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4,8,9,10-Tetraphenyl-1,3-diazaadamantan-6-one

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.044
wR factor = 0.118
Data-to-parameter ratio = 10.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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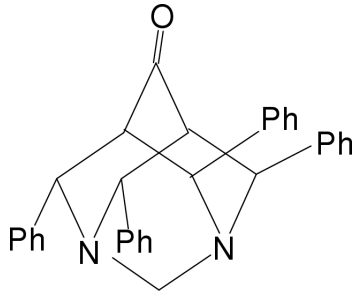
In the molecule of the title compound, $C_{32}H_{28}N_2O$, two of the four phenyl substituents occupy axial and the other two occupy equatorial positions relative to their respective C_5N rings of the adamantane framework. The crystal packing is characterized by weak C—H···O interactions. The packing features are distinctly different from those of the crystals of the methoxy- and chloro-substituted analogues.

Comment

The tendency of molecules to pack as closely as possible upon crystallization gives rise to a variety of intermolecular interactions. The complex nature of such interactions contributes to the difficulty in predicting crystal structures, which is recognized as a major problem similar to that of predicting protein folding. In this context, the design, synthesis and crystal structure determination of symmetrically shaped molecules are expected to provide insights into the nature of intra- and intermolecular interactions and their role in 'steering' a molecule to adopt a unique crystal structure. 1,3-Diazaadamantane systems are of pharmacological significance and are potentially interesting as anticholinergic compounds (Fernández *et al.*, 1990). We report here the crystal structure of a symmetrically shaped diazaadamantanone derivative, *viz*. 4,8,9,10-tetraphenyl-1,3-diazaadamantan-6-one, (I).



(I)

Fig. 1 shows the atom-numbering scheme, which complies with the standard adamantane framework numbering, as recommended by IUPAC. Recently, the crystal structures of derivatives of the title compound, namely 4,8,9,10-tetrakis(4-methoxyphenyl)-1,3-diazaadamantan-6-one benzene solvate (Krishnakumar, Vijayakumar *et al.*, 2001) and 4,8,9,10-tetrakis(4-chlorophenyl)-1,3-diazaadamantan-6-one (Krishnakumar, Subha Nandhini *et al.*, 2001) were elucidated in our laboratory. In all cases, two of the four phenyl substituents occupy axial and the other two occupy equatorial positions relative to their respective C_5N rings of the

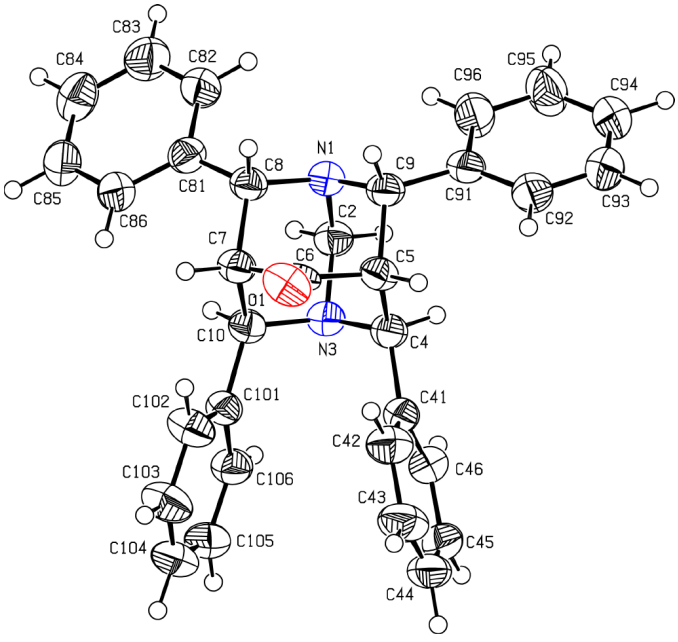


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids.

adamantane framework. Interestingly, in the crystal structure of the methoxy-substituted derivative, the molecule sits on a crystallographic mirror plane (along with the solvent benzene molecule) and serves as a good example of the retention of mirror symmetry by a molecule in the crystalline state. However, no such feature has been observed either in the crystal structure of (I) or in the structure of its chloro-substituted derivative. A molecular fit of (I) with its methoxy- and chloro-substituted analogues shows a nearly perfect match except for the slight rotations of the substituent phenyl rings. Thus, it seems there is no loss of molecular symmetry, though the molecule does not lie across the mirror plane, as in the case of the methoxy-substituted analogue. Though the adamantanone cage is inherently rigid and symmetrical, the fact that the overall symmetry of the molecule is sensitive to slight rotations of the phenyl substituents at positions 4, 8, 9 and 10 might possibly play a role in displacing the molecule from a potential mirror plane in the unit cell.

The distance between the centres of the phenyl substituents in the axial positions relative to the C_5N rings (*viz*. the C41–C46 and C101–C106 substituents in Fig. 1) is 3.775 (5) Å in (I), which is less than the value of 3.939 (6) Å observed in the electron-releasing methoxy derivative and greater than the value of 3.613 (7) Å observed in the electron-withdrawing chloro derivative.

The crystal packing is characterized by weak C—H···O interactions (Fig. 2 and Table 1). The packing features of (I) are distinctly different from those of its methoxy- and chloro-substituted analogues, as the packing of the former does not feature any specific interactions, whereas the packing of the latter is determined, not only by the C—H···O, but also by the Cl···Cl interactions.

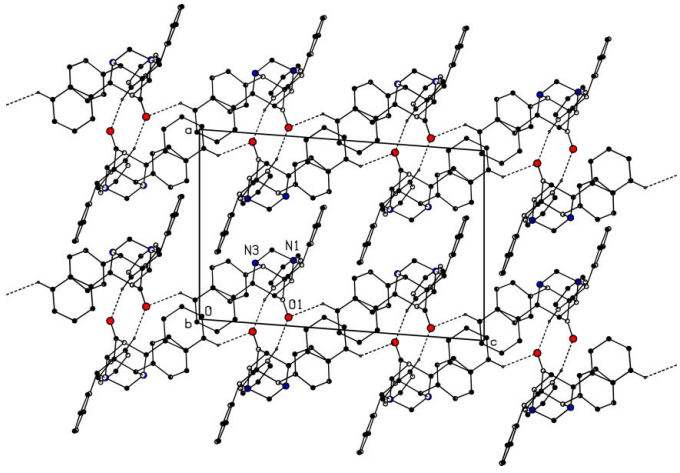


Figure 2
Crystal packing diagram, viewed down the *b* axis.

Experimental

The title compound was synthesized using the general method of preparation of 4,8,9,10-tetraaryl-1,3-diazaadamantane-6-ones as follows.

(*a*) Preparation of 2,4,6,8-tetraphenyl-3,7-diazabicyclo[3.3.1]-nonan-9-ones: 42.4 ml of benzaldehyde (0.4 mol), 15.4 g of dry ammonium acetate (0.2 mol) and 5.8 ml of acetone (0.1 mol) were mixed in 100 ml of ethanol, and the mixture was heated on a hotplate with constant shaking until the colour changed to pale orange (under the reaction conditions, ammonium acetate dissociates and liberates ammonia, which acts as the nitrogen source). The flask was immediately cooled under tap water, a sufficient amount of ether was added to the cold reaction mixture, and the precipitated 2,4,6,8-tetraphenyl-3,7-diazabicyclo[3.3.1]nonan-9-ones were removed by filtration and washed with an alcohol–ether mixture until the yellow colour disappeared. Generally, the yield was up to 50%.

(*b*) Preparation of 4,8,9,10-tetraphenyl-1,3-diazaadamantan-6-one: 2,4,6,8-tetraphenyl-3,7-diazabicyclo[3.3.1]nonan-9-one (2.2 g, 5 mmol) was taken up in benzene (50 ml), and 40% aqueous formaldehyde (10 ml) was added. During this period, the benzene-insoluble bicyclic compound was converted to the benzene-soluble adamantanone and two clear layers separated out. The benzene layer was separated, washed thoroughly with water and evaporated to yield the crude adamantanone. The crude adamantanone was crystallized from a benzene–chloroform mixture in a 1:1 ratio and the melting points were noted (Quast & Muller, 1980; Jackman *et al.*, 1982; Quast *et al.*, 1982; Sivasubramanian *et al.*, 1990; Jeyaraman *et al.*, 1992).

Colourless single crystals were obtained as transparent needles from a saturated solution of the title compound in a benzene–chloroform mixture by slow evaporation at room temperature.

Crystal data

$C_{32}H_{28}N_2O$
M_r = 456.56
Monoclinic, $P2_1/c$
a = 11.7347 (14) Å
b = 11.6976 (13) Å
c = 17.6391 (14) Å
β = 94.32 (1)°
V = 2414.4 (5) Å^3
Z = 4
D_x = 1.256 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 1016 reflections
θ = 16–32°
μ = 0.59 mm^{-1}
T = 293 (2) K
Needle, colourless
0.30 × 0.26 × 0.13 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.92, T_{max} = 0.93
9728 measured reflections
3425 independent reflections
2919 reflections with $I > 2\sigma(I)$
R_{int} = 0.098
θ_{max} = 58.9°
$h = -7 \rightarrow 13$
$k = -12 \rightarrow 11$
$l = -19 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.118
S = 1.08
3425 reflections
317 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.7546P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0063 (5)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C86—H86···O1^{i}	0.93	2.62	3.191 (2)	120
C105—H105···O1^{ii}	0.93	2.64	3.310 (2)	130

Symmetry codes: (i) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (ii) $x, \frac{1}{2}-y, z-\frac{1}{2}$.

All H atoms were generated geometrically and were allowed to ride on their parent atoms, with *SHELXL*97 (Sheldrick, 1997) defaults for bond distances and displacement parameters.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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