

2:1, with a disordered solvate molecule at the ($x,x,0$) position on the twofold axis. The refinement of the disordered ethyl acetate molecule gave some trouble; several attempts were made to interpret the confused difference map and to refine the six independent heavy atoms with population factors of 0.5, but there were always very high correlations between various parameters and an unacceptable molecular geometry. The best interpretation was to place the bridge O atom O1S on the twofold axis and to consider the C atoms of the acetyl and ethyl groups to be equivalent; in this interpretation, the carboxyl O atom O2S is the only atom with a population factor of 0.5. At the end of the refinement, the geometry of the group was quite acceptable but nevertheless, we considered the inclusion of the H atoms of the ethyl acetate molecule in the model to be of little significance.

Data collection and cell refinement: Enraf-Nonius software. Data reduction and structure refinement: *SDP-Plus* (Frenz, 1983). Structure solution: *MULTAN11/82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Software used to prepare material for publication: *PARST* (Nardelli, 1983) and *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71227 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1036]

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Structure of (\pm)-Tetrahydropalmatine

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Abstract

In 5,8,13,13a-tetrahydro-2,3,9,10-tetramethoxy-6H-dibenzo[*a,g*]quinolizine, according to the puckering parameters [Cremer & Pople (1975). *J. Am. Chem. Soc.* **97**, 1354–1558] the *trans* fused ring *B* [$Q = 0.518$ (5) Å, $\varphi = 145.4$ (7)°, $\theta = 51.6$ (6)°] and ring *C* [$Q = 0.529$ (4) Å, $\varphi = 328.2$ (5)°, $\theta = 48.2$ (4)°] of the quinolizine moiety both have almost perfect half-chair conformations. The mean value of the three C—N—C angles is 110.0 (3)° indicating sp^3 hybridization of the N atom. Molecules are held together by van der Waals interactions.

Comment

Tetrahydropalmatine is a tetrahydroprotoberberine alkaloid previously isolated from *Corydalis aurea*, *C. lutea* and *C. ochroleuca* (Glasby, 1975). We have isolated the same alkaloid from the roots of *C. cava*, as well as from the overground parts and roots of *C. solida* collected at the Fruška Gora mountain (Vojvodina). Isolation was performed as described by Gašić, Popović & Dragutinović (1985). The dihedral angle between the phenyl rings *A* and *D* is 25.8 (1)° as compared to 33.8 (1)° in isocorypalmatine (Ribár, Radivojević, Gašić, Kanyó & Golić, 1992) and 36.7 (1)° in corydaline (Ribár, Lazar, Radivojević, Engel, Gašić & Kanyó, 1992). The O3—C19 bond is perpendicular to the plane of phenyl ring *D*, while the O4—C20 bond is in the plane of the same ring. The O1—C21 and O2—C18 bonds are in the plane of phenyl ring *A*, as indicated

by the corresponding torsion angles. According to Zhao, Ren, Wu & Yu (1988), tetrahydropalmatine has an effect on blood vessel contraction.

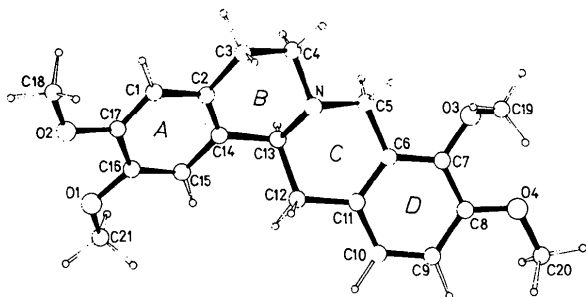


Fig. 1. Perspective view of the molecule showing the atomic numbering. The H atoms are shown but are not labelled.

N	0.5447 (1)	0.6535 (2)	0.1935 (4)	32 (1)
C1	0.6829 (1)	0.6748 (2)	0.1024 (5)	39 (1)
C2	0.6378 (1)	0.6594 (2)	0.1380 (5)	34 (1)
C3	0.6179 (1)	0.6917 (3)	0.3128 (5)	42 (1)
C4	0.5736 (1)	0.6517 (3)	0.3568 (5)	41 (1)
C5	0.4999 (1)	0.6274 (2)	0.2495 (5)	39 (1)
C6	0.4682 (1)	0.6192 (2)	0.0903 (5)	33 (1)
C7	0.4228 (1)	0.6146 (2)	0.1254 (5)	34 (1)
C8	0.3916 (1)	0.6042 (2)	-0.0158 (5)	36 (1)
C9	0.4074 (1)	0.5967 (2)	-0.1956 (5)	40 (1)
C10	0.4534 (1)	0.6016 (2)	-0.2309 (5)	38 (1)
C11	0.4845 (1)	0.6131 (2)	-0.0891 (5)	35 (1)
C12	0.5341 (1)	0.6184 (2)	-0.1276 (5)	39 (1)
C13	0.5622 (1)	0.6027 (2)	0.0457 (4)	32 (1)
C14	0.6124 (1)	0.6169 (2)	0.0138 (5)	33 (1)
C15	0.6333 (1)	0.5859 (2)	-0.1449 (5)	36 (1)
C16	0.6777 (1)	0.6004 (2)	-0.1794 (5)	41 (1)
C17	0.7028 (1)	0.6477 (2)	-0.0550 (5)	42 (1)
C18	0.7711 (2)	0.7130 (4)	0.0125 (8)	83 (2)
C19	0.3929 (2)	0.6967 (3)	0.3544 (6)	55 (1)
C20	0.3161 (1)	0.5763 (3)	-0.0988 (7)	61 (1)
C21	0.6814 (2)	0.5149 (3)	-0.4379 (7)	66 (1)

Experimental

Crystal data

$C_{21}H_{25}NO_4$

$M_r = 355.43$

Orthorhombic

Pbca

$a = 29.817 (12) \text{ \AA}$

$b = 17.001 (7) \text{ \AA}$

$c = 7.279 (5) \text{ \AA}$

$V = 3690 (3) \text{ \AA}^3$

$Z = 8$

$D_x = 1.280 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.54178 \text{ \AA}$

Cell parameters from 15 reflections

$\theta = 20\text{--}25^\circ$

$\mu = 0.68 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism

$0.60 \times 0.25 \times 0.25 \text{ mm}$

Colourless

Crystal source: alkaloid from

Corydalis cava and *C. solida*

Data collection

DAR-UMB diffractometer

ω - $\theta/2\theta$ scans

Absorption correction:

none

2325 measured reflections

2325 independent reflections

2210 observed reflections

$[I > 3\sigma(I)]$

$\theta_{\max} = 68^\circ$

$h = 0 \rightarrow 36$

$k = 0 \rightarrow 21$

$l = 0 \rightarrow 8$

3 standard reflections

frequency: 60 min

intensity variation: $< 2.5\%$

Refinement

Refinement on F

Final $R = 0.061$

$wR = 0.070$

$S = 3.85$

2210 reflections

259 parameters

Only H-atom U 's refined

$w = 5.605[\sigma^2(F_o) + 0.001671F_o^2]^{-1}$

$(\Delta/\sigma)_{\max} = 0.80$

$\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.30 \text{ e \AA}^{-3}$

Atomic scattering factors

from *SHELX76*

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
O1	0.7014 (1)	0.5736 (2)	-0.3284 (4)	66 (1)
O2	0.7466 (1)	0.6625 (2)	-0.1062 (4)	62 (1)
O3	0.4079 (1)	0.6187 (2)	0.3057 (3)	39 (1)
O4	0.3478 (1)	0.6030 (2)	0.0350 (4)	46 (1)

Table 2. Geometric parameters (\AA , $^\circ$)

O1—C16	1.372 (5)	C3—C4	1.520 (5)
O1—C21	1.410 (6)	C5—C6	1.502 (5)
O2—C17	1.381 (4)	C6—C7	1.380 (4)
O2—C18	1.420 (8)	C6—C11	1.397 (5)
O3—C7	1.387 (4)	C7—C8	1.398 (5)
O3—C19	1.444 (6)	C8—C9	1.397 (5)
O4—C8	1.357 (4)	C9—C10	1.398 (4)
O4—C20	1.431 (5)	C10—C11	1.401 (5)
N—C4	1.468 (5)	C11—C12	1.508 (4)
N—C5	1.465 (4)	C12—C13	1.538 (5)
N—C13	1.475 (4)	C13—C14	1.534 (4)
C1—C2	1.394 (4)	C14—C15	1.414 (5)
C1—C17	1.370 (5)	C15—C16	1.370 (4)
C2—C3	1.507 (5)	C16—C17	1.424 (5)
C2—C14	1.383 (5)		
C7—O3—C19	112.2 (3)	O4—C8—C9	125.3 (3)
C8—O4—C20	117.1 (3)	C7—C8—C9	118.4 (3)
C16—O1—C21	117.7 (3)	C8—C9—C10	119.8 (3)
C17—O2—C18	115.6 (4)	C9—C10—C11	121.5 (3)
C4—N—C5	107.7 (3)	C6—C11—C10	117.9 (3)
C4—N—C13	111.8 (3)	C6—C11—C12	120.7 (3)
C5—N—C13	110.4 (3)	C10—C11—C12	121.4 (3)
C2—C1—C17	120.7 (3)	C11—C12—C13	111.8 (3)
C1—C2—C3	117.9 (3)	N—C13—C12	107.7 (3)
C1—C2—C14	120.3 (3)	N—C13—C14	111.3 (3)
C3—C2—C14	121.8 (3)	C12—C13—C14	112.4 (3)
C2—C3—C4	110.9 (3)	C2—C14—C13	121.2 (3)
N—C4—C3	109.3 (3)	C2—C14—C15	119.2 (3)
N—C5—C6	112.8 (3)	C13—C14—C15	119.7 (3)
C5—C6—C7	118.7 (3)	C14—C15—C16	120.6 (3)
C5—C6—C11	120.6 (3)	O1—C16—C15	125.6 (3)
C7—C6—C11	120.7 (3)	O1—C16—C17	114.8 (3)
O3—C7—C6	119.1 (3)	C15—C16—C17	119.6 (3)
O3—C7—C8	119.3 (3)	O2—C17—C1	125.0 (3)
C6—C7—C8	121.6 (3)	O2—C17—C16	115.4 (3)
O4—C8—C7	116.2 (3)	C1—C17—C16	119.6 (3)
C6—C7—O3—C19	98.1 (4)	C16—C17—O2—C18	176.9 (3)
C9—C8—O4—C20	13.4 (5)	C17—C16—O1—C21	168.3 (4)

Data were corrected for Lorentz and polarization effects. A value for R_{int} is missing since only a unique data set was collected. The structure was solved by direct methods (Sheldrick, 1986) and refined with *SHELX76* (Sheldrick, 1976). Positions of H atoms were generated and included in structure-factor calculations with refined isotropic temperature factors (riding model). All calculations were performed on a PC/AT computer.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71157 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1026]

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2-Methyl-4-oxo-3H,5H-6-imidazo[3,4-b]-[1,2,4]triazepinecarbonitrile: Condensation Product of a β -Keto Ester with 1,5-Diamino-4-imidazolecarbonitrile under Basic Conditions

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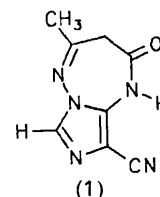
Abstract

In the triazepine, a double bond links atoms 1 and 2 [$C=N = 1.276(3) \text{ \AA}$] with no evidence of an alternative tautomer in which the double bond is between 2 and 3 [$C=C = 1.490(4) \text{ \AA}$]. ^1H NMR spectroscopy in d_6 -DMSO confirms that this is the only tautomer present

in solution. A hydrogen bond between the triazepine $N-H$ and the imidazo N atom in an adjacent molecule [$N \cdots N 2.950(3)$, $H \cdots N 1.99(2) \text{ \AA}$, $N-H \cdots N 172(2)^\circ$] links the molecules into infinite spirals along b .

Comment

Following our recent synthesis of 1,5-diamino-4-imidazolecarbonitrile in high yield (Alves, Booth, Freitas & Proença, 1992), we have undertaken a detailed study of its reactions with β -keto esters under basic conditions. It was clear from spectroscopic data that the reaction with sodium ethyl acetoacetate occurs by condensation of the 1- and 5-amino groups with both the keto and ester functions. However, it was impossible to decide from the available data whether the compound had structure (1) (formed by attack of the 1-amino group at the keto carbonyl and the 5-amino group at the ester carbonyl) or the alternative structure formed by inverting the ethyl acetoacetate group.



This work establishes (1) as the sole product in contrast to the finding of Bernardi, Viallefont & Zniber (1978) who reported that the reaction between 1,5-diamino-2-phenylimidazole and ethyl acetoacetate at the reflux temperature of xylene gives a mixture in which both the keto and ester carbonyls react with each of the amine substituents.

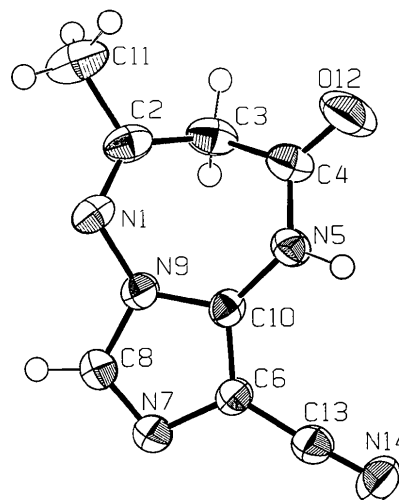


Fig. 1. The title molecule, showing atomic numbering scheme, drawn using ORTEPII (Johnson, 1976).