tions would introduce much closer C···H and/or H···H repulsive contacts between the rings, as suggested by an examination of a Dreiding molecular model of the complex. In the observed structure, these inter-ring C···H and H···H close contacts (those less than the van der Waals radii sum) range from 2·48 to 2·70 Å and 2·13 to 2·33 Å.

The authors are indebted to G. B. Robertson and P. O. Whimp (Research School of Chemistry, ANU, Canberra, Australia) for the collection of the intensity data, to Max O'Connor (La Trobe University, Victoria) for the crystals and to the Australian Research Grants Committee for financial support.

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The Crystal and Molecular Structure of 3-Methyl-mono-*o*-benzylautumnaline

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(*Received* 22 *June* 1976; *accepted* 24 *July* 1976)

The title compound ($C_{30}H_{37}NO_5$) crystallizes in space group $P\bar{1}$ with $a = 21{\cdot}657\,(4)$, $b = 13{\cdot}193\,(2)$, $c = 5{\cdot}291\,(1)$ Å; $\alpha = 105{\cdot}52\,(1)$, $\beta = 89{\cdot}39\,(1)$, $\gamma = 113{\cdot}03\,(1)°$; $Z = 2$. The structure was solved by direct methods from diffractometer data and refined anisotropically to $R = 0{\cdot}05$. A comparison of three automatic direct-methods computer systems, *MULTAN*, *SHELX* and *XCSD*, is presented. The analysis establishes that the compound is the *cis*-1,3 isomer. The molecule is considerably distorted from planarity through the combined effects of intra- and intermolecular forces.

Introduction

Biosynthetic studies of colchicine, the major alkaloid of *Colchicum autumnale* have shown that it is derived from the aromatic amino acids phenylalanine and tyrosine *via* the formation of autumnaline (Battersby, Herbert, McDonald, Ramage & Clements, 1972). To study the steric requirements of the enzyme-active sites in autumnaline the two stereoisomers of 3-methyl-mono-*o*-benzlyautumnaline (ratio 9:1) were prepared (Stachulski, 1974). We have undertaken the X-ray analysis of the minor isomer (I) to establish the relative stereochemistry of the active sites.

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Experimental

3-Methyl-mono-*o*-benzylautumnaline (I) (Fig. 1) crystallized as long needles from an ether–petroleum solution. After preliminary photographic work a crystal was mounted on a Syntex $P2_1$ diffractometer and the cell dimensions were determined by a least-squares refinement of 15 automatically centred reflexions. Cell constants and other crystal data are given in Table 1.

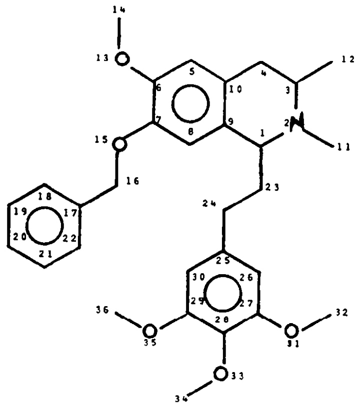

Fig. 1. 3-Methyl-mono-*o*-benzylautumnaline (I): chemical formula and numbering of atoms.

Table 1. *Crystal data*

3-Methyl-mono-*o*-benzylautumnaline, $C_{30}H_{37}NO_5$, m.p. 103 °C, triclinic, $P\bar{1}$. $a = 21{\cdot}657\,(4)$, $b = 13{\cdot}193\,(2)$, $c = 5{\cdot}291\,(1)$ Å. $\alpha = 105{\cdot}52\,(1)$, $\beta = 89{\cdot}39\,(1)$, $\gamma = 113{\cdot}03\,(1)°$. $M_r = 491$, $U = 1332{\cdot}9\,(4)$ Å^3, $D_x = 1{\cdot}22$ g cm^{-3}, $Z = 2$.

Intensities ($2\theta \leq 110°$) were collected at room temperature with graphite-monochromated Cu $K\alpha$ radiation. Measurements were made over a 2θ range of 2° plus the calculated α_1–α_2 separation by the $\omega/2\theta$ scan technique. The scan rate varied from 2 to 29° min^{-1}, depending on the intensity of the reflexion measured in a rapid preliminary scan. Background counts were taken at each end of the scan range for a period equal to half the scan time. The intensities of two standard reflexions were monitored every 25 reflexions: no significant reduction was observed. The intensities were corrected for Lorentz and polarization effects.

Structure determination and refinement

In order to examine the relative efficiency of different direct-methods systems available for the automatic solution of centrosymmetric structures we used the following programs:

(1) *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974): a multisolution phase-refinement technique utilizing a weighted tangent formula. The combined figure of merit is based on: (*a*) $M_{\text{abs.}}$ (Germain, Main & Woolfson, 1971), (*b*) ψ_0 test (Cochran & Douglas, 1955), (*c*) R_k (Karle & Karle, 1966).

(2) *SHELX* (Sheldrick, 1975): a multisolution technique utilizing Σ_2 sign expansion along a predetermined pathway with selective rejection tests based on: (*a*) $M_{\text{abs.}}$ (Germain *et al.*, 1971) during the expansion, (*b*) $\text{NQT} = -\Sigma E_{h+k}E_{h-k}(2E_h^2E_k^2 - E_h^2 - E_k^2)$. This value is related to the probability of the sign of the product $E_{h-k}E_{h+k}$ as derived by Giacovazzo (1974) when E_h, E_{h+k}, E_{h-k} are large, E_k small (or E_k large and E_h small).

(3) *XCSD* [a minicomputer system written by Oeser & Sheldrick (1975) for the ECLIPSE and NOVA computers]: a multisolution phase-refinement technique where the tangent formula is constrained to include trio phase relations which consist of one positive and two negative quartets (Hauptman, 1974*a*,*b*). The

Table 2. *Results of the three direct-method systems*

System	Phase sets	*E* values ($E_{\text{min.}}$ in parentheses)	Phase relations	Computing time (min)
MULTAN	2^8	220 (1·72)	2000	10
SHELX	2^{19}	570 (1·20)	5000	6
XCSD	2^7	475 (1·42)	4000	2

Figures of merit for the top phase sets

				Fraction of atoms correctly located from *E* map
MULTAN	$M_{\text{abs.}}$(0·8)*	ψ_0(1·2)	R_k (1·0)	
	1·093	2·36 × 10^2	22·50	
	†1·069	2·10 × 10^2	22·91	30/36
	1·020	2·08 × 10^2	25·98	
	1·021	2·08 × 10^2	26·17	
SHELX	$M_{\text{abs.}}$	NQT		
	0·999	−0·302		
	0·897	−0·288		32/36
	0·827	−0·276		
	†0·915	−0·183		
XCSD	NQEST	R_A		
	†−0·82	0·29		
	−0·54	0·40		36/36
	−0·48	0·44		
	−0·37	0·40		

* The weights given to the three figures of merit are in parentheses.

† Correct phase set.

Table 3. *Atom coordinates and e.s.d.'s* ($\times 10^4$)

	x	y	z
C(1)	1389 (1)	1484 (2)	2852 (5)
N(2)	931 (1)	1717 (2)	4805 (4)
C(3)	1118 (1)	2956 (2)	6080 (5)
C(4)	1809 (1)	3459 (2)	7598 (5)
C(5)	3010 (1)	3993 (2)	6461 (6)
C(6)	3481 (1)	3853 (2)	4800 (6)
C(7)	3272 (1)	2954 (2)	2435 (6)
C(8)	2600 (1)	2226 (2)	1823 (5)
C(9)	2119 (1)	2356 (2)	3551 (5)
C(10)	2326 (1)	3252 (2)	5837 (5)
C(11)	236 (1)	1148 (3)	3534 (6)
C(12)	612 (2)	3164 (3)	7980 (6)
O(13)	4160 (1)	4534 (2)	5244 (4)
C(14)	4408 (2)	5336 (3)	7808 (7)
O(15)	3781 (1)	2873 (2)	925 (4)
C(16)	3619 (2)	1902 (3)	−1369 (6)
C(17)	4278 (2)	1853 (3)	−2143 (6)
C(18)	4666 (2)	2481 (4)	−3634 (9)
C(19)	5302 (2)	2494 (5)	−4132 (10)
C(20)	5530 (2)	1823 (4)	−3276 (9)
C(21)	5161 (2)	1220 (4)	−1715 (12)
C(22)	4547 (2)	1255 (4)	−1086 (12)
C(23)	1354 (1)	261 (2)	2495 (5)
C(24)	1631 (1)	115 (2)	4966 (5)
C(25)	1721 (1)	−1001 (2)	4419 (5)
C(26)	2200 (1)	−1160 (2)	2772 (6)
C(27)	2276 (1)	−2196 (3)	2137 (6)
C(28)	1874 (1)	−3082 (2)	3150 (5)
C(29)	1408 (1)	−2913 (2)	4837 (5)
C(30)	1330 (1)	−1876 (2)	5471 (5)
O(31)	2731 (1)	−2431 (2)	516 (4)
C(32)	3126 (2)	−1560 (3)	−645 (7)
O(33)	1919 (1)	−4133 (2)	2362 (4)
C(34)	2387 (2)	−4258 (3)	3996 (8)
O(35)	1038 (1)	−3826 (2)	5763 (4)
C(36)	589 (2)	−3670 (3)	7669 (7)

rejection test is based on the value of NQEST (De Titta, Edmonds, Langs & Hauptman, 1975) and applied when about 200 phases have been determined. A reliability index R_A (Roberts, Petterson, Sheldrick, Isaacs & Kennard, 1973) is calculated from $E_{\text{obs.}}$ and $E_{\text{calc.}}$ (obtained by a point-atom structure factor calculation from the positions of the N strongest peaks in the E map).

The last two systems also include a similarity test based on sign products which are structure invariants, thus taking into account possible changes of unit-cell origin.

The three programs were run on an IBM 370/165 computer. The E maps of the four best different phase sets in each system were calculated. The results are summarized in Table 2. In each system the top E maps gave essentially the complete molecule with a common orientation but shifted relative to each other. In each system the E map yielding the correct structure was the one with the largest proportion of high peaks defining the molecule. Ranked according to the combined figures of merit, these were the second phase set in *MULTAN*, the fourth in *SHELX* and the first in *XCSD* (Table 2). These results reflect the power of NQEST in discriminating between correct and incorrect phase sets, as already observed by De Titta *et al.* (1975). The application of selective rejection tests during the phase-refinement procedure reduces computing time considerably.

The positional parameters of the nonhydrogen atoms were refined isotropically by full-matrix least squares (Sheldrick, 1975). The H atoms were introduced into the structure by applying the appropriate geometrical constraints. The refinement continued with anisotropic parameters for the heavy atoms and an overall temperature factor for the H atoms. The six methyls were treated as rigid groups, and the other H atoms refined so that the C—H vectors remained constant in magnitude and direction. At the last stages of refinement, individual group isotropic temperature factors were employed for the methyl H atoms, an overall temperature

Table 4. *Anisotropic temperature factors and e.s.d.'s* ($\text{Å}^2 \times 10^3$)

The temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^*)$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	35 (1)	42 (2)	41 (2)	14 (1)	7 (1)	18 (1)
N(2)	33 (1)	43 (1)	49 (1)	16 (1)	7 (1)	16 (1)
C(3)	44 (2)	42 (2)	50 (2)	16 (1)	11 (1)	23 (1)
C(4)	45 (2)	41 (2)	46 (2)	11 (1)	7 (1)	19 (1)
C(5)	42 (2)	41 (2)	53 (2)	13 (1)	2 (1)	15 (1)
C(6)	33 (2)	44 (2)	60 (2)	18 (2)	3 (1)	11 (1)
C(7)	35 (2)	49 (2)	53 (2)	20 (1)	10 (1)	17 (1)
C(8)	35 (2)	46 (2)	44 (2)	15 (1)	5 (1)	16 (1)
C(9)	36 (1)	37 (2)	42 (2)	17 (1)	4 (1)	16 (1)
C(10)	40 (2)	37 (2)	46 (2)	16 (1)	7 (1)	17 (1)
C(11)	37 (2)	57 (2)	75 (2)	22 (2)	10 (2)	18 (1)
C(12)	52 (2)	69 (2)	66 (2)	16 (2)	18 (2)	34 (2)
O(13)	34 (1)	61 (1)	77 (2)	11 (1)	2 (1)	5 (1)
C(14)	46 (2)	65 (2)	75 (2)	6 (2)	−10 (2)	0 (2)
O(15)	37 (1)	64 (1)	65 (1)	13 (1)	15 (1)	17 (1)
C(16)	49 (2)	64 (2)	63 (2)	12 (2)	13 (2)	26 (2)
C(17)	50 (2)	61 (2)	67 (2)	21 (2)	18 (2)	28 (2)
C(18)	96 (3)	174 (5)	130 (4)	107 (4)	67 (3)	93 (3)
C(19)	102 (3)	207 (6)	146 (4)	128 (4)	82 (3)	100 (4)
C(20)	74 (3)	118 (3)	118 (3)	55 (3)	43 (2)	61 (3)
C(21)	77 (3)	134 (4)	254 (7)	129 (5)	69 (4)	68 (3)
C(22)	73 (3)	122 (4)	227 (6)	121 (4)	70 (3)	55 (3)
C(23)	35 (1)	38 (2)	41 (2)	7 (1)	1 (1)	14 (1)
C(24)	48 (2)	40 (2)	40 (2)	10 (1)	2 (1)	21 (1)
C(25)	45 (2)	39 (2)	41 (2)	12 (1)	3 (1)	20 (1)
C(26)	44 (2)	44 (2)	56 (2)	18 (1)	8 (1)	20 (1)
C(27)	46 (2)	54 (2)	50 (2)	12 (1)	11 (1)	28 (2)
C(28)	54 (2)	39 (2)	49 (2)	9 (1)	3 (1)	25 (1)
C(29)	49 (2)	39 (2)	50 (2)	15 (1)	5 (1)	15 (1)
C(30)	45 (2)	43 (2)	45 (2)	12 (1)	6 (1)	21 (1)
O(31)	69 (1)	72 (1)	76 (2)	26 (1)	32 (1)	44 (1)
C(32)	63 (2)	82 (3)	82 (3)	29 (2)	33 (2)	30 (2)
O(33)	75 (1)	45 (1)	66 (1)	7 (1)	3 (1)	35 (1)
C(34)	109 (3)	60 (2)	85 (3)	20 (2)	−5 (2)	50 (2)
O(35)	72 (1)	46 (1)	88 (2)	29 (1)	29 (1)	25 (1)
C(36)	69 (2)	70 (2)	76 (2)	37 (2)	27 (2)	27 (2)

factor for the H atoms of the unsubstituted phenyl ring (as this exhibited a very large thermal motion), and another overall temperature factor for the remaining H atoms. The function minimized was $\Sigma\, w|F_o - k|F_c||^2$ with weights $w = [\sigma^2(F_o) + gF_o^2]^{-1}$; g was given a fixed value of 0·001 which yielded a small variation of the mean value of $(F_o - k|F_c|)^2$ as a function of F. Unobserved reflexions $[F_o < 3\sigma(F_o)]$ were excluded from the refinement.

The final agreement indices were: $R = \Sigma|F_o - k|F_c|| / \Sigma F_o = 0{\cdot}055$ and $R_w = \Sigma\, w^{1/2}|F_o - k|F_c|| / \Sigma\, w^{1/2} F_o = 0{\cdot}059$ for 351 refined parameters and 2810 unique observed reflexions.* Scattering factors were taken from Cromer & Mann (1968). Final atomic parameters are given in Tables 3, 4 and 5.

Table 5. *Hydrogen-atom coordinates* (×10⁴) *and isotropic temperature factors* (Å² ×10³)

	x	*y*	*z*	*U*²
H(1)	1216	1557	1029	56 (2)
H(3)	1118	3362	4558	56 (2)
H(41)	1783	3064	9163	56 (2)
H(42)	1962	4374	8435	56 (2)
H(5)	3169	4685	8276	56 (2)
H(8)	2438	1545	−11	56 (2)
H(111)	−91	1232	5056	73 (5)
H(112)	103	248	2557	73 (5)
H(113)	180	1569	2115	73 (5)
H(121)	149	2989	6859	96 (7)
H(122)	830	4056	9135	96 (7)
H(123)	505	2622	9278	96 (7)
H(141)	4948	5720	7769	96 (7)
H(142)	4293	4893	9312	96 (7)
H(143)	4216	6000	8242	96 (7)
H(161)	3300	1123	−913	56 (2)
H(162)	3363	2013	−2950	56 (2)
H(18)	4482	2986	−4464	150 (7)
H(19)	5616	3053	−5224	150 (7)
H(20)	6000	1769	−3832	150 (7)
H(21)	5345	701	−937	150 (7)
H(22)	4273	801	269	150 (7)
H(231)	1644	71	902	56 (2)
H(232)	833	−341	1992	56 (2)
H(241)	1284	131	6441	56 (2)
H(242)	2114	821	5705	56 (2)
H(26)	2515	−477	1983	56 (2)
H(30)	964	−1753	6786	56 (2)
H(321)	3443	−1930	−1781	94 (7)
H(322)	3436	−805	905	94 (7)
H(323)	2853	−1323	−1918	94 (7)
H(341)	2343	−5131	3228	129 (9)
H(342)	2294	−4099	6044	129 (9)
H(343)	2889	−3671	3827	129 (9)
H(361)	391	−4457	8231	97 (7)
H(362)	177	−3537	6883	97 (7)
H(363)	856	−2957	9377	97 (7)

Results and discussion

Molecular geometry

The bond lengths and angles uncorrected for librational motion are given in Tables 6 and 7 and a list of selected torsion angles in Table 8. A stereo view of the molecule is shown in Fig. 2. The stereoisomer studied here possesses the *cis*-1,3 arrangement and thus the major isomer has the *trans*-1,3 arrangement, a result which is of interest in relation to the findings obtained

Table 6. *Bond lengths and e.s.d.'s* (Å)

N(2)–C(1)	1·481 (3)	C(9)–C(1)	1·523 (3)
C(23)–C(1)	1·545 (3)	C(3)–N(2)	1·478 (3)
C(11)–N(2)	1·465 (3)	C(4)–C(3)	1·513 (4)
C(12)–C(3)	1·535 (4)	C(10)–C(4)	1·508 (3)
C(6)–C(5)	1·375 (4)	C(10)–C(5)	1·401 (4)
C(7)–C(6)	1·406 (4)	O(13)–C(6)	1·373 (3)
C(8)–C(7)	1·377 (4)	O(15)–C(7)	1·375 (3)
C(9)–C(8)	1·409 (3)	C(10)–C(9)	1·376 (4)
C(14)–O(13)	1·432 (4)	C(16)–O(15)	1·436 (4)
C(17)–C(16)	1·501 (4)	C(18)–C(17)	1·344 (5)
C(22)–C(17)	1·370 (5)	C(19)–C(18)	1·394 (5)
C(20)–C(19)	1·338 (5)	C(21)–C(20)	1·339 (5)
C(22)–C(21)	1·383 (5)	C(24)–C(23)	1·532 (3)
C(25)–C(24)	1·512 (3)	C(26)–C(25)	1·390 (4)
C(30)–C(25)	1·388 (4)	C(27)–C(26)	1·392 (4)
C(28)–C(27)	1·392 (4)	O(31)–C(27)	1·373 (3)
C(29)–C(28)	1·384 (4)	O(33)–C(28)	1·379 (3)
C(30)–C(29)	1·395 (4)	O(35)–C(29)	1·373 (3)
C(32)–O(31)	1·424 (4)	C(34)–O(33)	1·424 (4)
C(36)–O(35)	1·425 (4)		

Table 7. *Bond angles and e.s.d.'s* (°)

C(9)–C(1)–N(2)	113·8 (2)	C(23)–C(1)–N(2)	109·7 (2)
C(23)–C(1)–C(9)	109·9 (2)	C(3)–N(2)–C(1)	113·5 (2)
C(11)–N(2)–C(1)	109·1 (2)	C(11)–N(2)–C(3)	111·5 (2)
C(4)–C(3)–N(2)	108·6 (2)	C(12)–C(3)–N(2)	111·9 (2)
C(12)–C(3)–C(4)	109·1 (2)	C(10)–C(4)–C(3)	111·4 (2)
C(10)–C(5)–C(6)	121·1 (3)	C(7)–C(6)–C(5)	119·4 (2)
O(13)–C(6)–C(5)	125·2 (3)	O(13)–C(6)–C(7)	115·4 (2)
C(8)–C(7)–C(6)	119·5 (2)	O(15)–C(7)–C(6)	115·1 (2)
O(15)–C(7)–C(8)	125·4 (3)	C(9)–C(8)–C(7)	121·1 (2)
C(8)–C(9)–C(1)	118·8 (2)	C(10)–C(9)–C(1)	122·2 (2)
C(10)–C(9)–C(8)	119·0 (2)	C(5)–C(10)–C(4)	120·4 (2)
C(9)–C(10)–C(4)	119·6 (2)	C(9)–C(10)–C(5)	120·0 (2)
C(14)–O(13)–C(6)	117·0 (2)	C(16)–O(15)–C(7)	118·3 (2)
C(17)–C(16)–O(15)	106·3 (2)	C(18)–C(17)–C(16)	122·7 (3)
C(22)–C(17)–C(16)	120·3 (3)	C(22)–C(17)–C(18)	116·5 (3)
C(19)–C(18)–C(17)	121·5 (4)	C(20)–C(19)–C(18)	120·9 (4)
C(21)–C(20)–C(19)	118·5 (4)	C(22)–C(21)–C(20)	120·7 (4)
C(21)–C(22)–C(17)	121·5 (4)	C(24)–C(23)–C(1)	113·5 (2)
C(25)–C(24)–C(23)	112·4 (2)	C(26)–C(25)–C(24)	118·8 (2)
C(30)–C(25)–C(24)	121·8 (2)	C(30)–C(25)–C(26)	119·4 (2)
C(27)–C(26)–C(25)	120·3 (2)	C(28)–C(27)–C(26)	120·3 (2)
O(31)–C(27)–C(26)	124·2 (3)	O(31)–C(27)–C(28)	115·4 (2)
C(29)–C(28)–C(27)	119·3 (2)	O(33)–C(28)–C(27)	119·9 (2)
O(33)–C(28)–C(29)	120·7 (2)	C(30)–C(29)–C(28)	120·4 (2)
O(35)–C(29)–C(28)	115·5 (2)	O(35)–C(29)–C(30)	124·1 (2)
C(29)–C(30)–C(25)	120·3 (2)	C(32)–O(31)–C(27)	116·5 (2)
C(34)–O(33)–C(28)	114·7 (2)	C(36)–O(35)–C(29)	117·9 (2)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32078 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

by stereospecific tritiation of autumnaline (Battersby, McDonald & Stachulski, 1977).

In order to compare the geometrical features of the isoquinoline system in autumnaline with other similar systems which have been analysed by X-rays we searched the Connectivity File of the Cambridge Crystallographic Data Centre (Kennard, Watson, Allen, Motherwell, Town & Rodgers, 1975) for compounds containing this molecular fragment. The search was made with *CONNSER* (Motherwell, 1977), which matches the connectivity matrix of the atoms and bonds of the search structure with those of the Connectivity File. The search yielded 14 references, mainly to large fused-ring systems, of which nine cited atomic coordinates.

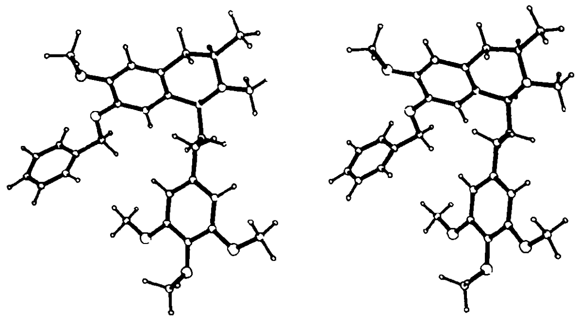

Fig. 2. Stereoscopic view of the molecule.

The bond lengths of the hetero ring taken from the published structures which were determined to a reasonable accuracy are given in Table 9, together with the values found in the present structure. The bond-scatter (s) values derived from equivalent bonds in these molecules range from 0·008 to 0·014 Å (Table 9). These values compare well with the bond-scatter of 0·011 Å obtained from the twelve aromatic bonds for rings *A* and *B* in (I). Ring *C* was not included in this analysis in view of the systematic errors in bond lengths resulting from its large thermal motion. It appears, therefore, that the variations in the equivalent bonds of the hetero ring in the molecules listed in Table 9 are due mainly to random errors, and the average values ($\bar{r}$) given may be taken as representative bond lengths. The variations in equivalent bond and torsion angles are much larger because of the influence of the different geometrical constraints which arise in these large fused-ring molecules.

Table 8. *Selected torsion angles* (°)

C(9)–C(1)–N(2)–C(3)	33·1	C(12)–C(3)–C(4)–C(10)	178·6	C(27)–C(28)–O(33)–C(34)	92·2
C(1)–N(2)–C(3)–C(4)	−62·5	C(11)–N(2)–C(1)–C(9)	158·1	C(30)–C(29)–O(35)–C(36)	−5·8
N(2)–C(3)–C(4)–C(10)	56·3	N(2)–C(1)–C(23)–C(24)	−66·1	C(5)–C(6)–O(13)–C(14)	10·2
C(3)–C(4)–C(10)–C(9)	−23·3	C(1)–C(23)–C(24)–C(25)	−168·6	C(8)–C(7)–O(15)–C(16)	−5·6
C(4)–C(10)–C(9)–C(1)	−6·2	C(23)–C(24)–C(25)–C(26)	65·9	C(7)–O(15)–C(16)–C(17)	−163·9
C(10)–C(9)–C(1)–N(2)	1·8	C(26)–C(27)–O(31)–C(32)	−2·7	O(15)–C(16)–C(17)–C(18)	−83·9

Table 9. *Bond lengths* (Å) *of the hetero ring in* 1,2,3,4-*tetrahydroisoquinoline derivatives*

	C(1)–N(2)	N(2)–C(3)	C(3)–C(4)	C(4)–C(10)	C(10)–C(9)	C(1)–C(9)
I(*a*)	1·481	1·478	1·513	1·508	1·376	1·523
II(*b*)	1·465	1·479	1·531	1·555*	1·396	1·548
III(*b*)	1·485	1·487	1·520	1·522	1·405	1·520
IV(*c*)	1·496	1·478	1·520	1·503	1·398	1·525
V(*d*)	1·457	1·460	1·515	1·510	1·392	1·532
VI(*e*)	1·470	1·465	1·506	1·524	1·404	1·523
VII(*f*)	1·465	1·474	1·583*	1·506	1·387	1·509
$\bar{r}$†	1·474	1·474	1·518	1·512	1·394	1·526
s‡	0·014	0·009	0·008	0·009	0·010	0·012

(*a*) Present analysis. (*b*) Karle, Estlin & Karle (1967). (*c*) Brown & Trefonas (1972). (*d*) Gokrinsky & Moss (1973). (*e*) Roques, Piquion, Fourme & André (1974). (*f*) Cameron, Freer, Doyle & Wright (1974).

* Bonds excluded from the analysis.

† $\bar{r} = \Sigma r_i/n$.

‡ $s = |\Sigma(r_i - \bar{r})^2/(n-1)|^{1/2}$.

The agreement between equivalent bonds involving the five ether O atoms is good. The average value of C_{sp^2}—O is 1·375 and O—C_{sp^3} is 1·429 Å with bond-scatters of 0·003 and 0·005 Å respectively. The methoxy groups, with the exception of O(33)—C(34), are nearly coplanar with the phenyl rings (Table 8). The relaxation of the close 1···6 interactions of the H atoms involved in these systems is achieved by a widening of the valency angles at O(13), O(15), O(31) and O(35) and the adjacent aromatic C(6), C(7), C(27) and C(29). O(33)—C(34) is nearly perpendicular to the phenyl ring, thus avoiding close contact with any of the adjacent methoxy groups.

The hetero ring adopts an approximate envelope shape in which C(3) deviates by 0·7 Å from the best plane through the other five atoms. The overall molecular conformation, as determined by the torsion angles about the chain C—C bonds, results mainly from intramolecular non-bonded interactions. The observed staggered conformations about C(1)—C(23) and C(23)—C(24) lead to minimal steric repulsions between the attached groups. The observed twists (88·4, 65·9°) at C(16)—C(17) and C(24)—C(25) probably result from intra- as well as intermolecular forces. All the methyl H atoms possess staggered orientations about the corresponding $C-CH_3$, $N-CH_3$ and $O-CH_3$ bonds.

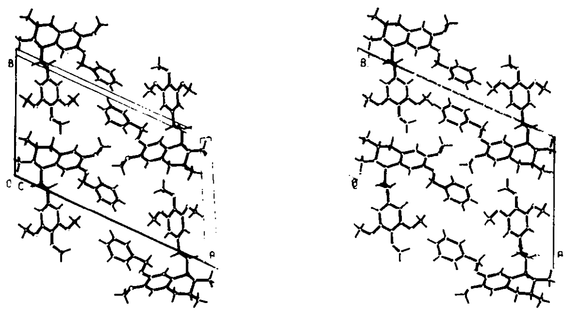

Fig. 3. Stereoscopic view of the packing arrangement along **c**.

Table 10. *Results of rigid-body analysis of ring C* [*including* C(16) *to* C(22)]

The eigenvectors of **L** and **T** are referred to the molecular system of inertia **I** which is referred to the crystal axes. All eigenvectors are given in terms of the corresponding direction cosines × 10^4.

	Eigenvalues		Eigenvectors		
	5·3 (at. wt Å^2)		−9750	159	2217
	13·0	**I**	−1623	6304	−7591
	18·3		−1519	−7761	−6121
(18·4°)*	103 × 10^{-3} rad^2		9978	243	623
(4·4)	6	**L**	602	−7309	−6798
(2·4)	2		290	6820	−7308
(0·31 Å)	94 × 10^{-3} Å^2		1480	4260	8925
(0·25)	62	**T**	522	−9046	4231
(0·21)	45		9876	−161	−1561

$$[\Sigma(\Delta U_{ij})^2/(6n-s)]^{1/2} = 0{\cdot}004\ (n=7,\ s=20)$$

Corrected bond lengths (Å)

C(16)—C(17)	1·508	C(19)—C(20)	1·392
C(17)—C(18)	1·399	C(20)—C(21)	1·396
C(17)—C(22)	1·424	C(21)—C(22)	1·389
C(18)—C(19)	1·399		

* The corresponding r.m.s. amplitudes are given in parentheses.

Molecular packing and thermal-motion analysis

The crystal structure is shown in Fig. 3. The molecules stack along the short axis and are linked together mainly by H···H and C···H interactions. The unsubstituted phenyl ring (*C*) is involved in rather weak interactions with methyl H atoms, resulting in the large observed thermal motion of this ring compared to the rest of the molecule. The results of a rigid-body-motion analysis (Schomaker & Trueblood, 1968) of the vibration tensors of the ring C atoms and the adjacent C(16) are summarized in Table 10. The r.m.s. of ΔU_{ij} (0·004 Å^2) compares well with the mean (0·003 Å^2) of $\sigma(U_{ij})$ for these atoms, thus indicating an approximate rigid-body motion for this group. The translational vibrations are nearly isotropic, whereas the librational motion is highly anisotropic with the largest libration (18·4°) about the first inertial axis which coincides approximately with the C(16)—C(17) single bond. In other words, ring *C* vibrates vigorously about C(16)—C(17), leading to significant shifts in the coordinates of four ring atoms [C(18), C(19), C(21), C(22)] towards this libration axis; hence the observed shortening of the related bond lengths. The corrected bond lengths are given in Table 10.

We thank Professor A. R. Battersby for suggesting the analysis and Dr G. M. Sheldrick for the computer programs and valuable discussions. We are grateful to the SRC for the provision of the diffractometer and to the MRC for financial support.

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Sodium Acetate Trihydrate: A Redetermination

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(*Received* 4 *May* 1976; *accepted* 30 *June* 1976)

$C_2H_3NaO_2.3H_2O$, monoclinic, *C*2/*c*; $a = 12{\cdot}353$ (5), $b = 10{\cdot}466$ (6), $c = 10{\cdot}401$ (6) Å, $\beta = 111{\cdot}69$ (4)°, 23 °C; $M_r = 136{\cdot}08$; $Z = 8$, $D_x = 1{\cdot}447$ g cm^{-3}; the material was recrystallized from aqueous solutions. The final *R* was 0·038 (2279 unique diffractometer data, Mo *Kα*, $2\theta \leq 65°$, isotropic H, anisotropic non-H). The Na^+ ion is coordinated by six O atoms in a distorted octahedral arrangement at distances of 2·349 to 2·512 Å. The C—O distances are 1·253 and 1·257 Å. Extensive hydrogen bonding in two dimensions, involving both carboxyl O atoms and the waters of hydration joins the acetate ions and waters of hydration into sheets parallel to (001); chains of O polyhedra coordinating the Na^+ ions connect the sheets to complete the three-dimensional structure.

Introduction

Crystals of the title compound are currently being used in a study of the ESR of methyl radicals in crystals (Rogers, 1975). The crystal and molecular structure determination of the title compound was undertaken to further elucidate the results of the ESR studies and to reveal the hydrogen-bonding network in the crystal.

A single crystal of approximate dimensions 0·25 × 0·29 × 0·89 mm [μ(Mo *Kα*) = 1·477 cm^{-1}] was sealed in a glass capillary tube with a drop of saturated aqueous solution to prevent loss of water from the crystal. The diffraction conditions hkl: $h + k = 2n$, $h0l$: $l = 2n$ ($h = 2n$), the absence of other non-related conditions, and the monoclinic symmetry indicate the space groups *C*2/*c* and *Cc*. Diffraction data were measured at 23 °C with a Picker FACS-I automatic diffractometer and Zr-filtered Mo *Kα* radiation. The cell parameters were determined by a least-squares fit to the angular settings (2θ, ω, χ, φ) of 12 reflections in the range $35 \leq 2\theta \leq 39°$, for which the α_1, α_2 doublet was clearly resolved [λ(Mo $K\alpha_1$) = 0·70926 Å]. The 2279 unique reflections (including 352 'unobserved') in the $+h + k \pm l$ region were collected for $2\theta \leq 65°$ with the θ–2θ scan method: a scan speed of 1° (2θ) min^{-1}; 10 s backgrounds; and scan ranges of 1·2° (2θ) plus the α_1,α_2 divergences. Three standard reflections measured after every 50 data were used to scale the data.

The data were reduced and standard deviations calculated as a function of counting statistics, as reported previously (Wei & Ward, 1976); the least-squares refinement weights were calculated from the standard deviations of the structure factors by weight (w) = $1/[\sigma^2 + (0{\cdot}02F)^2]$; an extinction correction was