

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

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.051

wR factor = 0.147

Data-to-parameter ratio = 10.9

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

In the title compound, $\text{C}_{32}\text{H}_{28}\text{N}_2\text{O} \cdot 0.5\text{C}_3\text{H}_6\text{O}$, the two axial and two equatorial phenyl substituents are essentially planar. There are no hydrogen-bonded interactions between the two independent molecules in the asymmetric unit. The crystal packing is characterized by $\text{C}-\text{H} \cdots \text{O}$ interactions. The solvent (acetone) molecule in the crystal structure significantly influences the packing, features of which are distinctly different from those of unsolvated 4,8,9,10-tetraphenyl-1,3-diazaadamantan-6-one and its methoxy- and chloro-substituted analogues.

Comment

The complex nature of intermolecular interactions contributes to the difficulty of predicting crystal structures; this is recognized as a difficult problem, similar to that of predicting protein folding. In this context, the presence of solvent molecules and their role in stabilizing a crystal structure is of much importance and interest, requiring detailed investigations. Solvent molecules have a variety of roles to play in crystal structures. Though their presence for some compounds is essential for a successful crystallization, it is often a cause of disorder and instability in crystal structures. When solvent molecules occur in crystals as participants in hydrogen-bonding networks, they may also be regarded as playing a role in stabilizing the crystal structure and increasing the complexity of the intermolecular interactions. A solvent molecule as a mere space filler, with no strong interactions between solvent and solute molecules, is nevertheless important and may have a role to play as a mediator between the intra- and intermolecular interactions. We report here the crystal structure of a symmetrical diazaadamantanone derivative, *viz.* 4,8,9,10-tetraphenyl-1,3-diazaadamantan-6-one, with acetone solvent incorporated in the structure. 1,3-Diazaadamantane systems are of pharmacological interest and are potentially interesting as anticholinergic compounds (Fernández *et al.*, 1990).

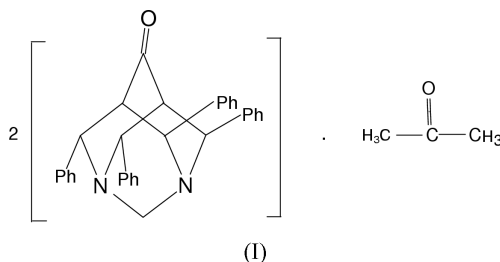


Fig. 1 shows the atom-numbering scheme of the title compound, (I), which complies with the standard adamantane

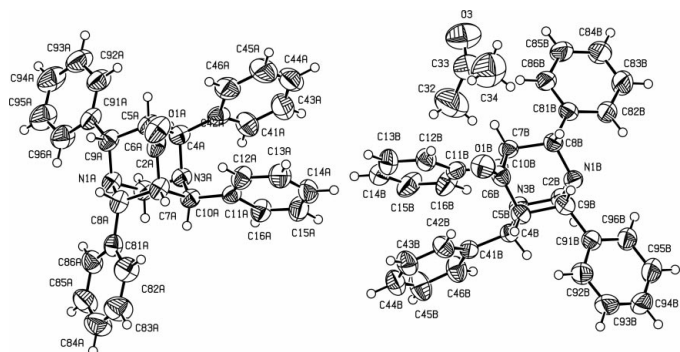


Figure 1
The asymmetric unit of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

framework numbering, as recommended by IUPAC. Recently, the crystal structures of derivatives of the title compound, 4,8,9,10-tetrakis(4-methoxyphenyl)-1,3-diazaadamantan-6-one benzene solvate (Krishnakumar, Vijayakumar *et al.*, 2001), 4,8,9,10-tetrakis(4-chlorophenyl)-1,3-diazaadamantan-6-one (Krishnakumar, Subha Nandhini *et al.*, 2001) and 4,8,9,10-tetraphenyl-1,3-diazaadamantan-6-one (Subha Nandhini *et al.*, 2002) were elucidated in our laboratory. 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 for the retention of mirror symmetry by a molecule in the crystal state. However, no such feature has been observed in the crystal structures of the chloro-substituted derivative or of 4,8,9,10-tetraphenyl-1,3-diazaadamantan-6-one.

In the present structure, two adamantane molecules are in the asymmetric unit; they are chemically equivalent but crystallographically independent. In addition, a solvent molecule (acetone) is also present. The four six-membered rings which constitute the diazaadamantanone cage adopt chair conformations, the preferred conformation for adamantanes, irrespective of substitution. A comparison of the torsion angles of the adamantane cage of the present structure with unsolvated 4,8,9,10-tetraphenyl-1,3-diazaadamantan-6-one (Subha Nandhini *et al.*, 2002) clearly shows that they are nearly the same.

The molecular fit of molecules *A* and *B* (Fig. 2) shows a nearly perfect match, except for slight rotations of the substituent phenyl groups. Thus, it seems there is no loss of molecular symmetry, though the molecule does not lie across a mirror plane, as in the case of 4,8,9,10-tetrakis(4-methoxyphenyl)-1,3-diazaadamantan-6-one benzene solvate (Krishnakumar, Vijayakumar *et al.*, 2001). Although the adamantane 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 the 4, 8, 9 and 10 positions might possibly play a role in displacing the molecule from a potential mirror in the crystal structure. Also, a very slight change observed in the positions of H atoms on C41 and C11 may be due to the presence of C—H...O interactions of the solvent (acetone) molecule with molecule *A*.

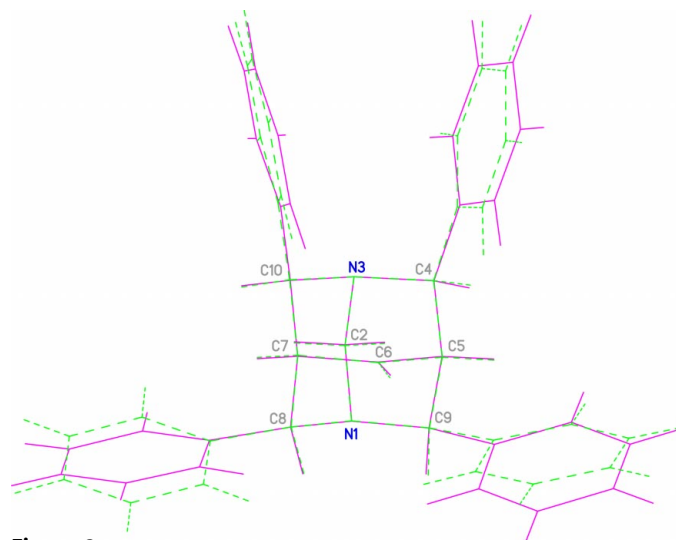


Figure 2
A least-squares superposition of the two independent molecules of (I) in the asymmetric unit.

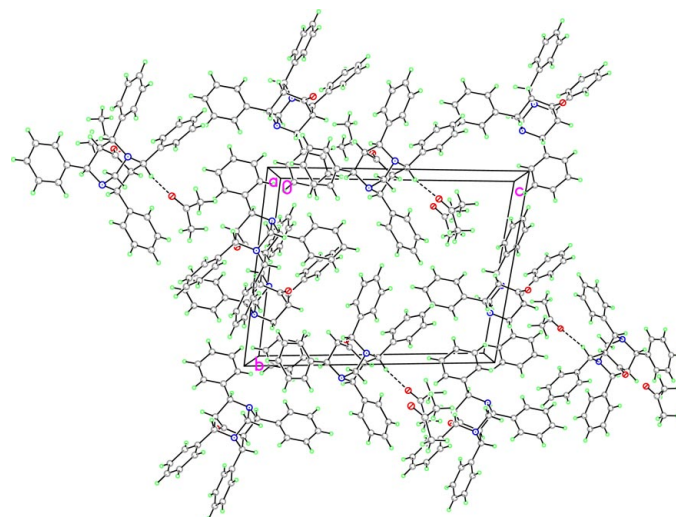


Figure 3
Packing diagram of the molecules, viewed down the *a* axis.

The distances between the centres of the phenyl rings in the axial positions and the C₅N rings are 3.833 and 3.730 Å in molecules *A* and *B*, respectively. The difference in these distances for molecules *A* and *B* may be due to the interactions between the π -electron cloud in the equatorial phenyl group and acetone molecule. The distances in the present structure are close to the value of 3.775 (5) Å observed in 4,8,9,10-tetraphenyl-1,3-diazaadamantan-6-one (Subha Nandhini *et al.*, 2002), less than the value of 3.939 (6) Å observed in the electron-releasing 4,8,9,10-tetra(4-methoxyphenyl)-1,3-diazaadamantan-6-one (Krishnakumar, Vijayakumar *et al.*, 2001), and greater than the value of 3.613 (7) Å observed in the electron-withdrawing 4,8,9,10-tetra(4-chlorophenyl)-1,3-diazaadamantan-6-one (Krishnakumar, Subha Nandhini *et al.*, 2001).

The crystal packing of (I) is illustrated in Fig. 3. The packing features are distinctly different from the previous unsolvated form and also from its methoxy- and chloro-substituted

analogues. The two independent molecules in the asymmetric unit have no hydrogen-bonded interactions between them. However, they each form a centrosymmetrically related hydrogen-bonded pair through C—H···O hydrogen bonds involving carbonyl O atoms. The crystal packing is characterized by these C—H···O hydrogen bonds and van der Waals interactions.

Experimental

The title compound was synthesized according to 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 added to 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 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-tetraaryl-3,7-diazabicyclo[3.3.1]nonan-9-one (2.2 g, 5 mmol) was added to 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. This was recrystallized from a 2:2:1 mixture of benzene, chloroform and acetone and the melting points were noted (Quast & Müller, 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 chloroform, benzene and acetone, by slow evaporation at room temperature.

Crystal data

$2C_{32}H_{28}N_2O \cdot C_3H_6O$	$Z = 2$
$M_r = 971.21$	$D_x = 1.223 \text{ Mg m}^{-3}$
Triclinic, $P1$	Cu $K\alpha$ radiation
$a = 12.6087 (14) \text{ \AA}$	Cell parameters from 1016 reflections
$b = 13.7214 (12) \text{ \AA}$	$\theta = 12\text{--}31^\circ$
$c = 17.056 (2) \text{ \AA}$	$\mu = 0.58 \text{ mm}^{-1}$
$\alpha = 92.76 (1)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 103.57 (1)^\circ$	Plate, colourless
$\gamma = 111.60 (1)^\circ$	$0.34 \times 0.26 \times 0.12 \text{ mm}$
$V = 2637.4 (5) \text{ \AA}^3$	

Data collection

Siemens SMART CCD diffractometer	7313 independent reflections
ω scans	5907 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.051$
$T_{\text{min}} = 0.853$, $T_{\text{max}} = 0.929$	$\theta_{\text{max}} = 58.9^\circ$
10907 measured reflections	$h = -10 \rightarrow 14$
	$k = -15 \rightarrow 15$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0611P)^2 + 0.8497P]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.147$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.11$	$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
7313 reflections	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
668 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0026 (2)

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C4A-H4A \cdots O3^i$	0.98	2.60	3.525 (3)	158
$C10A-H10A \cdots O3$	0.98	2.56	3.451 (3)	152
$C82A-H82A \cdots O1A^{ii}$	0.93	2.39	3.279 (3)	160
$C92B-H92B \cdots O1B^{iii}$	0.93	2.60	3.511 (3)	168

Symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $1 - x, -y, 1 - z$; (iii) $1 - x, 1 - y, -z$.

All the H atoms were generated geometrically and were allowed to ride on their parent atoms with *SHELXL97* (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: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97*.

The authors thank the UGC for the DRS programme.

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