Crystal and Molecular Structure and Absolute Stereochemistry of Cularine Methiodide

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The structure of cularine has been determined by three-dimensional *X*-ray diffraction analysis of its methiodide. Crystals are monoclinic, with $Z = 4$ in a unit cell of dimensions: $a = 22{\cdot}31(5)$, $b = 8{\cdot}43(12)$, $c = 11{\cdot}71(9)$ Å, $\beta = 90{\cdot}9(1)^\circ$, space group $P2_1$. The structure was solved from photographic data by the heavy-atom method and refined by least-squares to R 0·100 for 1416 observed reflexions. The absolute configuration has been determined by the method of anomalous dispersion as L(S)†. On the basis of this work all cularine-type alkaloids also have the L(S)-configuration.

THE alkaloids cularine (1),[1-3] cularimine (2),[2] cularicine (3),[4] and cularidine (4) [5] isolated from *Dicentra* and *Corydalis*, are characterised by the presence of an unusual 7,8-dioxygenated pattern and of a dihydrodibenzoxepin ring system. The structures of this type

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† See R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, 1965, **12**, 81.

[1] R. H. F. Manske, *Canad. J. Res.*, 1940, **18**, *B*, 97.

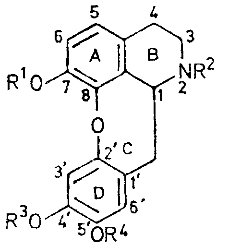
[2] R. H. F. Manske, *Canad. J. Res.*, 1938, **16**, *B*, 81.

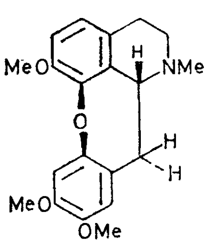
[3] R. H. F. Manske, *J. Amer. Chem. Soc.*, 1950, **72**, 55.

[4] R. H. F. Manske, *Canad. J. Chem.*, 1965, **43**, 989.

[5] R. H. F. Manske, *Canad. J. Chem.*, 1966, **44**, 561.

of alkaloid were confirmed by total syntheses.[6-10] The configuration of cularine was deduced by optical rotatory dispersion methods to be D(R) and hence the conformation (5) has been derived by combining information from its n.m.r. spectrum.[11] It was recently reported,





(1) $R^1 = R^2 = R^3 = R^4 = Me$ (5)

(2) $R^1 = R^3 = R^4 = Me, R^2 = H$

(3) $R^1 = H, R^2 = Me, R^3 + R^4 = CH_2$

(4) $R^1 = H, R^2 = R^3 = R^4 = Me$

however, that the absolute configuration of cularine (1) should be L(S) from chemical evidence.[12a] The present X-ray analysis of the methiodide of (1) was therefore undertaken in order to determine the absolute configuration and molecular structure of (1).

EXPERIMENTAL

The methiodide of (1) was recrystallised from methanol–ether as plates, m.p. 205 °C, elongated along the b axis. Since they were degraded gradually in air, a specimen was sealed in a thin-walled Lindemann glass capillary tube for data collection. Unit-cell dimensions were determined from a preliminary precession photograph and zero-layer Weissenberg photographs about the b axis. Equi-inclination Weissenberg photographs of the layers $h0$—$6l$ were obtained by use of Cu-K_α radiation from a crystal of dimensions 0·11 × 0·03 × 0·01 cm. Intensities were estimated visually. Interlayer scales were tentatively determined by use of Wilson's plots for each layer, and final values were obtained by comparison of F_o and F_c in each layer after all the atoms were located. Since the crystal was very thin, high-angle reflexions were hardly recorded. Of 1645 reflexions for which $\theta < 45°$, *ca.* 230 were too weak to be measured. Corrections for Lorentz and polarisation factors were made in the usual way, but no absorption correction was applied.

Crystal Data.—$C_{21}H_{26}INO_4$, $M = 483·35$. Monoclinic, $a = 22·31(5)$, $b = 8·43(12)$, $c = 11·7(9)$ Å, $\beta = 90·0(1)°$. $U = 2201·9$ Å^3, D_m (by flotation) $= 1·46$, $Z = 4$, $D_c = 1·46$, $F(000) = 976$. Space group $P2_2$ from systematic absences: $0k0$ for k odd. Cu-K_α radiation, $\lambda = 1·5418$ Å; μ(Cu-K_α) $= 124·69$ cm^{-1}.

Structure Determination.—The structure was solved by the heavy-atom method. The co-ordinates of the two independent iodine atoms were derived from the three-dimensional Patterson function, the y co-ordinate of one being taken arbitrarily as zero from the space-group symmetry. In the first three-dimensional Fourier synthesis phased with the iodine atoms only, 49 out of 52 light atoms were found clearly. Successive Fourier calculations revealed all the remaining non-hydrogen atom positions. Structural parameters were refined by the block-diagonal

TABLE 1

Final atomic co-ordinate (10^4) and temperature factors with their standard deviations

	x/a	y/b	z/c	B/Å^2
I(2)	272(17)	0(0)	2930(3)	*
I(1)	3691(16)	605(5)	3434(3)	*
C(21)	1821(21)	1238(60)	9679(41)	4·40(1·25)
C(22)	1278(20)	1939(58)	9596(38)	3·33(1·07)
C(23)	911(22)	2268(65)	8535(42)	4·43(1·24)
C(24)	1319(19)	1517(57)	7542(36)	3·02(1·03)
C(25)	961(20)	1759(60)	6446(37)	3·39(1·08)
C(26)	1432(22)	1293(63)	5420(43)	4·75(1·29)
N(27)	1722(14)	−310(46)	5637(27)	2·97(0·78)
C(28)	2132(17)	31(56)	6708(32)	2·73(0·92)
C(29)	2666(21)	856(72)	6321(40)	5·15(1·27)
C(210)	3197(21)	1097(63)	7209(40)	4·63(1·28)
C(211)	3711(16)	1823(47)	6947(31)	1·26(0·81)
C(212)	4180(23)	2159(66)	7642(44)	4·84(1·29)
C(213)	4131(23)	1340(64)	8883(43)	4·96(1·32)
C(214)	3601(19)	717(70)	9238(36)	4·36(1·10)
C(215)	3109(20)	258(73)	8461(38)	4·94(1·18)
C(216)	2633(12)	−252(38)	8822(22)	3·21(0·63)
C(217)	2060(18)	541(68)	8725(34)	3·73(0·99)
C(218)	1844(17)	727(62)	7663(32)	2·82(0·89)
O(219)	2154(15)	946(48)	10718(29)	6·20(0·92)
C(220)	1948(23)	1640(70)	11752(44)	5·07(1·30)
O(221)	4657(14)	1523(41)	9566(27)	4·58(0·79)
C(222)	4692(20)	451(76)	10571(37)	5·02(1·17)
O(223)	4741(12)	2641(36)	7470(23)	3·01(0·65)
C(224)	4790(22)	3122(65)	6203(43)	4·41(1·19)
C(225)	1228(23)	−1436(69)	5814(44)	5·14(1·34)
C(226)	2082(21)	−546(62)	4567(10)	4·36(1·21)
C(11)	1654(17)	5345(60)	3411(31)	2·95(0·91)
C(12)	1375(22)	6472(65)	2481(42)	4·63(1·26)
C(13)	1791(23)	6931(68)	1662(43)	4·74(1·26)
C(14)	2427(18)	6732(54)	1745(35)	2·45(0·95)
C(15)	2913(18)	7295(51)	1006(34)	2·05(0·89)
C(16)	3525(18)	6845(54)	1128(34)	2·32(0·94)
N(17)	3566(13)	5090(45)	1707(25)	2·95(0·75)
C(18)	3229(14)	5016(47)	2825(27)	1·13(0·75)
C(19)	3573(23)	5902(77)	3868(43)	6·25(1·48)
C(110)	3256(17)	5629(63)	4943(32)	2·85(0·87)
C(111)	3666(18)	6511(54)	5871(35)	2·53(0·95)
C(112)	3460(21)	6311(60)	6874(40)	4·22(1·22)
C(113)	2882(17)	5817(61)	7113(33)	3·07(0·96)
C(114)	2459(15)	5040(49)	6256(28)	1·51(0·78)
C(115)	2752(15)	5076(51)	5199(29)	1·81(0·82)
O(116)	2427(12)	4225(33)	4392(22)	2·64(0·63)
C(117)	2237(14)	5150(45)	3452(26)	0·94(0·73)
C(118)	2663(15)	5594(57)	2712(28)	1·73(0·76)
O(119)	1224(12)	4984(42)	4173(23)	4·24(0·70)
C(120)	603(16)	5038(54)	4087(30)	2·35(0·89)
O(121)	2660(13)	5734(47)	8253(24)	5·00(0·75)
C(122)	2115(17)	5267(60)	8507(31)	3·11(0·98)
O(123)	3718(15)	7057(44)	7924(29)	5·28(0·86)
C(124)	4701(20)	7541(60)	7703(39)	3·59(1·10)
C(125)	3286(19)	4002(57)	783(36)	2·98(1·02)
C(126)	4213(22)	4705(70)	1748(41)	5·11(1·26)

* Anisotropic temperature factors (×10^5) in the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I(1)	321(10)	2019(81)	916(32)	−425(51)	−325(28)	181(90)
I(2)	320(9)	1328(59)	677(26)	345(49)	150(24)	331(84)

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[6] T. Kametani and K. Fukumoto, *J. Chem. Soc.*, 1963, 4289.

[7] T. Kametani, S. Shibuya, S. Seino, and K. Fukumoto, *Tetrahedron Letters*, 1964, 25; *J. Chem. Soc.*, 1964, 4146.

[8] T. Kametani and S. Shibuya, *J. Chem. Soc.*, 1965, 5565.

[9] H. C. Hsu, T. Kikuchi, S. Aoyagi, and H. Iida, *J. Pharm. Soc. Japan*, 1972, **92**, 1030.

[10] H. Iida, H. C. Hsu, T. Kikuchi, and K. Kawano, *J. Pharm. Soc. Japan*, in the press.

[11] N. S. Bhacca, J. C. Craig, R. H. F. Manske, S. K. Roy, M. Shamma, and W. A. Slusarchyk, *Tetrahedron*, 1966, **22**, 1467.

[12] (*a*) J. Kunitomo, K. Morimoto, K. Yamamoto, Y. Yoshikawa, K. Azuma, and K. Fijitani, *Chem. Pharm. Bull. Japan*, 1971, **19**, 2197; (*b*) 'International Tables for X-Ray Crystallography', Kynoch Press, Birmingham, 1962, vol. III.

matrix least-squares method. Anisotropic temperature factors were applied to the iodine atoms, while the thermal motion of the light atoms was assumed to be isotropic. After several cycles of least-squares refinement, the discrepancy factor R was 0·100 for the observed reflexions. Final atomic co-ordinates and temperature factors are given in Table 1, with their standard deviations.

Computations were carried out on a HITAC 8500 computer in Tokyo Institute of Technology. The programs in the Universal Crystallographic Computation Program System (1967) were used with some modifications. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20693 (4 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Absolute Configuration.—Significant differences in intensity was found in each set of fourteen Bijvoet pairs appearing on the oscillation photographs around the b axis. For such pairs, $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ were calculated taking the values $\Delta f'$ $-1{\cdot}20$ and $\Delta f''$ $7{\cdot}00$ for the iodine atom with Cu-K_α radiation.[12b] The co-ordinate systems of real and reciprocal spaces were right-handed. As shown in Table 2, the inequalities observed in all pairs matched those calculated, for the structures of the two independent molecules M1 and M2 (Figure 1) which therefore represent the correct absolute configuration (6). It is clear, therefore, that cularine methiodide has the L(S)-configuration.

Since chemical studies have correlated the molecules in this group,[2,4,5] the present result leads to the conclusion that all cularine-type alkaloids have the L(S)-configuration.

Bhacca and co-workers have examined the o.r.d. curve of the cleaved product (7) with sodium and liquid ammonia. They then assigned the D(R)-configuration to cularine by applying the empirical correlation between o.r.d. and c.d. data for the 1-benzyltetrahydroisoquinoline series, the steric effect of a 2′-substituent being also taken into consideration.[13,14] The present X-ray result, however, shows that cularine has the opposite configuration (6). This suggests that the Cotton effect of the alkaloid having the substituent at the 8- or 2′-position cannot be compared directly, because the conformational change in the benzyl moiety would occur, as suggested by n.m.r. data.[15–17]

TABLE 2

Comparison between the structure factors in Bijvoet pairs (Cu-K_α radiation)

Indices			$I(hkl)$ $I(\bar{h}\bar{k}\bar{l})$	$F(hkl)$	$F(\bar{h}\bar{k}\bar{l})$
3	1	0	>	139	129
4	1	0	<	38	57
6	1	0	<	143	152
−5	1	0	>	71	54
−4	1	1	>	60	52
0	1	1	<	40	82
1	1	1	>	59	49
1	2	1	<	88	96
3	1	1	>	124	108
1	1	2	<	71	80
0	2	2	>	97	78
−1	1	2	<	67	74
2	2	2	<	57	69
8	1	4	<	66	72

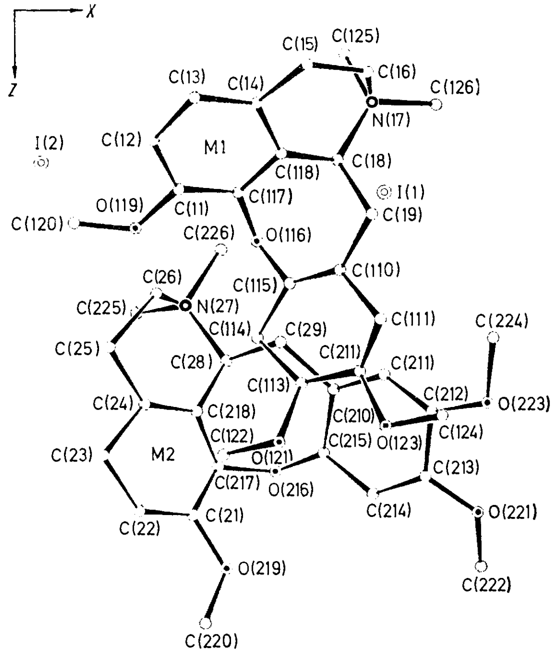
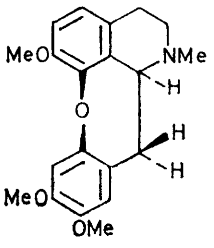
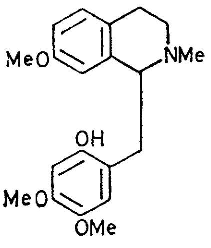


FIGURE 1 The molecules M1 and M2 in the asymmetric unit viewed along the b axis



(6)



(7)

Conformation.—There are some minor differences in conformation between the two molecules in the asymmetric unit. The conformations of the B rings are shown in Figure 2. The B ring of M2 adopts a half-chair conformation, while that of M1 has a distorted form. In both, the nitrogen atoms are tetrahedrally hybridised.

Views along C(115) · · · C(117) and C(215) · · · C(217) (Figure 3) show that the oxepin rings have a twist-boat

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[13] J. C. Craig, M. Martin-Smith, S. K. Roy, and J. B. Stenlake, *Tetrahedron*, 1966, **22**, 1335.

[14] J. C. Craig and S. K. Roy, *Tetrahedron*, 1965, **21**, 401.

[15] M. Tomita, T. Shingu, K. Fujitani, and H. Furukawa, *Chem. Pharm. Bull. Japan*, 1965, **13**, 921.

[16] G. Fraenkel, M. P. Cava, and D. R. Dalton, *J. Amer. Chem. Soc.*, 1967, **89**, 329.

[17] K. Ito, H. Furukawa, H. Tanaka, and S. Kato, *J. Pharm. Soc. Japan*, 1970, **90**, 1169.

shape, the oxygen atoms being the bow. The present result confirms the conformation of the ring given by Bhacca[11] and by Kametani.[18]

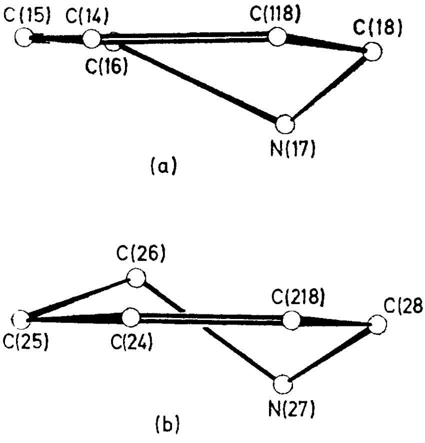

FIGURE 2 The conformation of ring B in (a) M1 viewed along C(11) ··· C(118), and (b) M2 along C(21) ··· C(218)

The molecules look like a hinge as a whole with atoms N(17), C(18), and O(116) in M1 and N(27), C(28), and O(216) in M2 as hinge joints. The angle of the hinge, namely the dihedral angle between the A and D rings is 54·3 in M1 and 59·4° in M2.

Bond Lengths and Angles.—Bond lengths and angles are shown in Tables 3 and 4, with their estimated standard deviations.

Since the crystal used was very thin and small, only 32% of the reflexions in the Cu sphere had measurable intensities, and the standard deviations for atomic co-ordinates were therefore rather large. The individual

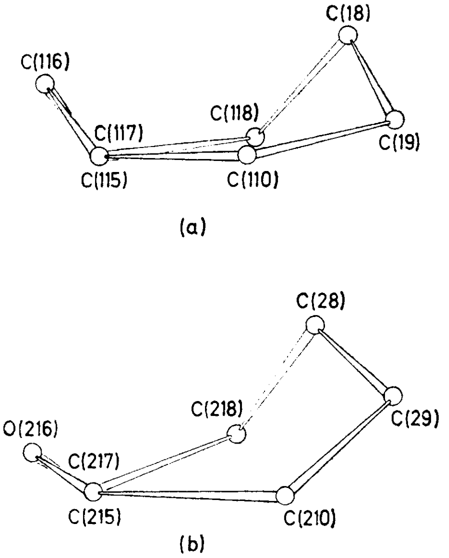

FIGURE 3 The conformation of ring C in (a) M1 viewed along C(115) ··· C(117), and (b) M2 along C(215) ··· C(217)

TABLE 3

Bond lengths (Å) with standard deviations

I(2) ··· N(27)	4·50(4)	O(223)–C(224)	1·54(6)
I(1) ··· N(17)	4·30(4)	C(11)–C(12)	1·57(8)
C(21)–C(22)	1·35(7)	C(11)–C(17)	1·31(6)
C(21)–C(217)	1·38(8)	C(11)–O(119)	1·35(6)
C(21)–O(219)	1·44(7)	C(12)–C(13)	1·40(8)
C(22)–C(23)	1·50(7)	C(13)–C(14)	1·43(7)
C(23)–C(24)	1·62(7)	C(14)–C(15)	1·48(6)
C(24)–C(25)	1·52(7)	C(14)–C(118)	1·57(7)
C(24)–C(218)	1·35(7)	C(15)–C(16)	1·422(6)
C(25)–C(26)	1·66(8)	C(16)–N(17)	1·63(6)
C(26)–N(27)	1·52(7)	N(17)–C(18)	1·52(6)
N(27)–C(28)	1·57(6)	N(17)–C(125)	1·48(7)
N(27)–C(225)	1·51(7)	N(17)–C(126)	1·54(6)
N(27)–C(226)	1·47(7)	C(18)–C(19)	1·62(8)
C(28)–C(29)	1·46(8)	C(18)–C(118)	1·36(6)
C(28)–C(218)	1·42(7)	C(19)–C(110)	1·47(8)
C(29)–C(210)	1·58(8)	C(110)–C(111)	1·59(7)
C(210)–C(211)	1·34(7)	C(110)–C(115)	1·26(7)
C(210)–C(215)	1·64(8)	C(111)–C(112)	1·28(7)
C(211)–C(212)	1·35(7)	C(112)–C(113)	1·39(7)
C(212)–C(213)	1·61(8)	C(112)–O(123)	1·49(6)
C(212)–O(223)	1·33(6)	C(113)–C(114)	1·52(7)
C(213)–C(214)	1·36(8)	C(113)–O(121)	1·43(7)
C(213)–O(221)	1·42(7)	C(114)–C(115)	1·41(6)
C(214)–C(215)	1·47(7)	C(115)–O(116)	1·38(5)
C(215)–O(216)	1·23(7)	O(116)–C(117)	1·41(5)
O(216)–C(217)	1·45(7)	C(117)–C(118)	1·35(6)
C(217)–C(218)	1·34(8)	O(119)–C(120)	1·39(6)
O(219)–C(220)	1·43(7)	O(121)–C(122)	1·32(7)
O(221)–C(222)	1·49(7)	O(123)–C(124)	1·39(6)

TABLE 4

Bond angles (deg.) with standard deviations

C(22)–C(21)–C(217)	119(5)	C(12)–C(11)–C(117)	119(4)
C(22)–C(21)–O(219)	126(5)	C(12)–C(11)–O(119)	109(4)
C(217)–C(21)–O(219)	114(5)	C(117)–C(11)–O(119)	131(5)
C(21)–C(22)–C(23)	128(5)	C(11)–C(12)–C(12)	113(5)
C(22)–C(23)–C(24)	103(4)	C(12)–C(13)–C(14)	126(5)
C(23)–C(24)–C(25)	105(4)	C(13)–C(14)–C(15)	131(4)
C(23)–C(24)–C(218)	128(5)	C(13)–C(14)–C(118)	116(4)
C(25)–C(23)–C(218)	127(5)	C(15)–C(14)–C(118)	112(4)
C(24)–C(25)–C(26)	105(4)	C(14)–C(15)–C(16)	125(4)
C(25)–C(26)–N(27)	111(4)	C(15)–C(16)–N(17)	109(4)
C(26)–N(27)–C(28)	102(4)	C(16)–N(17)–C(18)	112(3)
C(26)–N(27)–C(225)	102(4)	C(16)–N(17)–C(125)	103(3)
C(26)–N(27)–C(226)	106(4)	C(16)–C(17)–C(126)	105(4)
C(28)–N(27)–C(225)	112(4)	C(18)–N)17)–C(18)	112(3)
C(28)–N(27)–C(226)	116(4)	C(18)–N(17)–C(126)	117(4)
C(225)–N(27)–C(226)	117(4)	C(125)–N(17)–C(126)	106(4)
N(27)–C(28)–C(29)	108(4)	N(17)–C(18)–C(19)	113(4)
N(27)–C(28)–C(218)	116(4)	N(19)–C(18)–C(118)	110(4)
C(29)–C(28)–C(218)	115(5)	C(18)–C(19)–C(110)	110(5)
C(28)–C(29)–C(210)	118(5)	C(19)–C(110)–C(11)	103(4)
C(29)–C(210)–C(211)	123(5)	C(19)–C(110)–C(115)	135(5)
C(29)–C(210)–C(215)	116(4)	C(111)–C(110)–C(115)	121(5)
C(211)–C(210)–C(215)	121(5)	C(110)–C(111)–C(112)	111(4)
C(210)–C(211)–C(212)	128(5)	C(111)–C(112)–C(113)	125(5)
C(211)–C(212)–C(213)	113(5)	C(111)–C(112)–O(123)	124(5)
C(211)–C(212)–O(223)	134(5)	C(113)–C(112)–O(123)	108(4)
C(213)–C(212)–O(223)	110(4)	C(112)–C(113)–C(114)	125(4)
C(212)–C(213)–C(214)	121(5)	C(112)–C(113)–O(121)	123(5)
C(212)–C(213)–O(221)	113(4)	C(114)–C(113)–O(121)	112(4)
C(214)–C(213)–O(221)	126(5)	C(113)–C(114)–C(115)	106(4)
C(213)–C(214)–C(215)	124(5)	C(110)–C(115)–C(114)	130(5)
C(210)–C(215)–C(214)	110(5)	C(110)–C(115)–O(116)	119(4)
C(210)–C(215)–O(216)	125(5)	C(114)–C(115)–O(116)	110(4)
C(214)–C(215)–O(216)	122(5)	C(115)–O(116)–C(117)	113(3)
C(215)–O(216)–C(217)	126(4)	C(11)–C(117)–O(116)	113(4)
C(21)–C(217)–O(216)	119(5)	C(11)–C(117)–C(118)	131(4)
C(21)–C(217)–C(218)	124(5)	O(116)–C(117)–C(118)	117(4)
O(216)–C(217)–C(218)	116(5)	C(14)–C(118)–C(18)	126(4)
C(24)–C(218)–C(28)	122(5)	C(14)–C(118)–C(117)	114(4)
C(24)–C(218)–C(217)	117(5)	C(18)–C(118)–C(117)	120(4)
C(28)–C(218)–C(217)	121(5)	C(11)–O(119)–C(120)	131(4)
C(21)–O(219)–C(220)	119(4)	C(113)–O(121)–C(122)	124(4)
C(213)–O(221)–C(222)	114(4)	C(112)–O(123)–C(124)	109(4)
C(212)–O(223)–C(224)	108(4)		

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[18] T. Kametani, S. Shibuya, and W. D. Ollis, *J. Chem. Soc.* (*C*), 1967, 2877.

variations between bonds of the same type cannot therefore be considered significant. The mean bond lengths in the two independent molecules are: C(sp^2)–C(sp^2) 1·43, C(sp^2)–C(sp^3) 1·47, C(sp^3)–C(sp^2) 1·54, C(sp^2)–O(methoxy) 1·45, O–CH_3 1·46, C(sp^2)–O(ether bridge) 1·37, and C–N 1·53 Å. The bond angles around the N(17) and N(27) atoms have almost the tetrahedral value. The angles of the ether bridge (C–O–C) are 113 in M1 and 125° in M2.

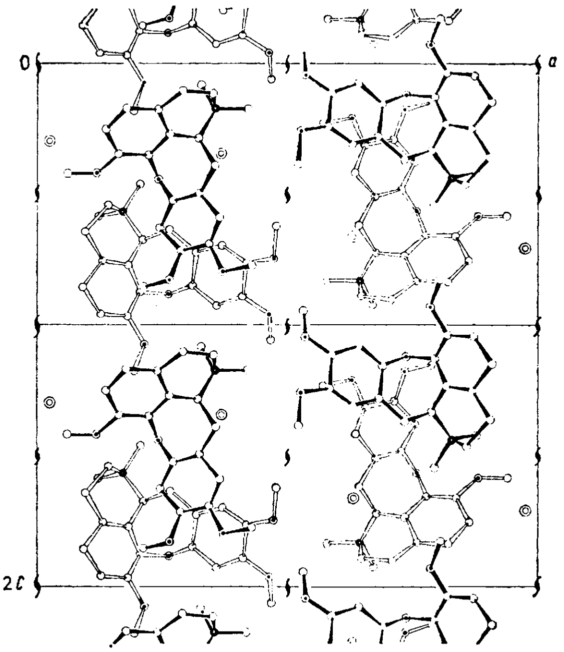

FIGURE 4 The crystal structure projected along the *b* axis

TABLE 5

Intermolecular distances <3·6 Å

C(26) · · · O(119^{I})	3·47	C(124) · · · C(213^{II})	3·51
C(26) · · · O(116^{I})	3·55	C(125) · · · C(214^{II})	3·60
C(29) · · · C(114^{I})	3·56	C(214) · · · C(125^{II})	3·39
O(119) · · · C(226^{II})	3·58	O(121) · · · C(15^{III})	3·52
O(121) · · · O(216^{II})	3·45	O(121) · · · C(125^{III})	3·57
O(123) · · · C(214^{II})	3·46	O(216) · · · C(15^{IV})	3·34
O(123) · · · C(215^{II})	3·09	O(219) · · · C(15^{IV})	3·53
O(123) · · · O(216^{II})	3·49		

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I x, y, z
II $x, 1 + y, z$
III $x, y, 1 + z$
IV $x, -1 + y, 1 + z$

Crystal Structure.—A packing diagram of the crystal viewed along the *b* axis is shown in Figure 4, and intermolecular distances <3·6 Å are listed in Table 5. Two independent molecules, with hinge-like form mentioned earlier, have the same orientation with respect to the *b* axis and can be related to each other by a non-crystallographic screw about the *b* axis, having *ca.* 70° rotation and 4 Å translation.

The relation of the iodide ion to the nearest nitrogen atom is different in the two molecules. As shown in Figure 5, the iodide ion I (1), lies below the plane formed by C(18), C(125), and C(126), while I (2) is above the plane formed by C(26), C(225), and C(226). The angle between the vector I(1) · · · N(17) and the first plane is 81·8°, and that between the vector I(1) · · · N(27) and the second plane is 79·5°. The $I^- \cdots N^+$ distances are 4·30 and 4·50 Å.

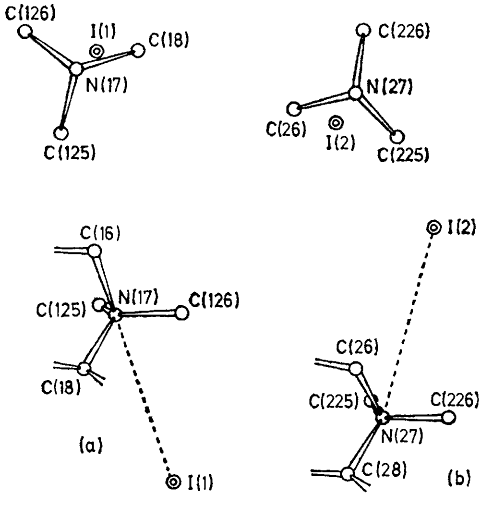

FIGURE 5 Relationship of the iodide ion to the nitrogen atom in (a) M1 and (b) M2

[2/2785 *Received, 11th December*, 1972]