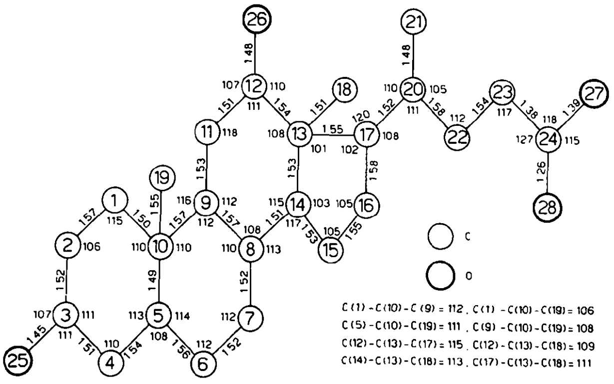

Fig. 4. Bond distances (Å) and angles (°) of DCA.

bond lengths and angles of DCA are given in Fig. 4. Their average e.s.d.'s are 0·027Å and 1·5° with maximum values of 0·037 Å and 2·1°.

Discussion. The low number of intensity data recorded (34% of the whole Cu $K\alpha$ sphere) have caused large standard deviations in the atomic coordinates and in the bond lengths and angles. Nevertheless, since the DCA geometry is known from the DCAETH crystal structure, the main interests of this work lie both in the determination of the DMS arrangement within the canals and in the possibility of locating the guest molecules by potential-energy calculations. The packing is equal to that of DCAETH (see Figs. 2 and 3). The O(31) coordinates probably represent an average position of the DMS and W O atoms, which were indistinguishable in the difference syntheses. The O atoms of DMS and W both form two hydrogen bonds with two O(26) atoms, the O···O distances being 2·74 and 2·77 Å, and are necessarily acceptor and donor in turn. Good van der Waals contacts exist among the DMS methyl groups. The S—C bonds of DMS nearly coincide with the two directions allowed for the C—C bond of ETH in DCAETH. Moreover the dimensions of the cavities suggest that molecules bulkier than DMS can be accommodated with difficulty without a change of the host lattice.

We thank Hilger & Watts for the data collection and the Consiglio Nazionale delle Ricerche for financial support.

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Absolute Configurations of the Stereoisomeric *N,N*-Dimethyl-4-methyl-4-phenyl-1,2,3,4-tetrahydro-2-naphthylamines*

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Abstract. $C_{19}H_{24}IN$, $M_r = 393·3$, orthorhombic, $P2_12_12_1$ (systematic absences: $h00$, h odd; $0k0$, k odd; $00l$, l odd), $a = 7·569$ (3), $b = 8·201$ (8), $c = 30·01$ (2) Å, $Z = 4$, $D_c = D_o$ (CCl_4/C_6H_6) = 1·40 Mg m^{-3}. The structure was refined to a final R of 0·038 for 1667 reflections. The absolute configuration, determined using anomalous dispersion by iodine, confirms tentative absolute configurations proposed earlier for this series of potent analgetics.

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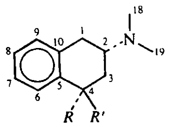
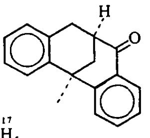
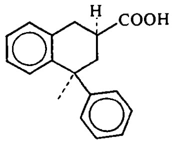
Introduction. In connection with our continuing interest in aminotetralins as potential analgetics of the morphine type (Martin, Parulkar, Gusseck, Anderson, Grunewald & White, 1969; Kandeel & Martin, 1973; Galpin, Kandeel & Martin, 1978), we have sought to determine the stereochemical and conformational relationships among the *N*,*N*-dimethyl-4-methyl-4-phenyl-1,2,3,4-tetrahydro-2-naphthylamines (I). The two racemates, (±)-(I*a*) and (±)-(I*b*), exhibit analgetic potency similar to codeine in mice (Kandeel & Martin, 1973). However, preliminary unpublished results indicate that one of the stereoisomers, (−)-(I*a*), is slightly more potent than morphine while (+)-(I*a*), (+)-(I*b*) and (−)-(I*b*) are similar to codeine in potency. The absolute stereochemistries shown for the enantiomers of (I*a*) and (I*b*) were tentatively assigned from the circular-dichroism spectra of the bridged ketones (II) (Galpin, Kandeel & Martin, 1978), derived from the precursor acids (III), using the modified octant rule for the C=O $n \rightarrow \pi^*$ transition of aryl ketones developed by Snatzke (1965). We now report an X-ray crystallographic study of the hydroiodide salt of (+)-(I*a*) undertaken to establish conclusively the absolute configurations in this series.



(+)-(I*a*) $R = \overset{11}{\mathrm{Me}}, R' = \overset{12\text{-}17}{\mathrm{C_6H_5}}$
(−)-(I*b*) $R = \mathrm{C_6H_5}, R' = \mathrm{Me}$



(II)



(III)

Colorless crystals of (+)-(I*a*) hydroiodide, m.p. 516 K, were grown from methanol. A needle 0·1 × 0·2 × 0·4 mm was mounted with the *b* axis parallel to the goniostat φ axis. The space group was determined to be $P2_12_12_1$. A Syntex four-circle computer-controlled diffractometer ($P2_1$) with a graphite monochromator (Mo $K\alpha$ radiation, λ = 0·71069 Å) and pulse-height analyzer was used for collection of intensities. The cell constants were determined by least-squares treatment of 16 reflections. The θ–2θ scan technique was employed with a variable scan rate of 0·5 to 29·3° min^{-1} (in 2θ), a scan range of 2·0°, and a background to scan time ratio of 1·0. 1964 reflections with $2\theta <$ 50° were collected and 1667 with $I > 3\sigma(I)$ were considered observed. There were no significant variations in the intensities of three check reflections that were monitored every 100 reflections. The intensities were corrected for Lorentz and polarization effects, but not absorption.

The iodine was located on a Patterson map. All but one of the nonhydrogen atoms were located on a Fourier map with iodine phasing, and the last nonhydrogen position (for a benzene C) was calculated. Full-matrix least-squares refinement of positional and isotropic thermal parameters of nonhydrogen atoms reduced *R* to 0·096. Anisotropic refinement brought *R* down to 0·048. Nineteen of the H atoms were located in difference maps, and calculated positions were used for the remaining five. Further refinement (anisotropic nonhydrogen atoms and isotropic H) brought *R* to the final value of 0·038. Four H atoms [H(N), H2(C1),

Table 1. *Fractional coordinates* ($\times 10^4$) *of the nonhydrogen atoms, with standard deviations in parentheses*

	x	*y*	*z*
I	3088 (1)	−466 (1)	−2951 (1)
N	2271 (7)	3713 (7)	−3018 (2)
C(1)	−640 (11)	2729 (9)	−3300 (3)
C(2)	850 (9)	3928 (8)	−3367 (2)
C(3)	90 (9)	5622 (9)	−3378 (2)
C(4)	−963 (10)	5889 (8)	−3812 (2)
C(5)	−2198 (9)	4423 (10)	−3890 (2)
C(6)	−3540 (10)	4536 (12)	−4206 (3)
C(7)	−4737 (12)	3294 (12)	−4278 (3)
C(8)	−4599 (12)	1898 (11)	−4031 (3)
C(9)	−3281 (12)	1740 (9)	−3722 (3)
C(10)	−2045 (12)	2986 (8)	−3652 (2)
C(11)	−2029 (14)	7440 (9)	−3761 (3)
C(12)	359 (10)	6096 (9)	−4200 (2)
C(13)	482 (10)	5030 (9)	−4552 (2)
C(14)	1696 (13)	5296 (13)	−4901 (3)
C(15)	2807 (13)	6609 (14)	−4885 (3)
C(16)	2707 (13)	7639 (13)	−4535 (3)
C(17)	1531 (12)	7398 (11)	−4194 (3)
C(18)	3940 (10)	4573 (12)	−3142 (3)
C(19)	1771 (13)	4180 (12)	−2559 (3)

Table 2. *Fractional coordinates* ($\times 10^3$) *of the hydrogen atoms, with standard deviations in parentheses*

	x	*y*	*z*
*H(N)	250	250	−300
H1(C1)	−105 (9)	291 (8)	−303 (2)
*H2(C1)	−14	161	−329
H(C2)	139 (7)	367 (7)	−362 (2)
H1(C3)	90 (8)	641 (8)	−337 (2)
H2(C3)	−68 (8)	570 (8)	−310 (2)
H(C6)	−366 (8)	546 (9)	−439 (2)
*H(C7)	−551	345	−450
H(C8)	447 (10)	110 (9)	−409 (2)
H(C9)	−328 (8)	84 (7)	−352 (2)
H1(C11)	−265 (8)	775 (8)	−401 (2)
H2(C11)	−123 (10)	806 (9)	−367 (2)
H3(C11)	−268 (9)	721 (9)	−355 (2)
H(C13)	−23 (8)	409 (7)	−452 (2)
H(C14)	185 (11)	464 (9)	−509 (2)
H(C15)	357 (10)	669 (9)	−516 (2)
H(C16)	378 (12)	862 (12)	−453 (3)
*H(C17)	145	819	−392
H1(C18)	502 (10)	422 (10)	−302 (3)
H2(C18)	420 (13)	431 (12)	−341 (3)
H3(C18)	369 (10)	580 (10)	−317 (3)
H1(C19)	98 (12)	352 (12)	−244 (3)
H2(C19)	150 (12)	514 (11)	−258 (3)
H3(C19)	263 (11)	375 (11)	−232 (3)

* Not successfully refined.

H(C7), and H(C17)] did not converge to reasonable positions and were included at calculated positions. The refinement was based on F_o, the quantity minimized being $\sum w(F_o - F_c)^2$. The scattering factors used were those of Hanson, Herman, Lea & Skillman (1964), except for the anomalous-dispersion factors for iodine (Lonsdale, 1962). No correction was applied for extinction.*

Table 3. *Bond lengths* (Å) *with standard deviations in parentheses*

N–C(2)	1·513 (9)	N–H(N)	1·01
N–C(18)	1·495 (10)	C(1)–H1(C1)	0·89 (6)
N–C(19)	1·482 (10)	C(1)–H2(C1)	1·00
C(1)–C(2)	1·511 (11)	C(2)–H(C2)	0·89 (5)
C(1)–C(10)	1·514 (12)	C(3)–H1(C3)	0·89 (6)
C(2)–C(3)	1·508 (10)	C(3)–H2(C3)	1·03 (6)
C(3)–C(4)	1·544 (10)	C(6)–H(C6)	0·94 (7)
C(4)–C(5)	1·544 (10)	C(7)–H(C7)	0·90
C(4)–C(11)	1·517 (11)	C(8)–H(C8)	0·98 (8)
C(4)–C(12)	1·547 (10)	C(9)–H(C9)	0·96 (6)
C(5)–C(6)	1·393 (10)	C(11)–H1(C11)	0·93 (6)
C(5)–C(10)	1·387 (10)	C(11)–H2(C11)	0·84 (8)
C(6)–C(7)	1·382 (13)	C(11)–H3(C11)	0·82 (7)
C(7)–C(8)	1·372 (14)	C(13)–H(C13)	0·95 (6)
C(8)–C(9)	1·370 (13)	C(14)–H(C14)	0·78 (7)
C(9)–C(10)	1·403 (11)	C(15)–H(C15)	0·90 (8)
C(12)–C(13)	1·375 (10)	C(16)–H(C16)	1·14 (9)
C(12)–C(17)	1·391 (12)	C(17)–H(C17)	1·05
C(13)–C(14)	1·412 (11)	C(18)–H1(C18)	0·94 (8)
C(14)–C(15)	1·369 (15)	C(18)–H2(C18)	0·87 (9)
C(15)–C(16)	1·354 (14)	C(18)–H3(C18)	1·03 (8)
C(16)–C(17)	1·370 (13)	C(19)–H1(C19)	0·88 (9)
		C(19)–H2(C19)	0·82 (8)
		C(19)–H3(C19)	1·04 (8)

Discussion. When crystals of the hydrobromide of (+)-(I*a*) proved unsuitable for X-ray analysis, we turned to the hydroiodide, which formed excellent crystals whose structure was readily solved. Tables 1 and 2 list fractional coordinates, Table 3 lists bond lengths, Table 4 bond angles and Table 5 selected torsion angles; Fig. 1 depicts the molecule and Fig. 2 the unit cell. The relative configuration assigned previously (Martin *et al.*, 1969) was easily verified. The absolute configuration in Fig. 1, proposed earlier (Kandeel &

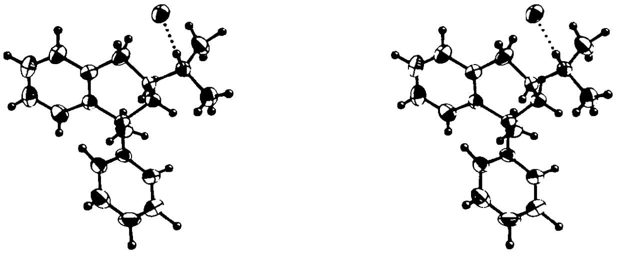


Fig. 1. Stereoscopic view of a (+)-(I*a*) hydroiodide molecule. H atoms are shown as spheres, and other atoms as 50% probability ellipsoids.

Table 4. *Bond angles* (°) *with standard deviations in parentheses*

C(2)–N–C(18)	111·9 (5)	C(5)–C(4)–C(12)	111·3 (6)	C(13)–C(12)–C(17)	117·2 (7)
C(2)–N–C(19)	115·7 (6)	C(11)–C(4)–C(12)	109·1 (7)	C(12)–C(13)–C(14)	121·1 (7)
C(2)–N–H(N)	105·7	C(4)–C(5)–C(6)	119·5 (6)	C(12)–C(13)–H(C13)	114 (2)
C(18)–N–C(19)	109·0 (5)	C(4)–C(5)–C(10)	122·4 (6)	C(14)–C(13)–H(C13)	125 (2)
C(18)–N–H(N)	109	C(6)–C(5)–C(10)	118·0 (6)	C(13)–C(14)–C(15)	119·8 (8)
C(19)–N–H(N)	105	C(5)–C(6)–C(7)	122·4 (6)	C(13)–C(14)–H(C14)	121 (4)
C(2)–C(1)–C(10)	109·9 (6)	C(5)–C(6)–H(C6)	121 (3)	C(15)–C(14)–H(C14)	118 (4)
C(2)–C(1)–H1(C1)	106 (3)	C(7)–C(6)–H(C6)	116 (3)	C(14)–C(15)–C(16)	119·0 (8)
C(2)–C(1)–H2(C1)	109	C(6)–C(7)–C(8)	118·9 (7)	C(14)–C(15)–H(C15)	115 (3)
C(10)–C(1)–H1(C1)	112 (3)	C(6)–C(7)–H(C7)	116	C(16)–C(15)–H(C15)	126 (3)
C(10)–C(1)–H2(C1)	115	C(8)–C(7)–H(C7)	125	C(15)–C(16)–C(17)	121·8 (8)
H1(C1)–C(1)–H2(C1)	105	C(7)–C(8)–C(9)	120·2 (7)	C(15)–C(16)–H(C16)	114 (3)
N–C(2)–C(1)	111·2 (6)	C(7)–C(8)–H(C8)	114 (3)	C(17)–C(16)–H(C16)	124 (3)
N–C(2)–C(3)	113·2 (5)	C(9)–C(8)–H(C8)	126 (3)	C(16)–C(17)–C(12)	121·1 (8)
N–C(2)–H(C2)	104 (2)	C(8)–C(9)–C(10)	121·2 (7)	C(16)–C(17)–H(C17)	122
C(1)–C(2)–C(3)	108·7 (6)	C(8)–C(9)–H(C9)	121 (3)	C(12)–C(17)–H(C17)	116
C(1)–C(2)–H(C2)	107 (2)	C(10)–C(9)–H(C9)	118 (3)	N–C(18)–H1(C18)	120 (3)
C(3)–C(2)–H(C2)	112 (2)	C(9)–C(10)–C(1)	118·1 (7)	N–C(18)–H2(C18)	108 (4)
C(2)–C(3)–C(4)	110·3 (6)	C(9)–C(10)–C(5)	119·3 (7)	N–C(18)–H3(C18)	109 (3)
C(2)–C(3)–H1(C3)	114 (3)	C(1)–C(10)–C(5)	122·6 (7)	H1(C18)–C(18)–H2(C18)	94 (4)
C(2)–C(3)–H2(C3)	105 (3)	C(4)–C(11)–H1(C11)	115 (3)	H1(C18)–C(18)–H3(C18)	120 (4)
C(4)–C(3)–H1(C3)	106 (3)	C(4)–C(11)–H2(C11)	99 (4)	H2(C18)–C(18)–H3(C18)	102 (4)
C(4)–C(3)–H2(C3)	113 (3)	C(4)–C(11)–H3(C11)	102 (3)	N–C(19)–H1(C19)	113 (4)
H1(C3)–C(3)–H2(C3)	109 (3)	H1(C11)–C(11)–H2(C11)	119 (3)	N–C(19)–H2(C19)	104 (4)
C(3)–C(4)–C(5)	109·3 (6)	H1(C11)–C(11)–H3(C11)	113 (3)	N–C(19)–H3(C19)	114 (3)
C(3)–C(4)–C(11)	108·0 (6)	H2(C11)–C(11)–H3(C11)	108 (3)	H1(C19)–C(19)–H2(C19)	117 (4)
C(3)–C(4)–C(12)	108·6 (6)	C(4)–C(12)–C(13)	123·6 (6)	H1(C19)–C(19)–H3(C19)	86 (4)
C(5)–C(4)–C(11)	110·4 (6)	C(4)–C(12)–C(17)	119·2 (7)	H2(C19)–C(19)–H3(C19)	123 (4)

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33927 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Selected torsion angles* (°)

C(1)–C(2)–C(3)–C(4)	−70·8	C(1)–C(2)–N–C(18)	165·5	C(3)–C(4)–C(12)–C(13)	116·0
C(2)–C(3)–C(4)–C(5)	47·2	C(3)–C(2)–N–C(18)	−71·7	C(3)–C(4)–C(12)–C(17)	−62·1
C(3)–C(4)–C(5)–C(10)	−12·6	C(1)–C(2)–N–C(19)	−68·9	C(5)–C(4)–C(12)–C(13)	−4·3
C(4)–C(5)–C(10)–C(1)	−0·8	C(3)–C(2)–N–C(19)	53·9	C(5)–C(4)–C(12)–C(17)	177·5
C(5)–C(10)–C(1)–C(2)	−19·9			C(11)–C(4)–C(12)–C(13)	−126·4
C(10)–C(1)–C(2)–C(3)	54·2			C(11)–C(4)–C(12)–C(17)	55·4

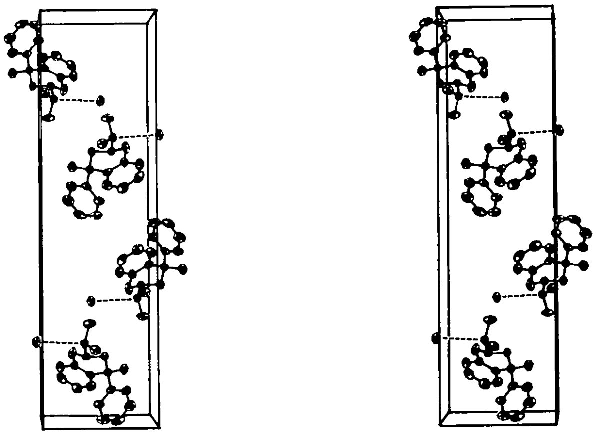

Fig. 2. Stereoscopic view of a unit cell in the *a* axis projection; the *b* axis is horizontal, and the *c* axis vertical.

Martin, 1973), was shown to be correct when it gave an *R* factor of 0·038 compared with 0·041 for the other enantiomer. As the other three stereoisomers have been unambiguously correlated with this one (Martin *et al.*, 1969; Kandeel & Martin, 1973), their configurations are also verified. The most potent analgetic of the four [(−)-(I*a*)] is thus the one most closely related to morphine in structure.

The cyclohexene-type ring is a typical half-chair, with the methyl and protonated dimethylamino groups pseudoequatorial. The protonated dimethylamino group adopts the staggered arrangement about the C(2)–N bond which puts H(N) and C(3) antiparallel [torsion angle H(N)–N–C(2)–C(3) is 169°]. H(N) is hydrogen bonded to the iodide ion [I–N distance 3·496 (6) Å]. The phenyl group is rotated to approximately bisect the C(3)–C(4)–C(11) angle, making the torsion angle C(5)–C(4)–C(12)–C(13) −4·3°. The angle between the aromatic rings, whose C atoms average 0·009 Å from the least-squares planes, is 106·0°.

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Monocrotaline: A Pyrrolizidine Alkaloid

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Abstract. $C_{16}H_{23}NO_6$, orthorhombic, $P2_12_12_1$, a = 10·16 (1), b = 11·44 (1), c = 13·63 (2) Å, D_m = 1·35, D_c = 1·363 Mg m^{-3}, μ(Cu $K\alpha$) = 0·78 mm^{-1}. Intensities were measured using the equi-inclination Weissenberg method; films were scanned with an automatic densitometer. The structure was refined to R = 0·0799. The ester carbonyl bonds are synparallel and directed below the plane of the 11-membered macro-ring.

Introduction. Monocrotaline, a pyrrolizidine alkaloid (PA) derived from retronecine, is commonly found in the plant family *Leguminosea* (genus *Crotalaria*) (Bull, Culvenor & Dick, 1968). The PA's are extremely toxic