Although the difference map indicated only one carbon peak, C(17) had to be assigned two positions with the same occupancies as the Cl(2) in order to satisfy the CH_2Cl_2 molecular geometry. The present geometry assignment of the solvent molecule is assumed to be the best one since it consumes the maximum extra electron density in that region of the cell while yielding a reasonable description of the disorder.

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Structure of Allocryptopine

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Abstract. 5,7,8,15-Tetrahydro-3,4-dimethoxy-6-methyl[1,3]benzodioxolo[5,6-*e*][2]benzazecin-14(6*H*)-one, $C_{21}H_{23}NO_5$, $M_r = 369{\cdot}40$, monoclinic, $P2_1/c$, $a = 18{\cdot}689\,(6)$, $b = 7{\cdot}253\,(3)$, $c = 14{\cdot}034\,(4)$ Å, $\beta = 108{\cdot}93\,(2)°$, $V = 1799{\cdot}4\,(25)$ Å^3, $Z = 4$, $D_x = 1{\cdot}363$ Mg m^{-3}, $F(000) = 784$, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}1052$ mm^{-1}, room temperature. Final $R = 0{\cdot}054$ for 1676 unique observed reflections. The skeleton of the molecule is similar to those of the other protopine-type alkaloids. The methyl of the methoxy group, which is *ortho* to the fused position, deviates far from the plane of the ring. This methyl group, the carbonyl O atom and the *N*-methyl group are on the same side of the ten-membered ring.

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Introduction. Allocryptopine is one of the protopine-type alkaloids, and has been isolated from several plants (*Papaveraceae, Fumariaceae, Ranunclaceae* and *Rutaceae*). The structural formula of this substance was given by Gadamer (1919) and was obtained by replacing the 3,4-methylenedioxy ring of protopine by 3,4-dimethoxy groups. The typical character of the protopine group is the presence of a ten-membered N heteroring which contains one carbonyl group (Manske & Holmes, 1954). It is of interest to see the influence of the replacement of the substituents on the dihedral angle between the two aromatic planes and to know the shapes of the two methoxy groups.

Experimental. Compound recrystallized from chloroform/methanol solution. Crystal 0·1 × 0·2 × 0·4 mm. Rigaku AFC-5 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell parameters refined by least-squares methods on the basis of 25 2θ values ($33 < 2\theta < 38°$). Intensity measurement performed to $2\theta = 50°$. ω–2θ scan technique, scan speed 2° min^{-1}. Three reference reflections showed no significant change in intensities, $0·990 < |F_o|/|F_o|_{\text{initial}} < 1·034$. Space group $P2_1/c$, determined from systematic absences ($0k0$, k odd; $h0l$, l odd). 2669 reflections measured, $0 \le h \le 20$, $0 \le k \le 8$, $-15 \le l \le 14$, 427 weak reflections classified as unobserved [$|F_o| \le 3\sigma(|F_o|)$], 566 zero, 1676 non-zero unique reflections, corrected for Lorentz–polarization, not for absorption, direct methods, *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Full-matrix least-squares refinements with anisotropic thermal parameters using *UNICS*II (1967) programs. All H atoms found from difference syntheses and refined with isotropic thermal parameters. Unit weights on all reflections. $\sum||F_o| - |F_c||^2$ minimized. Final $R = 0·054$, $wR = 0·052$, $S = 1·6$. $\Delta/\sigma < 0·3$ for non-H atoms and $< 0·8$ for H atoms. Max. and min. heights in final difference synthesis $\pm 0·2$ e Å^{-3}. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. *Final fractional coordinates and* B_{eq} *thermal factors for non-*H *atoms*

E.s.d.'s in parentheses are in the units of the least significant digit.

$$B_{\text{eq}} = \tfrac{4}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} b_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B_{eq}(Å^2)
O1	0·5436 (2)	0·5924 (6)	−0·3988 (2)	6·06 (13)
O2	0·5147 (2)	0·8967 (5)	−0·3991 (3)	6·17 (13)
O3	0·9295 (2)	0·6960 (5)	0·3071 (2)	5·34 (11)
O4	0·9314 (2)	0·3609 (5)	0·3897 (2)	5·65 (12)
O5	0·7427 (2)	0·4441 (5)	−0·0617 (2)	5·14 (12)
C1	0·6267 (2)	0·5789 (7)	−0·2186 (3)	4·42 (14)
C2	0·5809 (3)	0·6632 (7)	−0·3049 (3)	4·58 (16)
C3	0·5626 (3)	0·8486 (9)	−0·3049 (4)	5·61 (19)
C4	0·5931 (3)	0·9544 (8)	−0·2194 (3)	5·03 (18)
C5	0·6798 (3)	1·0002 (7)	−0·0472 (4)	4·95 (17)
C6	0·7669 (3)	0·9914 (7)	−0·0200 (4)	4·73 (17)
N7	0·7968 (2)	0·8139 (5)	0·0299 (3)	4·53 (12)
C8	0·8083 (2)	0·8257 (6)	0·1381 (3)	3·54 (14)
C9	0·8710 (3)	0·5783 (7)	0·2654 (3)	4·75 (17)
C10	0·8707 (3)	0·4038 (8)	0·3068 (3)	4·58 (17)
C11	0·8116 (3)	0·2819 (8)	0·2663 (4)	5·56 (19)
C12	0·7500 (3)	0·3389 (6)	0·1859 (3)	3·81 (15)
C13	0·6846 (3)	0·5742 (7)	0·0532 (4)	5·05 (17)
C14	0·7051 (2)	0·5642 (7)	−0·0420 (4)	5·56 (19)
C15	0·6570 (2)	0·6815 (7)	−0·1306 (4)	3·92 (15)
C16	0·6414 (3)	0·8687 (6)	−0·1329 (4)	4·44 (17)
C17	0·8103 (3)	0·6373 (7)	0·1823 (3)	4·05 (14)
C18	0·7500 (3)	0·5147 (7)	0·1440 (3)	4·27 (15)
C19	0·5019 (3)	0·7358 (7)	−0·4638 (4)	5·39 (18)
C20	1·0009 (3)	0·6416 (10)	0·2936 (4)	7·50 (24)
C21	0·9285 (3)	0·1857 (7)	0·4396 (4)	5·06 (18)
C22	0·8629 (3)	0·7489 (7)	0·0072 (4)	5·08 (18)

Discussion. The fractional atomic coordinates and thermal factors are listed in Table 1.* The bond lengths, bond angles and torsion angles are shown in Table 2. The molecular structure and the numbering scheme are given in Fig. 1 (Johnson, 1965). The 4,5-methylenedioxyphenylene nucleus (ring *A*) and the 3,4-dimethoxyphenylene nucleus (ring *C*) are very slightly boat formed, as are the corresponding rings of the protopine and cryptopine (Hall & Ahmed, 1968*a*,*b*) molecules. The maximum deviation from the mean plane is only 0·019 (6) Å. On the other hand, the ten-membered ring (ring *B*) has a buckled form in the middle of the ring. Ring *B* and its neighbours viewed along the N7···C14 direction are shown in Fig. 2. The structure of the allocryptopine molecule is essentially similar to those of protopine and cryptopine.

In the ten-membered ring, the carbonyl group (C14—O5) and the *N*-methyl group (N7—C22) are on the same side of ring *B*. The distances between atoms N7 and C14 and atoms C22 and O5 are 2·472 (6) and 3·076 (6) Å, respectively. For C14, the shortness of the C14—O5 bond length [1·206 (6) Å] and the flatness of the plane through C13, C15, O5 and C14 [C14 is about 0·124 (6) Å away from the plane through C13, C15 and O5] indicate that the atom C14 has ketonic character. The three bonds at N7 and the short N7···C14 distance are arranged nearly tetrahedrally around the N7 atom; the three C—N—C bond angles are 110·1 (4), 113·3 (4) and 113·4 (3)°. The torsion angles C10—C9—C17—C8 and C9—C17—C8—N7, which show the puckering direction of the N atom position in relation to the plane *C*, are 178·4 (4) and 125·7 (4)°, respectively. The dihedral angle between the mean planes of the two aromatic rings *A* and *C* is 42·17 (6)°. The distance between atoms N7 and C14 and the dihedral angle of this molecule are the shortest and the largest, respectively, among those of protopine

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44617 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Intramolecular bond distances (Å), bond angles (°) and torsion angles (°) with e.s.d.'s in parentheses*

O1—C2	1·375 (5)	C6—N7	1·485 (6)
O1—C19	1·435 (6)	N7—C8	1·465 (6)
O2—C3	1·379 (6)	N7—C22	1·451 (7)
O2—C19	1·450 (6)	C8—C17	1·496 (7)
O3—C9	1·361 (6)	C9—C17	1·404 (6)
O3—C20	1·462 (7)	C9—C10	1·393 (8)
O4—C10	1·371 (5)	C10—C11	1·385 (8)
O4—C21	1·460 (6)	C11—C12	1·388 (6)
O5—C14	1·206 (6)	C12—C18	1·404 (7)
C1—C2	1·379 (6)	C17—C18	1·399 (7)
C2—C3	1·388 (8)	C13—C18	1·514 (6)
C3—C4	1·382 (7)	C13—C14	1·506 (9)
C4—C16	1·401 (6)	C14—C15	1·534 (7)
C5—C16	1·520 (7)	C15—C16	1·387 (7)
C5—C6	1·548 (8)	C1—C15	1·395 (7)
C2—O1—C19	109·9 (4)	C9—C10—C11	121·3 (4)
C3—O2—C19	108·7 (4)	C9—C10—O4	116·5 (4)
C9—O3—C20	114·5 (4)	C11—C10—O4	122·2 (5)
C10—O4—C21	117·1 (4)	C10—C11—C12	119·0 (5)
		C11—C12—C18	119·9 (5)
C2—C1—C15	119·9 (5)	C18—C13—C14	111·4 (4)
C1—C2—C3	120·8 (4)	C13—C14—C15	116·2 (4)
C1—C2—O1	130·8 (5)	C13—C14—O5	124·9 (5)
C3—C2—O1	108·3 (4)	C15—C14—O5	116·5 (5)
C2—C3—C4	120·4 (5)	C14—C15—C1	112·6 (4)
C2—C3—O2	109·2 (4)	C14—C15—C16	128·7 (5)
C4—C3—O2	130·4 (6)	C16—C15—C1	118·7 (4)
C3—C4—C16	118·3 (5)	C4—C16—C5	114·4 (4)
C16—C5—C6	111·0 (5)	C4—C16—C15	121·7 (5)
C5—C6—N7	110·9 (4)	C15—C16—C5	123·6 (4)
C6—N7—C8	110·1 (4)	C8—C17—C9	121·8 (4)
C6—N7—C22	113·3 (4)	C8—C17—C18	120·8 (4)
C8—N7—C22	113·4 (3)	C9—C17—C18	117·3 (4)
N7—C8—C17	110·6 (4)	C12—C18—C17	121·7 (4)
C17—C9—C10	120·8 (5)	C12—C18—C13	120·1 (4)
C17—C9—O3	119·1 (4)	C13—C18—C17	118·2 (4)
C10—C9—O3	120·1 (4)	O1—C19—O2	103·9 (4)
C1—C15—C14—C13	−126·6 (4)	C4—C16—C5—C6	−119·2 (4)
C15—C14—C13—C18	−159·0 (3)	C16—C5—C6—N7	−70·6 (5)
C14—C13—C18—C12	−102·9 (5)	C5—C6—N7—C8	−84·7 (4)
		C6—N7—C8—C17	159·1 (3)
C8—C17—C9—C10	178·4 (4)	N7—C8—C17—C9	125·7 (4)

(2·555 Å, 27·8°) and cryptopine (2·581 Å, 30·1°) (Hall & Ahmed, 1968*a*,*b*).

In allocryptopine, in which two methoxy groups are present instead of the methylenedioxy group in ring *C* of protopine, the methyl C20 of the methoxy group attached to atom C9 deviates far from the plane of ring *C*. This result is the same as in the case of (−)-canadine (Sakai, Taira, Kamigauchi & Takao, 1987) where two methoxy groups are attached to the corresponding positions. This situation is thus most probably caused by the steric effect of the presence of the methylene group C8. The bond between atoms O3 and C20 is on the same side and nearly parallel to that of the atoms N7 and C22 of the tertiary amino group (Fig. 2). The distance between C20 and C22 is 4·085 (7) Å.

Calculations were carried out on a FACOM-M780 computer at the Data Processing Center, Kyoto University. The values for the molecular geometry were calculated using a part of the program package *KPPXRAY* (Taga, Higashi & Iizuka, 1985).

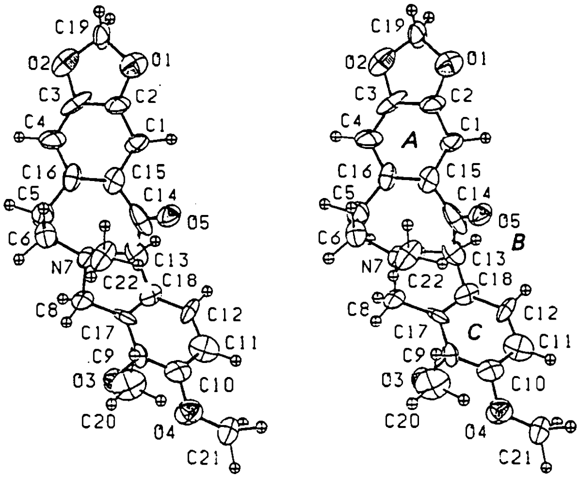

Fig. 1. Molecular structure with the atom-numbering scheme.

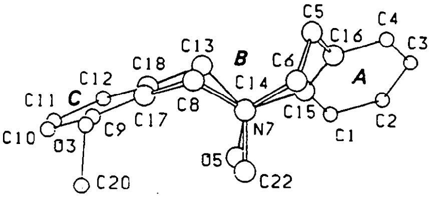

Fig. 2. The ten-membered ring with its neighbours viewed along the line joining atoms N7 and C14.

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