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4,8,9,10-Tetrakis(4-chlorophenyl)-1,3-diaza-adamantan-6-one

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.061
wR factor = 0.149
Data-to-parameter ratio = 14.9

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

In the title compound, $C_{32}H_{24}Cl_4N_2O$, all four six-membered rings which constitute the diazaadamantanone cage adopt chair conformations. The crystal structure is stabilized by Cl···Cl interactions and C—H···O hydrogen bonds.

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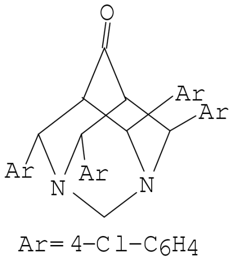
Comment

The present X-ray investigation on the title compound, 4,8,9,10-tetrakis(4-chlorophenyl)-1,3-diazaadamantan-6-one, (I), was carried out with a view to observing possible differences in the crystal and molecular structures upon exchange of substituents and to obtain some information about the nature of specific substituents or specific interactions. Moreover, crystallographic investigations on symmetrically shaped molecules are expected to provide insights into the nature and strength of intermolecular interactions and their role in effecting symmetry carry-over from the free state to the solid. Recently, the crystal structure of a methoxy-substituted analogue of the title compound, 4,8,9,10-tetrakis(4-methoxyphenyl)-1,3-diazaadamantan-6-one benzene solvate, was elucidated in our laboratory (Krishnakumar *et al.*, 2001).



(I)

Fig. 1 shows the crystallographic numbering scheme adopted. No significant differences in the geometry of the diazaadamantanone cage are seen as it is known to be inherently rigid and symmetrical. All four six-membered rings which constitute the diazaadamantanone cage adopt chair conformations; this is the most preferred conformation for adamantanones, irrespective of substitutions. A molecular fit of (I) with its methoxy-substituted analogue shows a near perfect fit, except for a slight rotation of the two axially substituted phenyl rings. Thus, it seems that there is no loss of molecular symmetry as a result of chloro substitution, though the molecule does not lie across the mirror plane as in the case of the methoxy-substituted analogue.

It is known that the regular hexagonal geometry of benzene is perturbed when the ring is substituted with strong electron-donating or electron-withdrawing groups (Domenicano &

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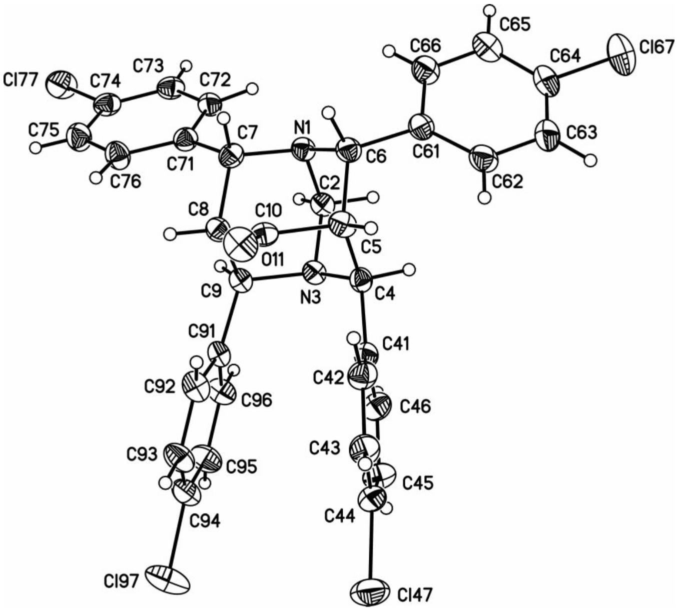

Figure 1
The molecular structure (*XP*; Siemens, 1990) with displacement ellipsoids drawn at the 50% probability level, showing the atom-numbering scheme adopted.

Murray-Rust, 1979; Domenicano *et al.*, 1983). However, in the title compound, the chloro substituent does not play any significant role in deforming the phenyl rings.

The crystal packing is stabilized by Cl···Cl interactions (Fig. 2) in addition to C—H···O hydrogen bonds. The two short Cl···Cl distances observed are: Cl47···Cl77$(1 - x, y + \frac{1}{2}, -z + \frac{3}{2})$ = 3.466 (3) Å and Cl67···Cl77$(x - 1, y + 1, z)$ = 3.346 (3) Å. These values are significantly shorter than the sum of the van der Waals radii and demonstrate the special nature of Cl···Cl interactions (Schmidt, 1971; Williams & Hsu, 1985) and their dominant role in determining the packing modes in crystal structures.

Experimental

Colourless single crystals of the title compound were obtained as transparent needles by slow evaporation of a benzene solution at room temperature.

Crystal data

$C_{32}H_{24}Cl_4N_2O$
$M_r = 594.33$
Monoclinic, $P2_1/c$
$a = 6.818 (3)$ Å
$b = 13.288 (4)$ Å
$c = 30.670 (14)$ Å
$\beta = 94.47 (3)^\circ$
$V = 2770 (2)$ Å^3
$Z = 4$

$D_x = 1.425$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–25°
$\mu = 4.12$ mm^{-1}
$T = 293 (2)$ K
Needles, colourless
0.34 × 0.22 × 0.18 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.42$, $T_{\max} = 0.48$
5739 measured reflections
5268 independent reflections
3549 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.036$
$\theta_{\max} = 70.1^\circ$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 16$
$l = -37 \rightarrow 37$
2 standard reflections every 200 reflections intensity decay: 2%

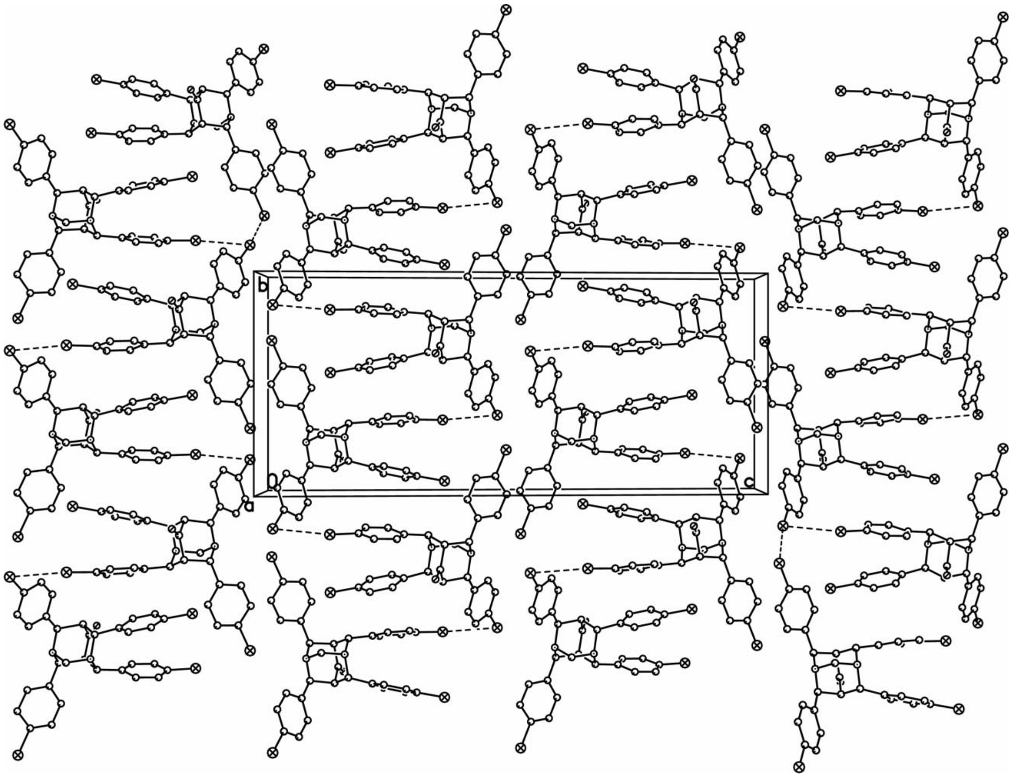

Figure 2
Packing of the molecules viewed down the *a* axis. Cl···Cl interactions are shown as dashed lines. H atoms have been omitted for clarity.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + 8.0771P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.061$	$(\Delta/\sigma)_{\max} < 0.001$
$wR(F^2) = 0.149$	$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$S = 1.16$	$\Delta\rho_{\min} = -0.40$ e Å^{-3}
5268 reflections	Extinction correction: *SHELXL*97
353 parameters	Extinction coefficient: 0.00100 (5)
H-atom parameters constrained	

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9···O11^{i}	0.98	2.58	3.428 (5)	144
C2—H2*B*···O11^{i}	0.97	2.50	3.357 (5)	148

Symmetry code: (i) $1 + x, y, z$.

The H atoms were placed at calculated positions and were allowed to ride on their respective parent atoms with HFIX instructions using *SHELXL*97 (Sheldrick, 1997) defaults.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL*97.

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