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4-Aza-9(10*H*)-acridone†

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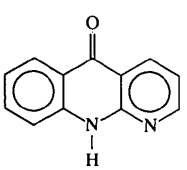
Abstract

The crystal packing of the title compound, $C_{12}H_8N_2O$, is dominated by hydrogen bonding and π–π-type interactions along the short axial direction. Each molecule is hydrogen bonded to two adjacent molecules which are part of the same stacked column. The N—H···N hydrogen bonds have an N···N distance of 2.95 Å.

Comment

The title compound, (I), has been employed as a reagent in the synthesis of potential DNA intercalative drugs (Denny, Atwell & Cain, 1977). During the attempted crystallization of one such intercalator, small yellow crystals formed which were subsequently shown by X-ray crystallography to be those of the title compound.



(I)

The majority of the bond lengths in compound (I) (between non-H atoms) are within 3σ of those of the parent 9(10*H*)-acridone compound, (II) (Potts & Jones, 1995), and most of the bond angles at the C atoms in the title compound fall in the range 118–120°. The angles falling outside this range are those involving atoms C9 and N10, and most of the angles that are part of the 4-aza ring. The bonds to atom N4 in (I) are significantly shorter than those to C4 in (II) and the internal ring angle at N4 is significantly smaller than that at C4. The two outer rings of the 4-aza three-ring system are individually planar, with no ring atoms deviating from their calculated planes by more than 0.01 Å. The central ring adopts a slight boat-type conformation with atoms C9 and N10 each deviating from the calculated ring plane by 0.036 (4) Å. Overall, the three-ring chromophore is approximately planar. The structure contains an intermolecular close approach of 2.14 Å between atoms O9 and H3($-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$), which results in a deviation for H3 of 0.21 (8) Å from the calculated six-membered ring plane.

The replacement of atom C4 in the parent acridone (II) with N4 in the present structure provides an extra potential hydrogen bond. The N—H···O hydrogen bond of compound (II) is replaced with an N—H···N bond involving N4 in (I). The hydrogen-bond pattern of (II) connects adjacent stacks of molecules extending through the crystal in a direction perpendicular to the π–π stacking direction. In compound (I), the stacking is also in the short axial direction, but the hydrogen bonding only links two stacked piles of molecules. Each molecule is hydrogen bonded to two adjacent molecules taking part in π–π stacking interactions such that the chain of hydrogen-bonded molecules extends

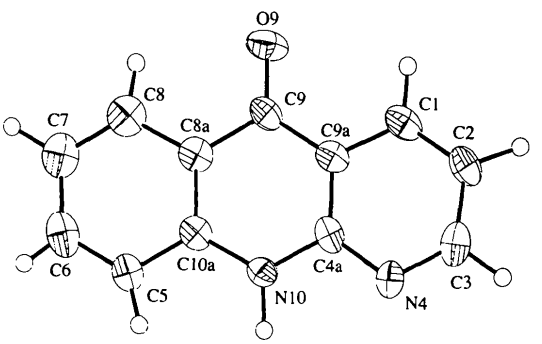


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of 4-aza-9(10*H*)-acridone showing 50% displacement ellipsoids and the atomic numbering scheme.

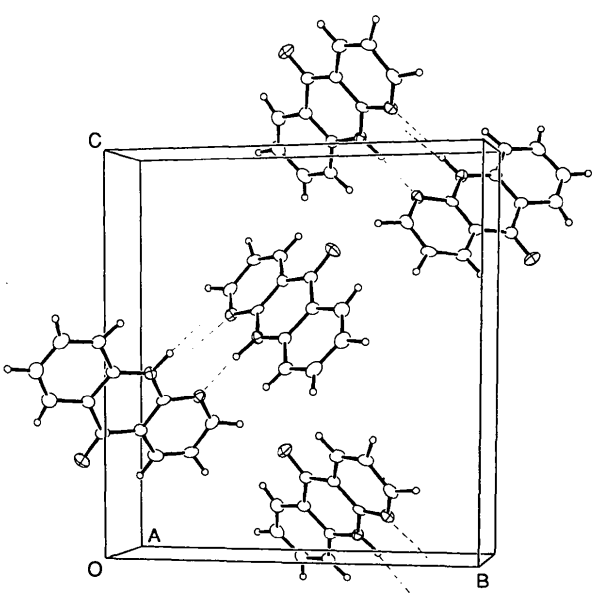


Fig. 2. Packing diagram of 4-aza-9(10*H*)-acridone. Hydrogen bonds are drawn with dashed lines.

† Alternative nomenclature: benzo[*b*][1,8]naphthyridin-10(5*H*)-one.

in the stacking direction. This bonding mode results in a change in space group from $P2_1/n$ in compound (II) to $P2_12_12_1$ in compound (I).

The hydrogen-bond pattern of (I) cannot occur in the $P2_1/n$ space group of the parent molecule. The space group $P2_1/n$ contains inversion symmetry which would not allow atoms N10 and N4 to face each other and form hydrogen bonds. Replacement of the glide planes and inversion centres with elements of rotational symmetry, such as the 2_1 screw axes in this case, allows the N atoms to attain a useful geometry for hydrogen-bond formation. The translational component of the screw axes allows the hydrogen bonding to occur down a chain of stacked molecules. In this way, the hydrogen bonding is maximized.

Experimental

A sample of the intercalative compound was generously supplied by Professor W. A. Denny of the Cancer Research Laboratory, Auckland University School of Medicine, New Zealand. The title compound was crystallized by evaporation from an ethanol solution.

Crystal data

$C_{12}H_8N_2O$
M_r = 196.20
Orthorhombic
$P2_12_12_1$
a = 4.8061 (10) Å
b = 13.262 (4) Å
c = 14.195 (4) Å
V = 904.8 (4) Å^3
Z = 4
D_x = 1.440 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 8.35–12.09°
μ = 0.095 mm^{-1}
T = 193 (2) K
Blade
0.30 × 0.08 × 0.06 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.919, T_{max} = 0.996
1063 measured reflections
1063 independent reflections

635 observed reflections [$I > 2\sigma(I)$]
θ_{max} = 25.97°
$h = 0 \rightarrow 5$
$k = -16 \rightarrow 0$
$l = -17 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: insignificant

Refinement

Refinement on F^2
$R(F)$ = 0.073
$wR(F^2)$ = 0.2109
S = 1.108
1063 reflections
167 parameters
All H-atom parameters refined except for H7

$w = 1/[\sigma^2(F_o^2) + (0.1110P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.269 e Å^{-3}
$\Delta\rho_{min}$ = −0.290 e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O9	0.4022 (11)	0.5760 (4)	0.7587 (3)	0.0458 (15)
N4	0.1358 (13)	0.2727 (4)	0.6018 (4)	0.0339 (15)
N10	0.4814 (12)	0.3762 (4)	0.5438 (4)	0.0307 (14)
C1	0.0433 (14)	0.4044 (6)	0.7510 (5)	0.037 (2)
C2	−0.1077 (16)	0.3181 (6)	0.7441 (5)	0.037 (2)
C3	−0.0510 (16)	0.2541 (6)	0.6679 (5)	0.040 (2)
C4a	0.2836 (14)	0.3589 (5)	0.6114 (4)	0.027 (2)
C5	0.8285 (15)	0.4808 (6)	0.4677 (5)	0.035 (2)
C6	0.9785 (17)	0.5666 (7)	0.4656 (6)	0.045 (2)
C7	0.9508 (16)	0.6407 (6)	0.5357 (6)	0.044 (2)
C8	0.7639 (18)	0.6251 (6)	0.6076 (6)	0.044 (2)
C8a	0.6047 (15)	0.5359 (5)	0.6126 (5)	0.032 (2)
C9	0.4141 (14)	0.5172 (5)	0.6907 (4)	0.031 (2)
C9a	0.2483 (15)	0.4278 (5)	0.6847 (4)	0.029 (2)
C10a	0.6345 (14)	0.4638 (5)	0.5406 (5)	0.030 (2)

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

O9—C9	1.241 (8)	C5—C6	1.348 (11)
N4—C3	1.322 (9)	C5—C10a	1.411 (10)
N4—C4a	1.352 (9)	C6—C7	1.404 (12)
N10—C4a	1.370 (8)	C7—C8	1.376 (11)
N10—C10a	1.377 (8)	C8—C8a	1.410 (10)
C1—C2	1.358 (11)	C8a—C10a	1.406 (9)
C1—C9a	1.397 (10)	C8a—C9	1.459 (10)
C2—C3	1.401 (10)	C9—C9a	1.431 (10)
C4a—C9a	1.395 (9)		
C3—N4—C4a	116.3 (6)	N4—C4a—C9a	124.4 (6)
C4a—N10—C10a	122.4 (6)	O9—C9—C9a	122.7 (6)
C1—C2—C3	117.5 (7)	C9a—C9—C8a	116.4 (6)
N4—C3—C2	124.5 (7)	C4a—C9a—C1	116.2 (7)
N4—C4a—N10	115.8 (6)	C1—C9a—C9	122.5 (6)

The fact that the crystal was weakly diffracting probably accounts for the high value of the R factor. Seven H atoms were located in difference Fourier maps and their coordinates and isotropic displacement parameters were fully refined. Atom H7 was assigned calculated coordinates and allowed to ride on atom C7 for refinement.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1053). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Denny, W. A., Atwell, G. J. & Cain, B. F. (1977). *J. Med. Chem.* **20**, 1242–1246.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Potts, G. D. & Jones, W. (1995). *Acta Cryst.* C**51**, 267–268.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

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4a-Phenylperhydro-1,4-dioxacyclopropa-[*cd*]pentalene

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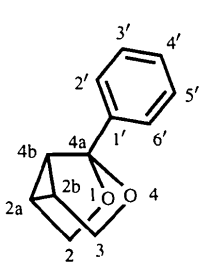
Abstract

The title compound, $C_{12}H_{12}O_2$, represents the first example of a molecule containing the perhydro-1,4-dioxacyclopropa[*cd*]pentalene ring system which has been subjected to single-crystal X-ray analysis.

Comment

We have been developing methods for the synthesis of molecular clefts based on cyclopropylidene dimers derived from ring-fused *gem*-dibromocyclopropanes (Banwell, Gable, Greenwood, Lambert, Mackay & Walter, 1995). As part of this work, we had occasion to attempt the dimerization of the dibromocarbene adducts of 4,7-dihydro-2-phenyl-1,3-dioxepin (Bulman-Page, Rayner & Sutherland, 1990) using methyl lithium. However, the major isolable product of the reaction was not the hoped-for dimer, but rather, a monomeric species. Given the propensity of certain cyclopropylidenes to undergo intramolecular C—H insertion (Banwell & Reum, 1991), it seemed plausible that this product was the title compound, (I), but the spectroscopic data obtained were inconclusive. Consequently, a single-crystal X-ray structure determination was undertaken, the results of which are reported here.



(I)

The 1,4-dioxacyclopropa[*cd*]pentalene framework associated with compound (I) closely resembles that of the all-carbon analogue (cyclopropa[*cd*]pentalene) and several molecules embodying this latter ring system have been the subject of X-ray crystallographic studies (Garcia-Garibay, Scheffer, Trotter & Wireko, 1990; Pokkuluri, Scheffer & Trotter, 1993*a*,*b*; Pokkuluri, Scheffer, Trotter & Yap, 1994; Pokkuluri & Trotter, 1994).

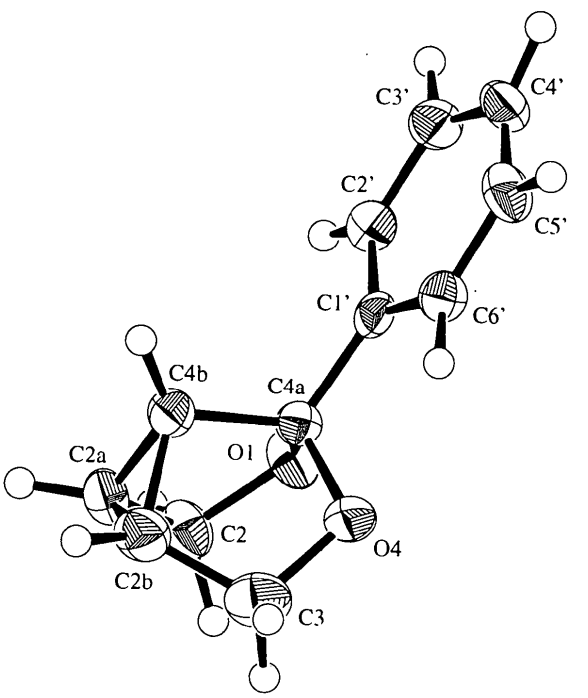


Fig. 1. View of 4a-phenylperhydro-1,4-dioxacyclopropa[*cd*]pentalene, (I), showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as circles of arbitrary radii.

Experimental

The title compound, (I), was prepared by treating the dibromocarbene adducts of 4,7-dihydro-2-phenyl-1,3-dioxepin with 2.2 equivalents of methyl lithium in diethyl ether at 193 K for 4 h. The reaction mixture was then allowed to warm to room temperature over a period of 4 h and quenched with water. The crude product obtained after extractive work-up was subjected to high-performance liquid chromatography (1:9 ethyl acetate/hexane elution, semi-preparative μ-Porasil column, flow rate 2 ml min^{-1}) and the appropriate fractions (t_R = 21 min) concentrated under reduced pressure to give the title compound (m.p. 380–381 K).

Crystal data

$C_{12}H_{12}O_2$
M_r = 188.23

Cu $K\alpha$ radiation
λ = 1.5418 Å