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Delphinifoline: a Lycoctonine Alkaloid with Configuration 1α-OH

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Abstract

Delphinifoline, $C_{23}H_{37}NO_7$, orthorhombic, $P2_12_12_1$, $a = 15{\cdot}750\ (5)$, $b = 16{\cdot}356\ (6)$, $c = 8{\cdot}415\ (2)$ Å, $V = 2166{\cdot}4$ Å^3, $D_c = 1{\cdot}347$ Mg m^{-3}, $Z = 4$, μ(Mo $K\alpha$) = $0{\cdot}1062$ mm^{-1}; $F(000) = 952$; $R = 0{\cdot}038$ for 1154 contributing reflections. The substitution pattern is 1α-OH, 4β-CH_2OCH_3, 6β-OH, 7α-OH, 8β-OH, 14α-OH, 16β-OCH_3, N-ethyl. The presence of an oxygenated functional group at C(7) established delphinifoline as a member of the lycoctonine family of alkaloids. The α configuration observed at C(1) is unexpected and calls into question the structural assignments of all alkaloids of this class.

Introduction

Delphinifoline was isolated as a minor alkaloid from *Aconitum delphinifolium* DC (Aiyar, Codding, Kerr, Benn & Jones, 1981) by chromatography on neutral alumina. Recrystallization from methanol yielded colourless needles, m.p. 491–493 K. The crystal chosen for analysis had dimensions $0{\cdot}15 \times 0{\cdot}10 \times 0{\cdot}20$ mm and was mounted about the c axis. Data were collected on a Picker FACS-I diffractometer operated in the $\theta/2\theta$ scan mode with a scan width $\Delta 2\theta = (1{\cdot}4 + 0{\cdot}692 \times \tan\theta)°$ and a scan rate of 1° min^{-1}. Background was measured for 20 s at either end of the scan. Of the 1642 reflections accessible with $2\theta < 45°$, 852 had intensities $I > 3\sigma(I)$ where $\sigma(I) = [T + S^2B + 0{\cdot}02I^2]^{1/2}$, T is the

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$) *for non-hydrogen atoms in delphinifoline*

$U_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$ where $\tilde{\mathbf{U}}$ is the diagonalized U_{ij} matrix. The e.s.d. for U_{eq} is $\sim 5 \times 10^{-3}$ Å^2.

	x	y	z	U_{eq} (Å^2)
C(1)	8147 (4)	3654 (5)	29 (9)	38
C(2)	7577 (5)	4329 (5)	−573 (9)	46
C(3)	6669 (5)	4039 (5)	−798 (9)	53
C(4)	6319 (5)	3549 (5)	636 (9)	38
C(5)	6929 (4)	3619 (4)	2118 (8)	32
C(6)	6611 (4)	3026 (4)	3417 (9)	35
C(7)	7194 (4)	2270 (4)	3265 (8)	28
C(8)	7905 (4)	2247 (5)	4530 (8)	34
C(9)	8376 (4)	3074 (5)	4554 (8)	30
C(10)	8512 (4)	3423 (4)	2897 (8)	26
C(11)	7812 (4)	3272 (4)	1626 (8)	26
C(12)	9402 (4)	3084 (5)	2353 (9)	34
C(13)	9700 (4)	2537 (4)	3714 (9)	32
C(14)	9291 (4)	2979 (4)	5100 (9)	32
C(15)	8509 (5)	1515 (4)	4326 (8)	32
C(16)	9371 (4)	1671 (4)	3527 (9)	32
C(17)	7581 (4)	2361 (4)	1591 (8)	28
C(18)	5449 (5)	3900 (5)	1062 (10)	52
C(19)	6204 (5)	2658 (5)	233 (9)	38
C(20)	6878 (5)	1346 (5)	−212 (10)	49
C(21)	7672 (6)	843 (5)	−406 (13)	69
C(22)	4745 (5)	5095 (5)	1902 (11)	69
C(23)	9877 (5)	274 (5)	3721 (12)	58
N	7016 (4)	2215 (3)	177 (7)	35
O(1)	8288 (3)	3041 (3)	−1177 (6)	47
O(2)	5523 (4)	4741 (3)	1502 (8)	61
O(3)	6620 (3)	3392 (3)	4997 (5)	41
O(4)	6705 (3)	1532 (2)	3365 (5)	40
O(5)	7482 (3)	2096 (3)	6040 (5)	41
O(6)	9429 (3)	2549 (3)	6564 (6)	47
O(7)	9998 (3)	1121 (3)	4172 (6)	43

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Table 2. *Bond lengths* (Å) *in delphinifoline*

C(1)–C(11)	1·574 (10)	C(1)–O(1)	1·444 (9)
C(1)–C(2)	1·511 (11)		
C(2)–C(3)	1·518 (12)		
C(3)–C(4)	1·549 (11)	C(4)–C(18)	1·527 (11)
		C(18)–O(2)	1·430 (10)
C(4)–C(5)	1·579 (10)	O(2)–C(22)	1·395 (10)
C(5)–C(6)	1·544 (10)		
C(5)–C(11)	1·557 (10)		
C(6)–C(7)	1·546 (9)	C(6)–O(3)	1·458 (9)
C(7)–C(17)	1·543 (9)	C(7)–O(4)	1·433 (7)
C(17)–C(11)	1·534 (9)		
C(17)–N	1·504 (9)		
N–C(19)	1·470 (9)	N–C(20)	1·476 (10)
		C(20)–C(21)	1·505 (12)
C(19)–C(4)	1·507 (11)		
C(7)–C(8)	1·544 (9)	C(8)–O(5)	1·456 (8)
C(8)–C(9)	1·544 (10)		
C(9)–C(10)	1·522 (9)		
C(10)–C(11)	1·555 (9)		
C(10)–C(12)	1·575 (10)		
C(12)–C(13)	1·528 (10)		
C(13)–C(14)	1·517 (10)	C(14)–O(6)	1·435 (9)
C(13)–C(16)	1·516 (9)	C(16)–O(7)	1·442 (8)
		O(7)–C(23)	1·449 (9)
C(16)–C(15)	1·536 (10)		
C(15)–C(8)	1·537 (10)		
C(14)–C(9)	1·519 (10)		

Table 3. *Bond angles* (°) *in delphinifoline*

C(11)–C(1)–C(2)	112·2 (6)	C(1)–C(11)–C(5)	112·4 (5)
C(11)–C(1)–O(1)	112·0 (6)	C(1)–C(11)–C(10)	106·6 (5)
C(2)–C(1)–O(1)	111·3 (6)	C(1)–C(11)–C(17)	116·7 (6)
C(1)–C(2)–C(3)	111·9 (7)	C(5)–C(11)–C(10)	113·0 (5)
C(2)–C(3)–C(4)	113·5 (6)	C(10)–C(11)–C(17)	109·6 (5)
C(3)–C(4)–C(5)	111·2 (6)	C(5)–C(11)–C(17)	98·5 (5)
C(3)–C(4)–C(18)	107·9 (6)	C(10)–C(12)–C(13)	105·2 (6)
C(3)–C(4)–C(19)	111·5 (6)	C(12)–C(13)–C(14)	99·6 (5)
C(5)–C(4)–C(18)	109·4 (6)	C(12)–C(13)–C(16)	111·4 (6)
C(5)–C(4)–C(19)	108·7 (6)	C(14)–C(13)–C(16)	112·3 (6)
C(18)–C(4)–C(19)	108·0 (6)	C(9)–C(14)–C(13)	102·7 (6)
C(11)–C(5)–C(6)	104·4 (5)	C(9)–C(14)–O(6)	117·0 (6)
C(11)–C(5)–C(4)	107·9 (6)	O(6)–C(14)–C(13)	111·2 (6)
C(6)–C(5)–C(4)	108·5 (6)	C(8)–C(15)–C(16)	117·8 (6)
C(7)–C(6)–O(3)	113·4 (5)	C(13)–C(16)–C(15)	114·3 (6)
C(7)–C(6)–C(5)	104·6 (5)	C(13)–C(16)–O(7)	108·0 (5)
O(3)–C(6)–C(5)	112·7 (6)	C(15)–C(16)–O(7)	109·7 (6)
C(6)–C(7)–C(8)	113·2 (5)	C(7)–C(17)–N	118·4 (5)
C(6)–C(7)–C(17)	103·4 (5)	C(7)–C(17)–C(11)	99·7 (5)
C(8)–C(7)–C(17)	110·3 (5)	C(11)–C(17)–N	108·0 (5)
C(7)–C(8)–C(9)	109·6 (6)	C(4)–C(19)–N	112·3 (6)
C(9)–C(8)–O(5)	110·9 (5)	C(17)–N–C(19)	114·2 (5)
C(7)–C(8)–O(5)	105·9 (5)	C(17)–N–C(20)	114·5 (5)
O(5)–C(8)–C(15)	104·4 (5)	C(19)–N–C(20)	110·7 (6)
C(7)–C(8)–C(15)	112·9 (6)	N–C(20)–C(21)	115·3 (7)
C(9)–C(8)–C(15)	112·8 (6)	C(18)–O(2)–C(22)	112·9 (6)
C(8)–C(9)–C(10)	112·6 (6)	C(4)–C(18)–O(2)	110·5 (6)
C(8)–C(9)–C(14)	111·7 (6)	C(6)–C(7)–O(4)	110·4 (5)
C(10)–C(9)–C(14)	100·5 (5)	C(17)–C(7)–O(4)	110·2 (5)
C(9)–C(10)–C(11)	118·1 (6)	C(8)–C(7)–O(4)	109·2 (5)
C(9)–C(10)–C(12)	105·0 (5)	C(16)–O(7)–C(23)	114·0 (6)
C(11)–C(10)–C(12)	112·0 (5)		

total peak count, B is the background count and S is the scale factor required to normalize the background to the time interval of the scan. Three reflections monitored during data collection showed no change in intensity during the experiment. Data were corrected for Lorentz and polarization factors.

The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971) and refined by full-matrix least squares to a final R value of 0·038 ($R_w = 0·051$). Those H atoms that could be located in difference maps were included in the model but were not refined. The function minimized was $\sum w|F_o - F_c|^2$ with $w = [\sigma^2(F) + 0·002F_o^2]^{-1}$. Reflections with $I \leq 3\sigma(I)$ were included in the refinement if $F_o \leq F_c$. The value of $[\sum w\Delta^2(m - n)]^{1/2}$ is 0·922. Scattering factors and anomalous-dispersion terms were taken from Cromer & Mann (1968). Programs are from XRAY 76 (Stewart, 1976), implemented on a Honeywell computer with a *MULTICS* operating system, and *FITMOL* from G. D. Smith, Medical Foundation, Buffalo.

Final atomic coordinates are given in Table 1.* Bond lengths are in Table 2 and bond angles in Table 3.

Results and discussion

The structure of delphinifoline is shown in Fig. 1. The numbering scheme is that proposed by Pelletier & Keith (1970) for C_{19} diterpenoid alkaloids. The unexpected feature of this structure is the α configuration of the substituent at C(1). Structural assignments in the lycoctonine alkaloids are based on the stereochemistry reported for (+)-de(oxymethylene)-lycoctonine hydroiodide monohydrate (Przybylska & Marion, 1956), in which the A ring is reported to have a chair form with the C(1) substituent on the opposite side of the ring. In a more recent paper, Cygler, Przybylska & Edwards (1982) report a C(1) α substituent in the acetoxy lactam acid from 4-amino-4-deoxymethyleneanhydrolycoctonam. Since all lycoctonines have been assumed to have the same stereochemistry at C(1), these results cast some doubt on structural assignments in this class of alkaloids. It is possible that there is an error in the early work since the structure was done in projection. The structure of the de(oxymethylene) derivative is being redetermined (M. Przybylska, private communication). At this point it is not clear whether both configurations are available to the substituent on C(1) or whether the structural assignments of all alkaloids of this class should be revised.

In a previous paper (Codding & Kerr, 1981) we have compared the conformations of alkaloid A and three

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36522 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

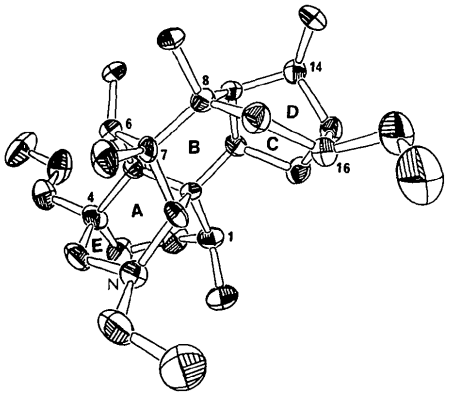
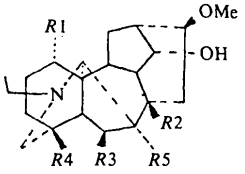


Fig. 1. A perspective drawing of delphinifoline showing the numbering scheme used in the text.

Table 4. *Torsional angles* (°) *for alkaloid A and delphinifoline*

The sign of the angle is positive if a clockwise rotation will cause the first named atom to eclipse the last. An asterisk indicates significant change.



(I) Alkaloid A: R_1 = OH, R_2 = OCH_3, R_3 = OAc, R_4 = CH_3, R_5 = H

(II) Delphinifoline: R_1 = OH, R_2 = OH, R_3 = OH, R_4 = CH_2OCH_3, R_5 = OH

	(I)	(II)
Ring *A*		
C(1)–C(2)–C(3)–C(4)	48·9 (9)	47·4 (9)
C(2)–C(3)–C(4)–C(5)	10·4 (9)	11·1 (9)
C(3)–C(4)–C(5)–C(11)	−57·1 (7)	−59·7 (7)
C(4)–C(5)–C(11)–C(1)	47·2 (9)	50·5 (7)*
C(5)–C(11)–C(1)–C(2)	9·8 (10)	5·6 (8)*
C(11)–C(1)–C(2)–C(3)	−58·9 (9)	−56·5 (8)*
Ring *B*		
C(7)–C(8)–C(9)–C(10)	−40·6 (8)	−39·8 (8)
C(8)–C(9)–C(10)–C(11)	34·6 (8)	34·7 (8)
C(9)–C(10)–C(11)–C(17)	−47·6 (7)	−49·7 (8)
C(10)–C(11)–C(17)–C(7)	65·9 (6)	65·1 (6)
C(11)–C(17)–C(7)–C(8)	−77·6 (6)	−76·2 (6)
C(17)–C(7)–C(8)–C(9)	64·4 (7)	64·6 (7)
Ring *C*		
C(9)–C(10)–C(12)–C(13)	2·9 (7)	2·1 (7)
C(10)–C(12)–C(13)–C(14)	−32·2 (7)	−31·2 (6)
C(12)–C(13)–C(14)–C(9)	49·6 (7)	50·3 (6)
C(13)–C(14)–C(9)–C(10)	−48·1 (7)	−49·3 (6)
C(14)–C(9)–C(10)–C(12)	26·9 (7)	28·0 (7)
Ring *D*		
C(9)–C(14)–C(13)–C(16)	−66·8 (7)	−67·7 (7)
C(14)–C(13)–C(16)–C(15)	19·6 (9)	20·5 (8)
C(13)–C(16)–C(15)–C(8)	26·7 (9)	26·9 (9)
C(16)–C(15)–C(8)–C(9)	−21·5 (9)	−24·1 (8)
C(15)–C(8)–C(9)–C(14)	−29·0 (9)	−25·4 (8)*
C(8)–C(9)–C(14)–C(13)	72·9 (7)	70·4 (7)

Table 4 (*cont.*)

	(I)	(II)
Ring *E*		
N–C(17)–C(11)–C(5)	70·6 (6)	71·1 (6)
C(17)–C(11)–C(5)–C(4)	−76·6 (6)	−73·0 (6)*
C(11)–C(5)–C(4)–C(19)	64·9 (7)	63·4 (7)
C(5)–C(4)–C(19)–N	−44·7 (8)	−47·7 (8)*
C(4)–C(19)–N–C(17)	42·4 (8)	48·6 (8)*
C(19)–N–C(17)–C(11)	−57·8 (7)	−62·6 (7)*
Ring *F*		
C(5)–C(6)–C(7)–C(17)	−17·3 (7)	−18·2 (6)
C(6)–C(7)–C(17)–C(11)	43·6 (7)	45·0 (6)
C(7)–C(17)–C(11)–C(5)	−51·3 (7)	−53·1 (6)
C(17)–C(11)–C(5)–C(6)	40·1 (7)	42·2 (6)
C(11)–C(5)–C(6)–C(7)	−41·3 (8)	−14·9 (7)
Side chains		
C(16)–C(15)–C(8)–O(5)	−137·8 (7)	−144·6 (6)*
C(8)–C(15)–C(16)–O(7)	148·4 (6)	148·4 (6)
C(15)–C(16)–O(7)–C(23)	153·8 (7)	69·8 (8)*
C(17)–C(7)–C(6)–O(3)	−140·5 (6)	−141·4 (5)
C(5)–C(11)–C(1)–O(1)	−109·7 (7)	−120·4 (6)*
C(12)–C(13)–C(14)–O(6)	174·1 (6)	176·2 (5)
N–C(17)–C(7)–O(4)		46·6 (7)
C(2)–C(3)–C(4)–C(18)		131·1 (7)
C(3)–C(4)–C(18)–O(2)		−61·0 (8)
C(4)–C(18)–O(2)–C(22)		179·8 (5)
C(19)–N–C(20)–C(21)		176·2 (7)
C(4)–C(19)–N–C(20)		179·7 (6)

aconitine-type alkaloids with the same basic skeleton: condelphine, chasmanine and delphisine. Although the substituent at C(7) clearly established delphinifoline as a lycoctonine alkaloid, the extreme rigidity of the skeleton invites comparison. In all of these structures, the gross features are the same. Rings *A* and *D* are boats; rings *B* and *E* are distorted chairs; ring *C* is an envelope with C(14) at the flap; ring *F* is a half-chair with an approximate twofold axis through C(6).

Torsional angles in alkaloid A and in delphinifoline are compared in Table 4. Although the substitution patterns in the two alkaloids are similar in bulk and in stereochemistry subtle differences are reflected in the conformations. Those torsional angles that are significantly different in the two structures are marked with an asterisk.

In both compounds, the boat conformation of ring *A* is stabilized by hydrogen bonding between the N and the hydroxyl group on C(1). However, in alkaloid A, the hydroxyl group accepts a proton from N while in delphinifoline the unprotonated N accepts a proton from the hydroxyl. This change in hydrogen-bonding pattern increases the N···O distance of 2·670 (8) from the 2·643 (8) Å observed in alkaloid A and affects the conformation of ring *A* by increasing the pucker at C(5) in delphinifoline and flattening it at C(2). There are also small but significant changes in torsional angles in ring *E*. These differences and others are compared in Fig. 2. The drawing is a composite with the structure of delphinifoline superposed on that of

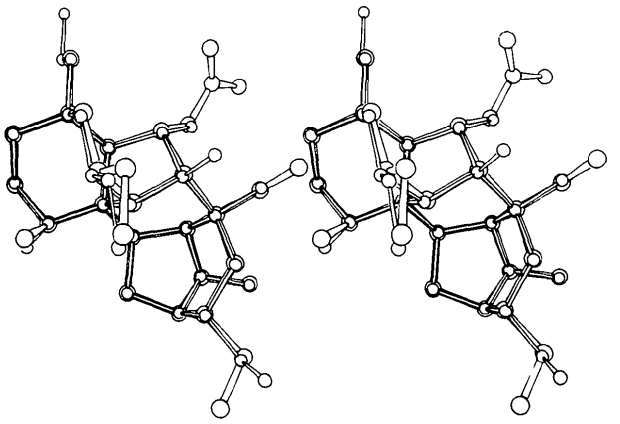


Fig. 2. A composite stereoview of delphinifoline and alkaloid A. The large spheres and wide bonds represent alkaloid A.

alkaloid A. The large spheres and wide bonds represent alkaloid A.

The hydroxyl substituent at C(7) is the feature that distinguishes lycoctonine alkaloids from the aconitines. It should also be noted that Figs. 1 and 2 clearly show that this group is in the α position although conventional formulae for lycoctonines are frequently drawn as if the substituent were β. Although the substituent is important in determining the physiological activity of the compound, it has remarkably little effect on the conformation of the skeleton. Only small changes are observed in rings *B* and *F*.

Other differences between the two structures can be attributed to differences in hydrogen bonding. Ring *D* is a boat flattened at C(15). The change in torsional angle at C(8)–C(9) occurs because O(5), the OH group on C(8), hydrogen bonds to O(3) in delphinifoline. O(3) accepts from O(5) and donates to O(7) of a symmetry-related molecule. It is interesting to note that although the hydroxyl, O(4), is relatively close to both O(5) (2·719 Å) and N (2·96 Å) there is no evidence that it forms hydrogen bonds with either of them. An examination of the model suggests that the geometry is not favourable for significant overlap of orbitals. This might explain why the proton on O(4) was not located in difference maps. Details of the hydrogen bonding are shown in Table 5.

Table 5. *Hydrogen bonding in delphinifoline*

Positions of H atoms were not refined.

	O···*A*	O–H	H···*A*	∠O–H···*A*
O(1)···N	2·670 (8) Å	1·02 Å	1·75 Å	148°
O(3)···O(7)	2·764 (7)	1·10	1·70	161
O(5)···O(3)	2·664 (7)	0·90	1·90	142
O(4)···O(5)	2·723 (6)			
O(4)···N	2·948 (7)			
O(1)···O(6)	2·737 (7)			

Conclusion

The hydroxyl group on C(1) is on the same side of the ring as the N bridge. The configuration is opposite to that reported in de(oxymethylene)lycoctonine hydroiodide monohydrate (Przybylska, 1961; Przybylska & Marion, 1956) but in agreement with the more recent results on a derivative of anhydrolycoctonam (Cygler, Przybylska & Edwards, 1982). These observations suggest that structures of some or all of the alkaloids of this family should be revised.

A comparison of delphinifoline with alkaloid A and with other alkaloids with this skeleton shows that the skeleton is extremely rigid. The conformations of the rings remain virtually unchanged in spite of a wide variation in substitution patterns.

The boat conformation in ring *A* is stabilized by hydrogen bonding between the N and a hydroxyl or methoxy group on position C(1). The proton may be donated by the N, as is the case with alkaloid A or by the hydroxyl as in delphinifoline.

However, there are several examples of molecules with similar skeletons in which ring *A* has the chair form. This occurs when there is no oxygenated function at C(1) (Przybylska, 1976); when the protonated N and the oxygenated function are on opposite sides of the ring as in (+)-de(oxymethylene)-lycoctonine hydroiodide hydrate (Przybylska, 1961); and might be expected when the boat form is destabilized by α substituents at C(1) and C(3). It is interesting to note that jesaconitine (Pelletier, DeCamp, Finer-Moore & Ichinohe, 1979) and aconitine (Codding, 1981) both have methoxy and hydroxyl groups at positions C(1) and C(3) respectively. However, jesaconitine crystallized as the perchlorate has a boat configuration while aconitine, as the free base, has a chair.

These observations suggest that the energy barrier between boat and chair forms is relatively low for ring *A* in these compounds.

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Structure of 13-Methyl-2,10-dioxatricyclo[4.4.4.0^{1,6}]tetradecane at 96 K

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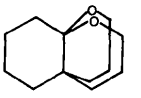
Abstract

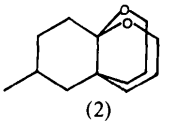
The structure of the title compound has been determined at room temperature (RT) and with improved accuracy at 96 K. $C_{13}H_{22}O_2$, $M_r = 210{\cdot}3$, is triclinic, space group $P\bar{1}$: $a = 6{\cdot}420\ (3)$, $b = 8{\cdot}734\ (4)$, $c = 11{\cdot}520\ (5)$ Å, $\alpha = 68{\cdot}59\ (3)$, $\beta = 82{\cdot}37\ (3)$, $\gamma = 80{\cdot}27\ (3)°$, $V = 590{\cdot}95$ Å^3, μ(Mo $K\alpha$) = 0·083 mm^{-1} at RT; $a = 6{\cdot}347\ (3)$, $b = 8{\cdot}685\ (2)$, $c = 11{\cdot}336\ (3)$ Å, $\alpha = 68{\cdot}47$, $\beta = 82{\cdot}37\ (4)$, $\gamma = 80{\cdot}09\ (3)°$, $V = 572{\cdot}05$ Å^3, μ(Mo $K\alpha$) = 0·086 mm^{-1} at 96 K; $Z = 2$, $D_c = 1{\cdot}182$ (RT) and 1·221 Mg m^{-3} (96 K). The low-temperature data extend to sin $\theta/\lambda = 0{\cdot}86$ Å^{-1} and include 5988 independent reflexions. The structure was solved by direct methods and refined to $R = 0{\cdot}033$ for 4080 reflexions with $I \geq 3\sigma_I$. The bond-length difference between the two chemically equivalent, conformationally inequivalent, geminal C—O bonds in the *sc*, *ap* conformation is 0·026 (1) Å, and other pairs of chemically equivalent bonds do not differ by more than 0·003 Å. The molecule behaves as a rigid body with its main librational and translational axes nearly parallel to the principal molecular axis with the smallest moment of inertia. The disordered crystal structure of the unsubstituted propellane, 2,10-dioxatricyclo-[4.4.4.0^{1,6}]tetradecane, $C_{12}H_{20}O_2$, is briefly described. At 103 K the orthorhombic unit cell has $a = 12{\cdot}26\ (1)$, $b = 12{\cdot}22\ (1)$, $c = 13{\cdot}79\ (1)$ Å, $Z = 8$, probable space group $P2_1ca$.

Introduction

The two equivalent, geminal C—O bonds of the dioxapropellane (1) become conformationally non-equivalent in the expected chair–chair–chair form of the molecule. Our attempt to obtain experimental evidence for a difference in length between such bonds was thwarted by disorder in the crystal structure of (1) (see Appendix). The methylated title compound (2) was therefore prepared. Details of the synthesis will be given elsewhere; here we report on its crystal structure.



(1)



(2)

Details of the analysis

The substance (m.p. 319 K) was crystallized from ether at 258 K and a first data set collected with a Hilger & Watts Y290 diffractometer at room temperature. Although the structure could be solved by direct methods the data were not good enough to yield results of the desired accuracy. A single crystal of better quality (dimensions 0·15 × 0·3 × 0·55 mm) was grown by sublimation in an evacuated capillary tube and a new, more extensive, data set (sin θ/λ limit

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