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9-Methyl-10-(4-methylphenyl)-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione

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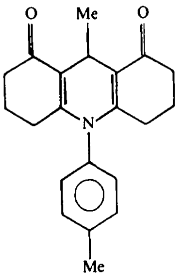
Abstract

The title molecule, $C_{21}H_{23}NO_2$, includes a partially hydrogenated acridine ring system. The central ring adopts a conformation which is predominantly boat in form (Δ_{cs} = 2°) while the two outer six-membered rings have approximate chair and twist-boat conformations (Δ_{c2} = 2.6 and 8.6°), respectively. The molecule has approximate mirror symmetry with the phenyl ring in the non-crystallographic mirror plane. There is considerable folding along the bonds at the ring junctions. The packing of molecules involves van der Waals interactions.

Comment

Aminoacridinyl derivatives have general uses in medicine, especially as antitumour agents, and have also been used as antibacterial agents for wound therapy (Acheson, 1956). The aminoacridine group enables the molecule to intercalate with DNA (Karle, Cysk & Karle, 1980; Lerman, 1961; Nandi, Debnath & Maiti, 1990; Reddy, Seshadri, Sakore & Sobell, 1979; Sakore, Reddy & Sobell, 1979; Peacocke & Skerrett, 1956). This intercalation is essential for biological activity. The present study of the title compound (I) is part of a series of investigations of the crystal structures of acridine derivatives.



(I)

Bond lengths and angles agree well with those in related acridinyl derivatives (Chu & van der Helm, 1976, 1977; Selladurai, Subramanian & Ramakrishnan, 1990; Selladurai, Subramanian & Natarajan, 1989). The bonds around the N(10) atom are nearly coplanar indicating sp^2 hybridization (Hempel, Hull, Bogucka-Ledochowska & Dauter, 1979). The dihedral angle between rings I and III is 20.5 (1)°. In similar compounds this angle varies between 10 and 19.5° (Clark, Hall, Denny & Stewart, 1986). The dihedral angle between the phenyl ring and the mean plane of the acridine ring system is 89.3 (1)°.

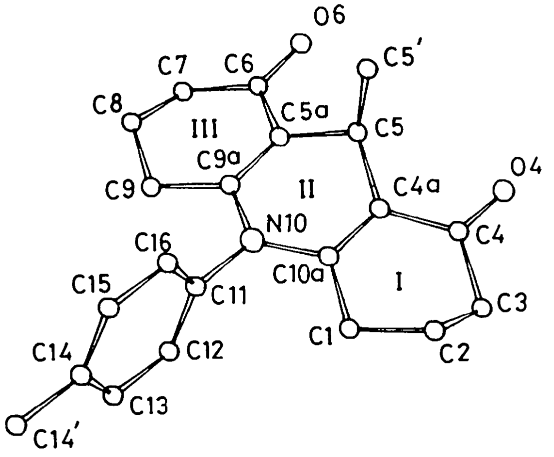


Fig. 1. View of the molecular geometry of the title compound showing the numbering scheme adopted.

Experimental

Crystal data

$C_{21}H_{23}NO_2$
M_r = 321.4
Monoclinic
$P2_1/c$
a = 9.108 (1) Å
b = 11.405 (2) Å
c = 17.482 (2) Å
β = 102.8 (1)°
V = 1770.8 (8) Å^3
Z = 4
D_x = 1.206 Mg m^{-3}
D_m = 1.210 Mg m^{-3}
D_m measured by flotation

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 20 reflections
θ = 15–25°
μ = 0.57 mm^{-1}
T = 293 K
Rectangular blocks
0.45 × 0.40 × 0.35 mm
Deep red

Data collection

Enraf–Nonius CAD-4 diffractometer

$R_{\rm int}$ = 0.021
$\theta_{\max}$ = 60°

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$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.812$, $T_{\max} = 0.901$
3000 measured reflections
2831 independent reflections
2611 observed reflections $[I > 3\sigma(I)]$

$h = 0 \rightarrow 12$
$k = -12 \rightarrow 13$
$l = 0 \rightarrow 17$
3 standard reflections monitored every 100 reflections
intensity variation: <2%

Refinement

Refinement on F
$R = 0.066$
$wR = 0.069$
$S = 1.105$
2611 reflections
309 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.008779F^2]$
$(\Delta/\sigma)_{\max} = 0.085$
$\Delta\rho_{\max} = 0.5$ e Å^{-3}
$\Delta\rho_{\min} = -0.4$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
C(1)	1.0415 (3)	0.2023 (2)	−0.0524 (1)	4.91 (7)
C(2)	1.1861 (5)	0.1736 (5)	−0.0749 (2)	8.97 (14)
C(3)	1.2797 (5)	0.0868 (4)	−0.0332 (2)	8.15 (12)
C(4)	1.2906 (3)	0.0839 (2)	0.0540 (2)	4.93 (7)
C(4a)	1.1670 (2)	0.1343 (2)	0.0833 (1)	3.80 (6)
O(4)	1.3982 (2)	0.0373 (2)	0.0987 (1)	6.78 (7)
C(5)	1.1770 (3)	0.1307 (2)	0.1702 (1)	4.34 (6)
C(5′)	1.2732 (3)	0.2301 (3)	0.2113 (2)	6.35 (9)
C(5a)	1.0204 (3)	0.1363 (2)	0.1854 (1)	4.06 (7)
C(6)	0.9911 (3)	0.0814 (3)	0.2557 (1)	5.48 (9)
O(6)	1.0896 (3)	0.0275 (3)	0.3008 (1)	9.48 (10)
C(7)	0.8353 (3)	0.0910 (3)	0.2708 (2)	6.25 (9)
C(8)	0.7615 (3)	0.2046 (4)	0.2398 (2)	6.69 (11)
C(9)	0.7577 (3)	0.2182 (3)	0.1534 (1)	5.03 (7)
C(9a)	0.9079 (2)	0.1934 (2)	0.1353 (1)	3.72 (6)
N(10)	0.9278 (2)	0.2296 (2)	0.0618 (1)	3.83 (5)
C(10a)	1.0508 (3)	0.1884 (2)	0.0342 (1)	3.64 (6)
C(11)	0.8151 (2)	0.3021 (2)	0.0123 (1)	3.59 (6)
C(12)	0.6948 (3)	0.2511 (2)	−0.0385 (1)	4.48 (6)
C(13)	0.5891 (3)	0.3230 (3)	−0.0870 (1)	4.77 (7)
C(14)	0.6026 (3)	0.4435 (2)	−0.0843 (1)	4.44 (6)
C(14′)	0.4891 (4)	0.5199 (3)	−0.1377 (2)	6.88 (10)
C(15)	0.7244 (3)	0.4923 (2)	−0.0327 (1)	4.86 (7)
C(16)	0.8305 (3)	0.4220 (2)	0.0166 (1)	4.29 (7)

Table 2. *Selected geometric parameters* (Å, °)

C(1)—C(2)	1.492 (6)	C(7)—C(8)	1.504 (5)
C(1)—C(10a)	1.506 (3)	C(8)—C(9)	1.511 (4)
C(2)—C(3)	1.401 (6)	C(9)—C(9a)	1.498 (3)
C(3)—C(4)	1.506 (5)	C(9a)—N(10)	1.399 (3)
C(4)—C(4a)	1.455 (4)	N(10)—C(10a)	1.396 (3)
C(4)—O(4)	1.231 (3)	N(10)—C(11)	1.447 (3)
C(4a)—C(5)	1.502 (3)	C(11)—C(12)	1.377 (3)
C(4a)—C(10a)	1.355 (3)	C(11)—C(16)	1.375 (3)
C(5)—C(5′)	1.513 (4)	C(12)—C(13)	1.399 (3)
C(5)—C(5a)	1.509 (4)	C(13)—C(14)	1.380 (4)
C(5a)—C(6)	1.456 (3)	C(14)—C(14′)	1.507 (4)
C(5a)—C(9a)	1.358 (3)	C(14)—C(15)	1.382 (3)
C(6)—O(6)	1.221 (4)	C(15)—C(16)	1.397 (3)
C(6)—C(7)	1.504 (4)		
C(2)—C(1)—C(10a)	112.7 (2)	C(8)—C(9)—C(9a)	111.8 (2)
C(1)—C(2)—C(3)	119.3 (3)	C(5a)—C(9a)—C(9)	123.3 (2)
C(2)—C(3)—C(4)	116.0 (4)	C(9)—C(9a)—N(10)	116.7 (2)
C(3)—C(4)—O(4)	121.1 (3)	C(5a)—C(9a)—N(10)	120.1 (2)
C(3)—C(4)—C(4a)	117.7 (3)	C(9a)—N(10)—C(11)	119.9 (2)
C(4a)—C(4)—O(4)	121.1 (3)	C(9a)—N(10)—C(10a)	119.7 (2)
C(4)—C(4a)—C(10a)	120.9 (2)	C(10a)—N(10)—C(11)	120.2 (2)
C(4)—C(4a)—C(5)	117.9 (2)	C(4a)—C(10a)—N(10)	120.6 (2)
C(5)—C(4a)—C(10a)	121.1 (2)	C(1)—C(10a)—N(10)	116.2 (2)
C(4a)—C(5)—C(5a)	109.2 (2)	C(1)—C(10a)—C(4a)	123.2 (2)
C(4a)—C(5)—C(5′)	111.0 (2)	N(10)—C(11)—C(16)	119.0 (2)
C(5′)—C(5)—C(5a)	110.8 (2)	N(10)—C(11)—C(12)	120.1 (2)
C(5)—C(5a)—C(9a)	121.0 (2)	C(12)—C(11)—C(16)	120.8 (2)
C(5)—C(5a)—C(6)	119.2 (2)	C(11)—C(12)—C(13)	119.1 (2)
C(6)—C(5a)—C(9a)	119.8 (2)	C(12)—C(13)—C(14)	121.3 (2)
C(5a)—C(6)—C(7)	118.3 (2)	C(13)—C(14)—C(15)	118.4 (2)
C(5a)—C(6)—O(6)	121.1 (2)	C(13)—C(14)—C(14′)	120.7 (2)
O(6)—C(6)—C(7)	120.7 (2)	C(14′)—C(14)—C(15)	120.8 (2)
C(6)—C(7)—C(8)	111.3 (3)	C(14)—C(15)—C(16)	121.1 (2)
C(7)—C(8)—C(9)	111.0 (3)	C(11)—C(16)—C(15)	119.3 (2)

Table 3. *Selected torsion angles* (°) *and puckering parameters* (Å, °) (*Cremer & Pople*, 1975)

Ring I	
C(2)—C(1)—C(10a)—C(4a)	−12.1 (4)
C(10a)—C(1)—C(2)—C(3)	32.6 (5)
C(1)—C(2)—C(3)—C(4)	−38.7 (6)
C(2)—C(3)—C(4)—C(4a)	23.6 (5)
C(3)—C(4)—C(4a)—C(10a)	−4.0 (4)
C(4)—C(4a)—C(10a)—C(1)	−1.1 (4)
Ring II	
C(5)—C(4a)—C(10a)—N(10)	−8.0 (3)
C(10a)—C(4a)—C(5)—C(5a)	27.9 (3)
C(4a)—C(5)—C(5a)—C(9a)	−29.8 (3)
C(5)—C(5a)—C(9a)—N(10)	11.6 (3)
C(5a)—C(9a)—N(10)—C(10a)	11.9 (3)
C(9a)—N(10)—C(10a)—C(4a)	−13.9 (3)
Ring III	
C(6)—C(5a)—C(9a)—C(9)	8.8 (4)
C(9a)—C(5a)—C(6)—C(7)	−0.5 (4)
C(5a)—C(6)—C(7)—C(8)	−32.0 (4)
C(6)—C(7)—C(8)—C(9)	56.2 (4)
C(7)—C(8)—C(9)—C(9a)	−48.4 (3)
C(8)—C(9)—C(9a)—C(5a)	16.3 (3)

Ring	$Q(2)$	$Q(3)$	$Q(t)$	$\phi(2)$	$\theta(2)$
I	0.223 (4)	−0.171 (4)	0.281 (5)	−105.0 (7)	127.6 (5)
II	0.283 (2)	0.089 (2)	0.297 (2)	−63.8 (5)	72.5 (4)
III	0.404 (3)	0.247 (3)	0.474 (4)	−167.3 (4)	58.5 (3)

Cell refinement and data reduction: *SDP* (Frenz, 1978). Program used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program used to refine structure: *SHELX*76 (Sheldrick, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983) and *PLUTO* (Motherwell & Clegg, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond lengths involving H atoms, complete geometry, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: HA1062). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Di(2-pyridinio)methanediol Dinitrate

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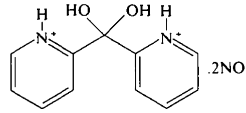
Abstract

An X-ray structural analysis of the title compound [2,2′-(dihydroxymethylene)dipyridinium dinitrate, $C_{11}H_{12}N_2O_2^{2+}.2NO_3^-$] revealed that it was a doubly protonated derivative of di-2-pyridyl ketone (dpk) which had also undergone a hydration reaction at the ketone to form a geminal diol. Extensive hydrogen bonding involving the O atoms of the diol contribute to the high stability of the molecule. The geometry about the bridging *sp*^{3} C atom is almost that of a regular tetrahedron. However, the two pyridine rings are twisted such that the molecule conforms closely to non-crystallographic twofold symmetry. The bond distances and angles within the pyridine rings are normal and there is no apparent strain or distortion.

Comment

We have been actively investigating the coordination chemistry of the ligand di-2-pyridyl ketone (dpk) since it exhibits unusual structural chemistry when in the presence of transition metal cations (Wang, Richardson, Briggs, Jacobson & Jensen, 1986). We have reported several structures involving dpk in this journal (Sommerer & Abboud, 1993; Sommerer, Westcott & Abboud, 1994) and elsewhere (Sommerer, Jensen & Jacobson, 1990; Sommerer, Baker, Jensen, Hamza & Jacobson, 1993). In the course of our current work with this molecule, we have isolated and structurally characterized a doubly protonated derivative of dpk which has also undergone a hydration reaction at the ketone to form a geminal diol, (I). A thermally stable diol of this form is quite novel and we are not aware of any others which have been characterized in the solid state to date. Stable geminal diols, of which the hydrates of chloral and hexafluoroacetone are two notable examples, are usually generated from electron-deficient carbonyl compounds, including polyhalogenated aldehydes and ketones and α-keto aldehydes (March, 1985). The two protonated pyridine rings in hydrated dpk serve this purpose and add to the stabilization of the molecule.



The crystal structure of the title compound was found to consist of di(2-pyridinio)methanediol cations each balanced by two nitrate anions. There is extensive hydrogen bonding involving the O atoms of the diol (Fig. 1), which contributes to the stability of the molecule. The geometry about the bridging *sp*^{3} C atom is close to tetrahedral with a slight expansion of the O1*a*—C1—O1*b* angle to 113.89 (14)°. This distortion from regular tetrahedral geometry is likely to result from the repulsion of the lone-pair electrons of O1*a* and O1*b*. The bonds and the angles within the pyridine rings show no irregularities. The dihedral angles between P_1 (the plane defined by the atoms C1, O1*a* and O1*b*) and P_2 (the plane defined by N1, C2, C3, C4, C5 and C6) is 125.1 (1)°, and the angle formed between P_1 and P_3 (N1′, C2′, C3′, C4′, C5′ and C6′) is 120.2 (1)°. The dihedral angle between P_2 and P_3 is 92.49 (6)°. The pyridine