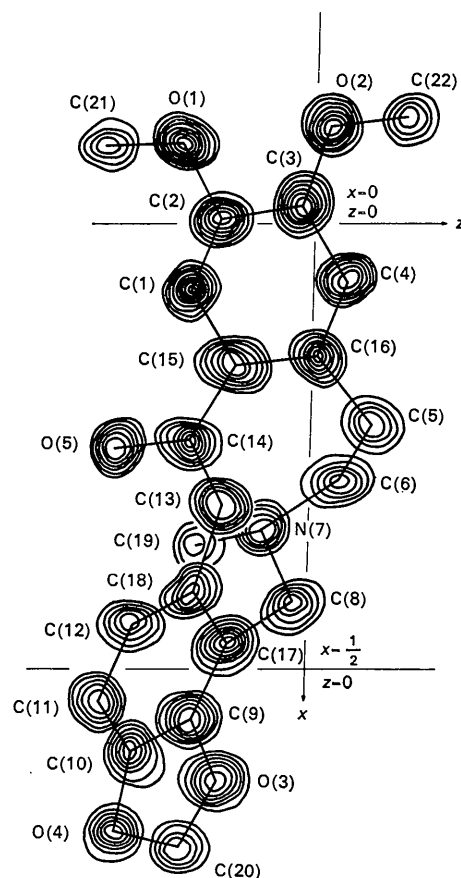


Fig. 1. Composite drawing of the cryptopine molecule from the *E*-map.

Table 1. *Fractional coordinates, vibration tensor components (\AA^2) for the expression $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + 2U_{23}b^*c^*kl + \dots)]$, and their e.s.d.'s (all quantities $\times 10^4$)*

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
C(1)	-4223 (3)	3781 (5)	3636 (3)	293 (21)	411 (27)	297 (20)	-17 (42)	72 (33)	-11 (41)
C(2)	-5092 (3)	3506 (5)	3986 (3)	285 (21)	440 (28)	322 (22)	-56 (43)	-32 (35)	-11 (42)
C(3)	-5169 (3)	2825 (5)	4859 (3)	285 (22)	451 (30)	413 (25)	-7 (46)	196 (36)	18 (42)
C(4)	-4372 (3)	2492 (6)	5367 (3)	343 (22)	553 (31)	293 (22)	1 (46)	156 (35)	28 (47)
C(5)	-2668 (3)	2383 (6)	5673 (3)	343 (22)	657 (34)	254 (20)	94 (47)	-2 (35)	60 (49)
C(6)	-2076 (3)	1113 (6)	5254 (3)	355 (24)	442 (30)	384 (25)	198 (46)	-74 (38)	-17 (44)
N(7)	-1543 (2)	1733 (4)	4486 (2)	295 (17)	375 (22)	345 (19)	118 (34)	4 (28)	4 (34)
C(8)	-678 (3)	2459 (6)	4827 (3)	287 (21)	470 (29)	385 (23)	56 (46)	-106 (35)	26 (45)
C(9)	580 (3)	3446 (5)	3791 (3)	247 (21)	384 (27)	452 (25)	-86 (45)	-72 (36)	67 (40)
C(10)	919 (3)	4397 (6)	3119 (3)	311 (22)	503 (31)	403 (25)	-18 (46)	73 (38)	-151 (44)
C(11)	392 (3)	5507 (6)	2704 (3)	413 (27)	557 (34)	454 (28)	219 (52)	52 (42)	-235 (51)
C(12)	-522 (3)	5649 (6)	3023 (3)	380 (25)	422 (31)	593 (31)	177 (51)	-122 (46)	-22 (47)
C(13)	-1845 (3)	4923 (5)	4045 (3)	304 (22)	356 (28)	515 (28)	17 (45)	38 (39)	147 (41)
C(14)	-2535 (3)	3780 (5)	3628 (3)	264 (21)	508 (30)	303 (22)	125 (44)	-13 (33)	107 (43)
C(15)	-3409 (3)	3452 (5)	4156 (3)	256 (21)	410 (28)	305 (22)	-86 (42)	-25 (33)	-32 (40)
C(16)	-3487 (3)	2834 (5)	5042 (3)	285 (21)	485 (30)	305 (22)	-60 (43)	-36 (35)	67 (42)
C(17)	-315 (3)	3536 (5)	4110 (3)	257 (21)	389 (27)	370 (23)	-6 (42)	-24 (33)	-38 (40)
C(18)	-862 (3)	4701 (5)	3707 (3)	293 (21)	391 (28)	418 (25)	-39 (44)	-44 (36)	-44 (41)
C(19)	-1374 (3)	617 (6)	3761 (3)	512 (28)	481 (32)	472 (28)	-120 (50)	173 (46)	25 (52)
C(20)	2077 (3)	2853 (6)	3623 (3)	305 (24)	582 (36)	692 (34)	-5 (58)	103 (46)	2 (49)
C(21)	-5858 (3)	4681 (7)	2685 (3)	324 (24)	812 (42)	506 (30)	389 (60)	-232 (44)	45 (54)
C(22)	-6143 (3)	1805 (7)	6030 (3)	404 (25)	846 (44)	465 (28)	141 (58)	302 (44)	-267 (57)
O(1)	-5912 (2)	3831 (4)	3522 (2)	249 (14)	673 (24)	444 (17)	221 (35)	-88 (25)	17 (32)
O(2)	-6049 (2)	2523 (4)	5138 (2)	278 (14)	775 (26)	463 (17)	222 (38)	131 (27)	-78 (34)
O(3)	1243 (2)	2388 (4)	4074 (2)	273 (14)	584 (24)	695 (22)	259 (39)	134 (28)	127 (32)
O(4)	1827 (2)	4007 (4)	2947 (2)	292 (16)	741 (27)	673 (22)	95 (41)	261 (30)	-37 (34)
O(5)	-2491 (2)	3373 (4)	2826 (2)	297 (14)	729 (24)	293 (16)	0 (33)	33 (25)	8 (33)

N(7)–C(19), respectively. It also makes angles of 85.0, 95.2, and 102.3° with C(14)–C(13), C(14)–C(15), and C(14)–O(5), respectively.

Discussion

Effect of the weighting scheme

The mean differences in the final parameters of the two refinements with different weighting schemes as described previously were about 0.5 of the corresponding e.s.d.'s, and the largest differences were below 1.8 times the e.s.d.'s. The mean and the maximum changes in the bond lengths and angles were as follows: 0.002 and 0.006 Å in bonds not involving hydrogen atoms, 0.02 and 0.06 Å in the C–H bonds, 0.13 and 0.4° in angles not involving C–H bonds, and 0.9 and 4.2° in angles involving C–H bonds. The largest difference of 4.2° was observed for the H(16)–C(20)–H(17) angle which was 120.3° for the results of weighting scheme (1), and 116.1° for those of weighting scheme (2). The latter value was obviously closer to that for the tetrahedral angle which was to be expected there.

The second weighting scheme, therefore, resulted in a slight improvement in the overall agreement between the observed structure amplitudes and calculated structure factors, and also in the general dimensions for the bond lengths and angles, although the individual differences in these dimensions were always well below the significance level.

Bond lengths and angles

Comparison of the lengths of the individual C–C, C–N, and C–O bonds in the protopine and cryptopine

molecules by means of the *t* test shows that $P > 5\%$ for 21 bonds, $5\% \geq P > 1\%$ for six bonds, and $1\% > P$ for three bonds, namely C(1)–C(2), C(2)–C(3), and C(13)–C(18), for which the bond lengths in the two structures differ by 0.020, 0.019, and 0.020 Å, respectively. A significant difference of 0.026 Å is also observed in the N(7)···C(14) distance across the ten-

Table 2. *Fractional coordinates ($\times 10^3$) and isotropic temperature factors (\AA^2) of the hydrogen atoms, and their e.s.d.'s*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	-417 (3)	416 (5)	296 (3)	2.8 (0.9)
H(2)	-442 (2)	199 (4)	597 (2)	1.7 (0.7)
H(3)	-225 (3)	336 (5)	582 (3)	3.9 (1.0)
H(4)	-289 (3)	203 (5)	628 (3)	3.2 (0.9)
H(5)	-247 (3)	25 (5)	501 (3)	4.3 (1.0)
H(6)	-162 (2)	64 (5)	578 (3)	2.7 (0.8)
H(7)	-22 (3)	159 (5)	500 (3)	3.4 (0.9)
H(8)	-83 (2)	309 (5)	541 (3)	2.9 (0.9)
H(9)	61 (3)	617 (5)	216 (3)	3.5 (0.9)
H(10)	-92 (3)	647 (5)	273 (3)	3.5 (0.9)
H(11)	-207 (2)	598 (5)	383 (2)	2.4 (0.8)
H(12)	-184 (3)	490 (5)	475 (3)	3.0 (0.9)
H(13)	-199 (3)	30 (5)	345 (3)	4.7 (1.1)
H(14)	-102 (3)	107 (5)	323 (3)	4.0 (1.0)
H(15)	-109 (3)	-43 (6)	399 (3)	5.1 (1.2)
H(16)	232 (3)	189 (6)	333 (3)	5.9 (1.3)
H(17)	252 (3)	339 (5)	410 (3)	4.8 (1.1)
H(18)	-553 (3)	576 (5)	278 (3)	3.7 (1.0)
H(19)	-552 (3)	408 (6)	219 (3)	5.5 (1.2)
H(20)	-649 (3)	491 (5)	249 (3)	4.7 (1.1)
H(21)	-590 (3)	255 (5)	651 (3)	3.4 (0.9)
H(22)	-677 (3)	169 (5)	614 (3)	3.6 (0.9)
H(23)	-580 (3)	67 (6)	600 (3)	6.0 (1.3)

Table 3 (cont.)

Table with multiple columns of numerical data, organized in groups of 10 columns. Each group has a header row with 'K FO FC' and a corresponding data row. The data consists of integers, some with negative signs, and some with subscripts or superscripts. The table is dense and covers a wide range of values.

Table 3 (cont.)

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
H= 10, L = 1	1 749 -29	2 499 -17	5 689 -32	6 113 -114	1 389 -63	0 237 -240	1 215 215	3 414 58	5 64 -72	5 528 -38	3 336 12	H= 16, L = -9	H= 10, L = -9	1 749 -29	2 499 -17	H= 16, L = -9	1 749 -29	2 499 -17	H= 10, L = -9	1 749 -29	2 499 -17	H= 10, L = -9	1 749 -29	2 499 -17	H= 10, L = -9	1 749 -29	2 499 -17	H= 10, L = -9	1 749 -29	2 499 -17		

membered ring of each structure. The *t* test on corresponding angles in the protopine and cryptopine molecules, excluding those involving C–H bonds, shows significant differences varying between 2.2° and 12.0°

in the ten angles at atoms O(1), O(2), C(1), C(2), C(3), and C(4). These differences appear to be due mainly to the presence of the two methoxyl groups in cryptopine in place of one of the five-membered rings of

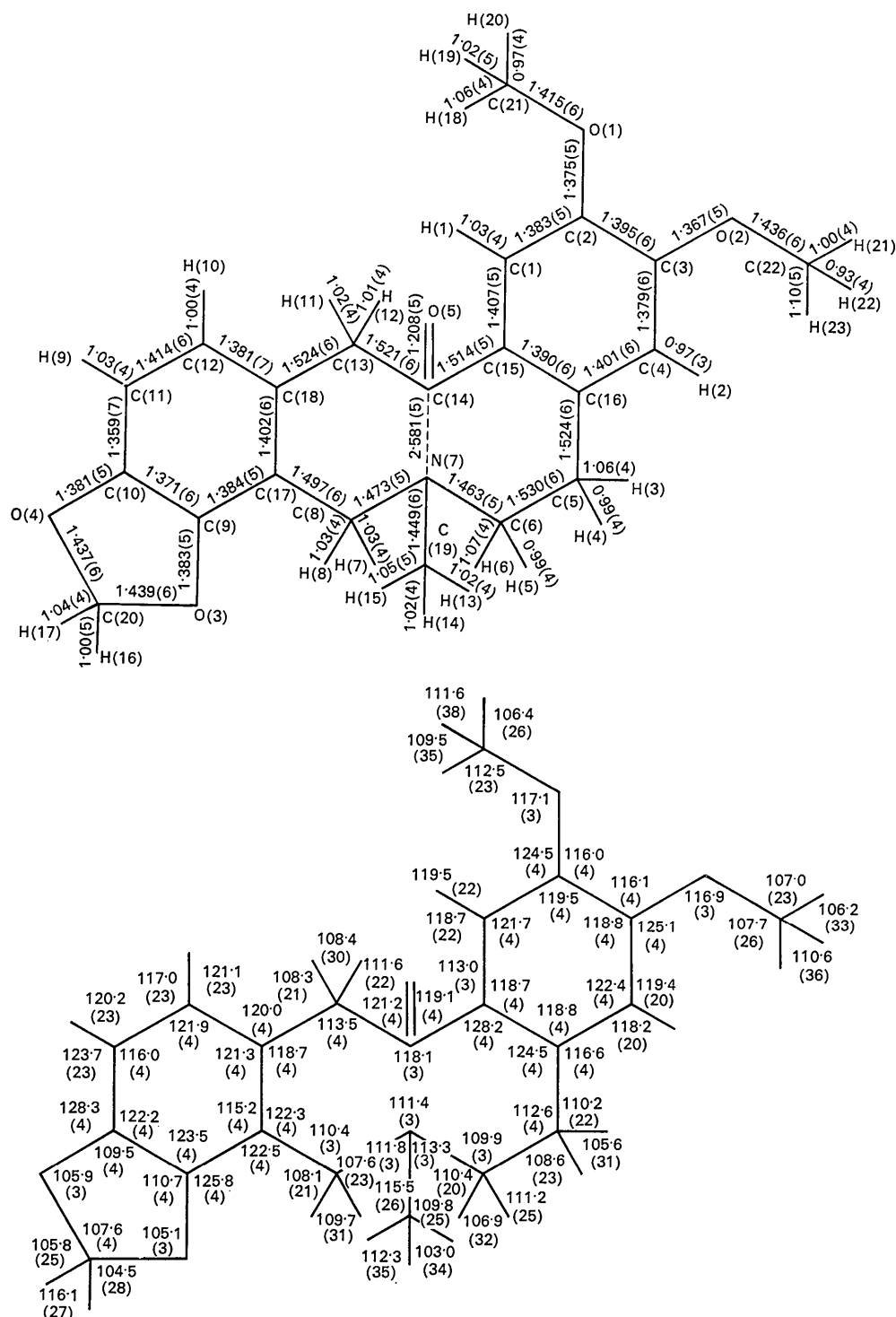


Fig. 2. Bond lengths (Å) and angles (°), and their e.s.d.'s in parentheses. The e.s.d.'s are $\times 10^2$ for the C–H bonds, $\times 10^3$ for the other bonds, and $\times 10$ for the angles.

protopine. The differences for the remaining 33 angles are all within 2.0° , and the t test shows that $P > 5\%$ for 19 angles, $5\% \geq P > 1\%$ for seven angles, $1\% \geq P > 0.1\%$ for three angles, and $0.1\% > P$ for four angles, namely, C(1)–C(15)–C(16), C(5)–C(6)–N(7), C(8)–C(17)–C(18), and C(17)–C(9)–O(3), which show differences of 2.0 , 1.9 , 2.0 , and 2.0° , respectively.

The mean values for the various types of bond in cryptopine are listed in Table 4 together with the corresponding mean values for protopine, and the corresponding average values calculated by Sutton (1965). The e.d.s.'s of these mean values have not been included in the Table since there is strong indication that the lengths of the individual bonds of the same type are affected to a certain extent by the character of the adjoining bonds. This is most significant in the aromatic C–C bonds which range from 1.363 to 1.418 Å ($\sigma_{r.m.s.} = 0.003$ Å) in protopine, and from 1.359 Å to 1.407 Å ($\sigma_{r.m.s.} = 0.006$ Å) in cryptopine. However, the overall mean values for the different types of bond as listed in Table 4 are about the same in the two structures, and the largest difference of 0.010 Å in the carbon–oxygen double bond is not significant since it involves only one observation in each case.

In cryptopine, the three bonds at each of the carbon atoms of the benzene rings are very nearly coplanar, since the mean angle at each of these atoms varies from 119.95° to 120.00° . The mean angle at C(14) is 119.5° as compared with 119.3° in protopine. The mean angle at each of the other carbon atoms is between 109.27° and 109.47° thus showing that the four bonds at each of these atoms conform closely to a tetrahedral arrangement. Also, as found in protopine, the three C–N bonds and the N(7)···C(14) distance across the ten-membered ring are tetrahedrally arranged around the nitrogen atom, and the mean angle between them is 109.39° .

Intermolecular distances

The shortest intermolecular distance between the different types of atom in this structure are H···H, 2.39 ; H···O, 2.46 ; H···C, 2.71 ; O···O, 3.35 ; O···C,

3.03 ; and C···C, 3.58 Å. The nearest intermolecular contact to the nitrogen atom is from a hydrogen atom which is at a distance of 3.908 Å away from it, thus showing that the nitrogen atom is well buried in the cryptopine molecule, as is the case in the protopine molecule.

Planarity of the rings

Each of the aromatic six-membered rings is slightly non-planar and has a slight boat form. The equation of the mean plane of the first ring through atoms C(1), C(2), ... C(15), referred to the orthogonal set of axes $X' = ax + cz \cos \beta$, $Y' = by$, $Z' = cz \sin \beta$, and calculated according to the procedure described by Blow (1960) is

$$0.0351X' - 0.9129Y' - 0.4067Z' + 5.3577 = 0, \quad (1)$$

$\chi^2 = 65$, $P < 0.1\%$, and these atoms lie within $+0.015$ and -0.022 Å from that plane. Similarly, the equation of the mean plane of the second ring through atoms C(9), C(10), ... C(18) is

$$0.2953X' + 0.6457Y' + 0.7042Z' - 5.9780 = 0, \quad (2)$$

$\chi^2 = 14.8$, $1\% > P > 0.1\%$, and the deviations of these atoms from their mean plane are within $+0.010$ and -0.008 Å. The angle between the normals to these two planes is 30.1° as compared to 27.8° in protopine.

The carbon–oxygen double bond C(14)–O(5) makes angles of 41.1 and 33.1° with planes (1) and (2), respectively, as compared with 37.4 and 35.0° , respectively, in protopine. The ten-membered ring has a similar shape to that in protopine with atoms O(5) and C(19) lying on the same side of the ring. The two bonds N(7)–C(19) and C(14)–O(5) are skew with respect to each other, the angle between them is 26.5° , and the distance C(19)···O(5) is 3.17 Å. The corresponding values in protopine are 27.9° and 3.19 Å respectively. The mean plane of the four atoms N(7), C(19), C(14), and O(5) makes angles of 69.1° and 63.0° with planes (1) and (2) respectively, while in protopine these two angles are both equal to 60.7° .

Table 4. Mean values for the various types of bond in protopine and cryptopine and the corresponding averages given by Sutton (1965)

Bond type	Protopine	Cryptopine	Sutton's average
C–C aromatic	1.388 Å	1.389 Å	1.394 ± 0.005 Å
C–C single	1.512	1.518	$1.506 \pm 0.005^{(a)}$ $1.53 \pm 0.01^{(b)}$
C–N	1.462	1.462	$1.472 \pm 0.005^{(c)}$
C–O double	1.218	1.208	$1.215 \pm 0.005^{(d)}$
C–O single, type (a)	1.381	1.377	$1.371 \pm 0.016^{(e)}$
C–O single, type (b)	1.425	1.432	$1.426 \pm 0.005^{(f)}$
C–H	1.02	1.02	1.06 to 1.09

(a) in the presence of a carbon–oxygen double bond

(b) in the presence of an aromatic bond

(c) for a trivalent nitrogen

(d) for a ketone group

(e) in conjugated heterocyclic compounds

(f) in saturated heterocyclic compounds

Conclusions

The X-ray analyses of protopine and cryptopine have shown conclusively their molecular structures in the crystalline form. In both molecules, the ten-membered ring is severely buckled, with the nitrogen atom N(7) well buried within it, and is held very close to the C(14) atom which lies across the ring from it. The distance N(7)···C(14) is only 2.57 ± 0.01 Å, which is much shorter than the sum of the van der Waals radii of these two atoms. The three C–N bonds and the C(14)···N(7) distance across the ring are very nearly tetrahedrally arranged around the nitrogen atom. Therefore, in forming derivatives of protopine and cryptopine in which the nitrogen atom is tetravalent, it would be necessary to invert the nitrogen atom so that a fourth atom other than C(14) may be attached to N(7). This inversion would also be accompanied by a considerable increase in the N(7)···C(14) distance. On the other hand, no inversion would be required if the fourth bond is formed between N(7) and C(14) thus transforming the ten-membered ring into two six-membered rings with N(7)–C(14) shared between them.

The carbon–oxygen double bond has ketonic character, makes about $39^\circ \pm 2^\circ$ with the plane of the aromatic six-membered ring nearest to it, and about $34^\circ \pm 1^\circ$ with the other. Each six-membered ring has a very slight boat form, and the angle between them is 152.2° in protopine and 149.9° in cryptopine. The atoms C(19) and O(5) are separated by a distance of 3.18 ± 0.01 Å which is just about the sum of the van der Waals radii of these two atoms.

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Al–O and Si–O Tetrahedral Distances in Aluminosilicate Framework Structures

BY J. B. JONES

Department of Geology, The University of Adelaide, South Australia

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A new determinative curve has been derived for estimating tetrahedral aluminum from the observed tetrahedral bond lengths in aluminosilicate framework structures. The end values of Si–O, 1.603 Å, and Al–O, 1.761 Å, derived from 13 feldspar analyses only, do not differ significantly from those obtained by considering an additional 19 other framework structures.

Introduction

Smith & Bailey (1963) in their second review of aluminum and silicon to oxygen tetrahedral distances, after examining the available information for framework structures, recommended the use of a straight line relationship of aluminum content *versus* tetrahedral distance. Their actual line based on accurately determined feldspar structures extended from 1.606 Å for Si–O to 1.757 Å for Al–O, but because of various

uncertainties they recommended the use of the rounded off figures 1.61 and 1.75.

In the case of the feldspars this rounding off has the effect of placing the line above the majority of the mean T–O distances for frameworks of composition $AlSi_3O_8$ and below the means for those with compositions close to $Al_2Si_2O_8$. Since Smith & Bailey's review four new feldspar determinations have become available and the structures of a number of other frameworks have been completed.