

1,3,5-Triphenyladamantane and
1,3,5,7-tetraphenyladamantaneIshtvan Boldog,^a Andrey B. Lysenko,^a Eduard B. Rusanov,^b
Alexander N. Chernega^b and Konstantin V.
Domasevitch^{a*}^aInorganic Chemistry Department, National Taras Shevchenko University of Kiev, Volodimirska Street 64, Kiev 01033, Ukraine, and ^bInstitute of Organic Chemistry, Murmanskaya Street 5, Kiev 02094, Ukraine
Correspondence e-mail: dk@univ.kiev.ua

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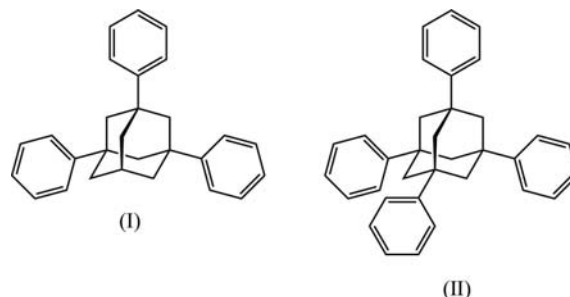
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In 1,3,5-triphenyladamantane, C₂₈H₂₈, (I), and 1,3,5,7-tetraphenyladamantane, C₃₄H₃₂, (II), the molecules possess symmetries 3 and $\bar{4}$, and are situated across threefold and fourfold improper axes, respectively. The molecules aggregate by means of extensive C—H... π interactions. In (I), the pyramidal shape of the molecules dictates the formation of dimers through a 'sixfold phenyl embrace' pattern. The dimers are linked to six close neighbors and constitute a primitive cubic net [H... π = 2.95 (2) and 3.02 (2) Å]. Compound (II) is isomorphous with tetraphenyl derivatives EPh₄ of group 14 (*E* = C—Pb) and ionic salts [EPh₄][BPh₄] (*E* = P, As and Sb). The multiple C—H... π interactions arrange the molecules into chains, with a concerted action of CH (phenyl) and CH₂ (adamantane) groups as donors [H... π = 3.15 (2) and 3.44 (2) Å, respectively]. The additional interactions with the methylene groups (four per molecule) are presumably important for explaining the high melting point and insolubility of (II) compared with the EPh₄ analogs.

Comment

Derivatives of adamantane attract a broad interdisciplinary interest as rigid molecular scaffolds for sustaining the structures of polyfunctional species, which find various applications in the chemistry of supramolecular systems, macromolecules, dendrimers and polymers. Thus, adamantanes substituted in the four available bridgehead positions represent a family of rigid tetrahedral building blocks for the synthesis of hydrogen- and coordination-bonded framework polymers, and they are paradigmatic for the general principles of crystal design. In particular, the fivefold-interpenetrated diamondoid framework of adamantane-1,3,5,7-tetracarboxylate (Ermer, 1988) was of paramount significance for the development of crystal engineering and for stimulating many further efforts in this field (Moulton & Zaworotko, 2001).

In recent years, considerable attention has been focused on the synthesis and utilization of nanosized adamantane derivatives extended by a rigid 1,4-phenylene spacer (Reichert & Mathias, 1994). Following this methodology, such species as carboxylates (Kim *et al.*, 2001), phosphonates (Jones *et al.*, 2006) and sulfonates (Hoffart *et al.*, 2005) were accessible by functionalization of phenyl-substituted adamantanes. However, supramolecular relations in such systems may be complicated, and close alignment of large shape-complementary tectons of high molecular symmetry could be prevalent for the crystal packing. This militates against the preparation of very open structures and makes the synthesis more difficult owing to the very poor solubility of the organic tectons. When exploring the evident potential of extended adamantanes for the development of framework solids (Chen *et al.*, 2000), the structures of the simpler phenyl derivatives are particularly interesting. The latter may be considered as prototypal building blocks, which assemble into framework structures through C—H... π interactions between the multiple phenyl functions (Nishio *et al.*, 1998). These interactions clearly define the elegant structure of 1,3-diphenyladamantane, which contains supramolecular helices (Tukada & Mochizuki, 2003). Even more illustrative supramolecular relations may be anticipated for rigid tri- and tetrasubstituted molecules since multivalency of the building blocks and inherently defined and proper binding geometry are equally important factors for organization of the framework. Concerted C—H... π interactions are presumably responsible for the unusual properties of a tetraphenyl derivative, which is an exceptionally high-melting (690–692 K) and insoluble solid (Newman, 1972). We have examined polyfunctional 1,3,5-triphenyladamantane, (I), and 1,3,5,7-tetraphenyladamantane, (II), and report their structures here.



Molecules of (I) have 3 symmetry in the crystalline state, with the C4—H4 group lying on a threefold axis (Fig. 1), and therefore there is only one independent phenyl group. This phenyl group adopts a nearly eclipsed conformation to one of the C—C bonds of the adamantane carrier [*e.g.* C2ⁱ—C1—C5—C6 = –6.71 (16)°; symmetry code: (i) –*x* + *y*, –*x* + 1, *z*; see also Table 1], similar to the conformation in 1,3-diphenyladamantane (Tukada & Mochizuki, 2003).

The most peculiar feature of the crystal packing of (I) is a pairwise association of the molecules, leading to the formation of a tight 'supramolecular cube' (Fig. 2). The dimer possesses $\bar{3}$ symmetry and is supported by very characteristic C—H... π interactions between the six phenyl rings. Each pair of interacting rings adopts an interplanar angle of 73.55 (4)°. These

weak interactions are directional and the H atom is situated almost exactly above the neighboring ring centroid, the angle of the $H \cdots \pi$ axis to the plane of the aromatic ring being $83.1(10)^\circ$ (Table 2). Such a mode of shape-complementary association, often recognized as a 'sixfold phenyl embrace', is characteristic for pyramidal triphenyl-substituted molecules, and has been observed for several triphenylphosphines (Scudder & Dance, 2000), triphenylgermanium halogenides (Prince *et al.*, 2002) and even for charged species, such as triphenyltellurium cations (Närhi *et al.*, 2004). A distance of $6.136(2) \text{ \AA}$ between the centroids of the adamantane frame-

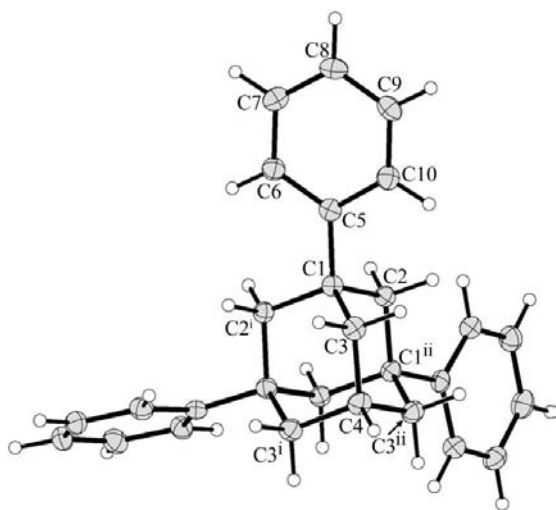


Figure 1
The structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. The threefold axis lies along the C4–H4 direction. [Symmetry codes: (i) $-x + y, -x + 1, z$; (ii) $-y + 1, x - y + 1, z$.]

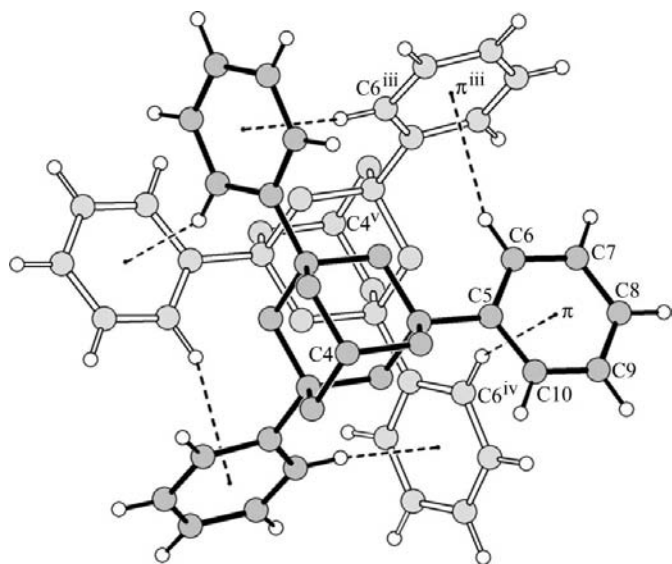


Figure 2
The supramolecular cube formed by two molecules of (I) by means of concerted $C-H \cdots \pi$ interactions (shown as dashed lines) between six phenyl groups. Atoms C4 and C4' are situated on the improper threefold axis. [Symmetry codes: (iii) $y - \frac{1}{3}, -x + y + \frac{1}{3}, -z + \frac{1}{3}$; (iv) $x - y + \frac{2}{3}, x + \frac{1}{3}, -z + \frac{1}{3}$; (v) $-x + \frac{2}{3}, -y + \frac{4}{3}, -z + \frac{1}{3}$.]

works indicates very tight coupling of the molecules constituting the dimer.

One additional group, C10–H10, is involved in an inter-dimer $C-H \cdots \pi$ interaction, which is comparable in strength to that above, with a $H \cdots \pi^{\text{vi}}$ separation of $2.95(2) \text{ \AA}$ [symmetry code: (vi) $y, -x + y, -z$; Fig. 3]. In total, the six phenyl groups of the dimer provide connections to six closest neighbors. Thus, the entire structure is very simple and may be regarded as a primitive cubic lattice with the supramolecular dimers as the net points. Alternatively, the structure may be described as a three-dimensional $C-H \cdots \pi$ phenyl stack of NbO topology, with bulky adamantane groups populating the framework cages.

Molecules of (II) have $\bar{4}$ symmetry in the crystal [atoms C2 and C2' are located on an inversion axis; symmetry code: (i) $y, -x, z$; Fig. 4] and display the expected tetrahedral geometry (Table 3), with the following angles subtended by the C_g –Ph vectors [C_g is the centroid of the adamantane group at $(0, 0, 0)$]: $C4-C_g-C4^{\text{ii}} = 106.74(6)^\circ$ and $C4-C_g-C4^{\text{iii}} = 110.86(6)^\circ$ [symmetry codes: (ii) $-x, -y, z$; (iii) $-y, x, -z$].

The structure is isomorphous with a family of tetraphenyl derivatives $E\text{Ph}_4$ of group 14 elements ($E = \text{C, Si, Ge, Sn}$ and Pb ; Claborn *et al.*, 2002) and also with tetraphenylsmium(IV) (Stavropoulos *et al.*, 1987). All the members of this family uniformly crystallize in the tetragonal space group $P\bar{4}2_1c$ with very similar unit-cell parameters. Ionic salts of the type $[E\text{Ph}_4][\text{BPh}_4]$ ($E = \text{P, As}$ and Sb) also adopt such a structure, while crystallizing in a supercell of $P\bar{4}2_1c$ with ordered positions of the ionic counterparts (Lloyd & Brock, 1997). Thus, (II) is a simple expanded analog of the above tetrahedral molecules, with a $C_g \cdots C(\text{Ph})$ separation [$3.1006(16) \text{ \AA}$] formally corresponding to the $E-C$ bonds of $E\text{Ph}_4$. The structure of (II) is organized by means of very extensive $C-H \cdots \pi$ interactions, leading to a packing index of 70.4. Although the value resides exactly at the mid-point of the 65–75% range expected for organic solids (Dunitz, 1995), it only slightly exceeds the parameters for the related $E\text{Ph}_4$ struc-

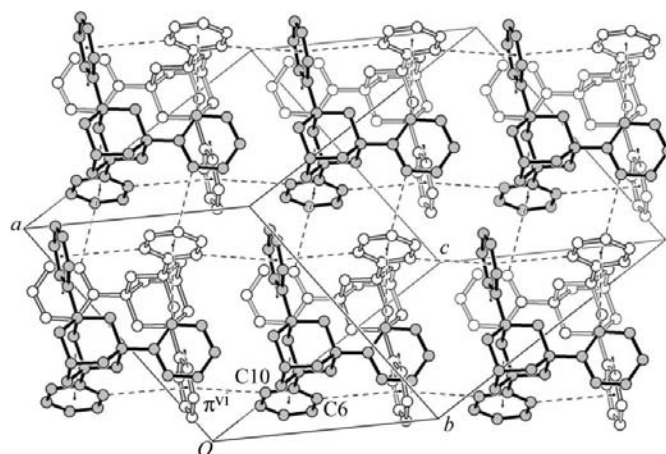


Figure 3
A view of the structure of (I), showing $C-H \cdots \pi$ interactions (dashed lines) between neighboring dimeric supramolecular entities. The same connectivity occurs also in the direction which is orthogonal to the plane of the drawing. [Symmetry code: (vi) $y, -x + y, -z$.]

tures, e.g. 69.3 for $E = \text{Si}$ and 69.9 for $E = \text{C}$ (Claborn *et al.*, 2002). In this context, it is interesting to query why these materials are so different in view of their properties, since (II) possesses an exceptionally low solubility in all common solvents and also an incomparably high melting point.

The primary supramolecular pattern is a one-dimensional chain, running along the c axis, in which the molecules are stacked like the pieces of a puzzle, yielding concerted cycles of four edge-to-face phenyl–phenyl interactions [$\text{C5}–\text{H5} \cdots \pi^v = 3.15(2) \text{ \AA}$; symmetry code: (v) $y, -x, -z + 1$; Figs. 5 and 6]. In the chain, the molecules of (II) are related by translation along the c -axis direction [$7.2032(6) \text{ \AA}$] and are packed even more closely than in tetraphenylmethane [$7.287(2) \text{ \AA}$; Robbins *et al.*, 1975]. The interchain bonding occurs by means of double $\text{C6}–\text{H6}/\text{C7}–\text{H7} \cdots \pi^{vi}$ [symmetry code: (vi) $y + \frac{1}{2}, x - \frac{1}{2}, z + \frac{1}{2}$] interactions, yielding a typical herring-bone arrangement of the phenyl groups (Fig. 6 and Table 4). These interactions are consistent with those in tetraphenyllead ($\text{H} \cdots \pi = 3.28 \text{ \AA}$; $\text{C} \cdots \pi = 3.949$ and 3.958 \AA ; Preut & Huber, 1993) and are somewhat stronger than those in tetraphenylmethane ($\text{H} \cdots \pi = 3.43$ and 3.73 \AA ; $\text{C} \cdots \pi = 4.166$ and 4.306 \AA).

The set of $\text{C}–\text{H} \cdots \pi$ interactions affords a three-dimensional stack (Fig. 7), and this motif is common for all of the present family. The most notable feature of the packing, which is applicable to (II) only, is a set of directional $\text{C2}–\text{H2} \cdots \pi^v$ contacts with the methylene group [$\text{H} \cdots \pi = 3.44(2) \text{ \AA}$ and $\text{C}–\text{H} \cdots \pi = 177.6(15)^\circ$; Fig. 5]. Such distal interactions are unlikely to be attributed to hydrogen bonding and presumably they originate in very weak dispersion forces. However, the co-operative effect of four such geometrically favored interactions per molecule of (II) may be significant (Suezawa *et al.*, 2001). This contributes to the overall energy of the supramolecular structure as an additional force compared with the isomorphous tetraphenyl derivatives of group 14. The fact that

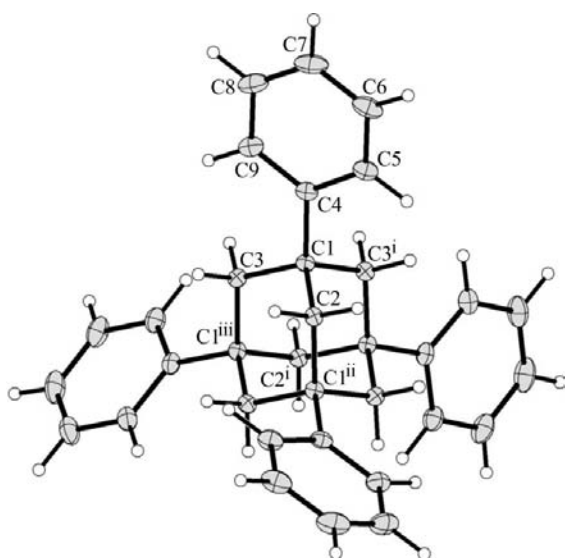


Figure 4
The structure of (II), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 35% probability level. The improper fourfold axis passes through atoms C2 and C2'. [Symmetry codes: (i) $y, -x, -z$; (ii) $-x, -y, z$; (iii) $-y, x, -z$.]

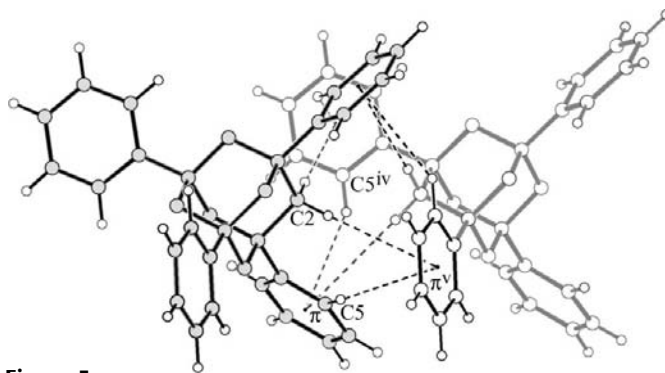


Figure 5
Multiple $\text{C}–\text{H} \cdots \pi$ interactions between pairs of molecules of (II), which lead to the formation of one-dimensional chains. Note the concerted interaction employing pairs of aromatic and aliphatic CH groups. [Symmetry codes: (iv) $-y, x, 1 - z$; (v) $y, -x, -z + 1$.]

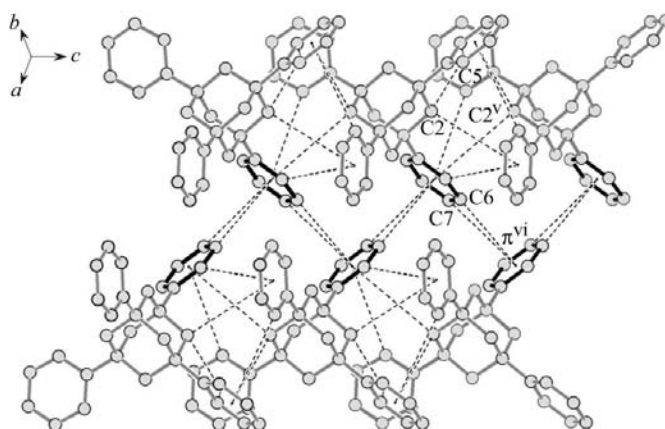


Figure 6
A view of the structure of (II), showing chains running along the c -axis direction. The $\text{C}–\text{H} \cdots \pi$ interactions between the chains produce a characteristic herring-bone phenyl motif (which is shown with bold bonds). [Symmetry codes: (v) $y, -x, -z + 1$; (vi) $y + \frac{1}{2}, x - \frac{1}{2}, z + \frac{1}{2}$.]

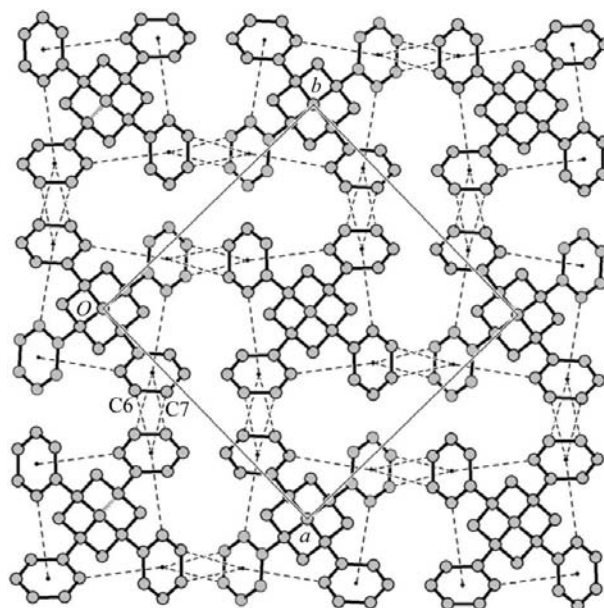


Figure 7
Projection of the structure of (II) on to the ab plane. The dashed lines indicate $\text{C}–\text{H} \cdots \pi$ interactions.

the concerted interactions C5–H5– π^v and C2–H2– π^v facilitate the densest interaction between the molecules may be applicable for other phenyl-substituted adamantanes as a special type of ‘supramolecular synthon’ organizing molecules in the solid state. In (I), such interactions are negated by the formation of the more prevalent ‘sixfold phenyl embrace’ pattern and there are no close contacts with the methylene group. However, the aforementioned synthon is relevant for 1,3-diphenyladamantane [C–H·· π = 3.39 Å (Ph) and 3.52 Å (CH₂); Tukada & Mochizuki, 2003], 1,3,5,7-tetrakis(4-phosphonophenyl)adamantane [C–H·· π = 3.28 Å (Ph) and 3.52 Å (CH₂); Jones *et al.*, 2006] and 1,3,5,7-tetrakis(4-ethynylphenyl)adamantane [C–H·· π = 3.55 Å (Ph) and 3.52 Å (CH₂); Galoppini & Gilardi, 1999].

In brief, the title structures are important as general and basic prototypes for intermolecular interactions between extended polyaryl-substituted adamantanes, which are currently arousing growing interest as molecular scaffolds in supramolecular chemistry. A comparison of (II) and a series of isomorphous tetraphenyl-substituted molecules allows the postulation of the significance of the weakest forces, such as methylene– π interactions.

Experimental

Compounds (I) and (II) were synthesized in a 15–20 g scale by Friedel–Crafts reaction of 1-bromoadamantane and benzene in the presence of *tert*-butyl bromide according to the procedure of Newman (1972). Crude (I) was washed repeatedly with ether to remove traces of mono- and diphenyladamantanes and then crystallized from hot toluene as large colorless prisms. Compound (II), which is insoluble in all common solvents, was purified from partially phenylated adamantanes by continuous extraction with hot toluene in a Soxhlet apparatus. For crystallization, the resulting colorless powder (15 mg) and xylene (8 ml, mixture of isomers) were sealed in a Pyrex tube and heated at 473 K for 2 d. Slow cooling to room temperature over a period of 70 h provided small colorless prisms of (II) in a quantitative yield.

Compound (I)

Crystal data

C ₂₈ H ₂₈	Z = 6
M _r = 364.50	Mo K α radiation
Trigonal, R $\bar{3}$	μ = 0.07 mm ⁻¹
a = 13.0230 (4) Å	T = 173 K
c = 19.8046 (13) Å	0.24 × 0.23 × 0.16 mm
V = 2908.8 (2) Å ³	

Data collection

Siemens SMART CCD area-detector diffractometer	3995 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1345 independent reflections
T _{min} = 0.978, T _{max} = 0.989	1039 reflections with I > 2 σ (I)
	R _{int} = 0.027

Refinement

R[F ² > 2 σ (F ²)] = 0.039	123 parameters
wR(F ²) = 0.103	All H-atom parameters refined
S = 1.04	$\Delta\rho_{\max}$ = 0.20 e Å ⁻³
1345 reflections	$\Delta\rho_{\min}$ = -0.20 e Å ⁻³

Table 1

Selected torsion angles (°) for (I).

C2 ⁱ –C1–C5–C10	177.26 (11)	C3–C1–C5–C10	56.10 (15)
C2–C1–C5–C10	-63.37 (14)		

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

Table 2

Geometry of C–H·· π interactions (Å, °) for (I).

π denotes the centroid of the phenyl ring and φ is the angle of the H·· π axis to the plane of the phenyl ring.

Contact	C·· π	H·· π	C–H·· π	φ
C6–H6·· π^{iii}	3.8598 (14)	3.02 (2)	147.0 (10)	83.1 (10)
C10–H10·· π^{vi}	3.8389 (13)	2.95 (2)	152.0 (10)	81.0 (10)

Symmetry codes: (iii) y - $\frac{1}{3}$, -x + y + $\frac{1}{3}$, -z + $\frac{1}{3}$; (vi) y, -x + y, -z.

Compound (II)

Crystal data

C ₃₄ H ₃₂	Z = 2
M _r = 440.60	Mo K α radiation
Tetragonal, P $\bar{4}$ ₂ c	μ = 0.07 mm ⁻¹
a = 12.8260 (11) Å	T = 213 K
c = 7.2032 (6) Å	0.26 × 0.23 × 0.22 mm
V = 1184.97 (17) Å ³	

Data collection

Stoe IPDS diffractometer	643 reflections with I > 2 σ (I)
4632 measured reflections	R _{int} = 0.028
822 independent reflections	

Refinement

R[F ² > 2 σ (F ²)] = 0.035	110 parameters
wR(F ²) = 0.084	All H-atom parameters refined
S = 0.92	$\Delta\rho_{\max}$ = 0.24 e Å ⁻³
822 reflections	$\Delta\rho_{\min}$ = -0.14 e Å ⁻³

Table 3

Selected torsion angles (°) for (II).

C3–C1–C4–C5	179.64 (15)	C3 ⁱ –C1–C4–C5	-58.51 (19)
C2–C1–C4–C5	60.75 (17)		

Symmetry code: (i) y, -x, -z.

Table 4

Geometry of C–H·· π interactions (Å, °) for (II).

π denotes the centroid of the phenyl ring and φ is the angle of the H·· π axis to the plane of the phenyl ring.

Contact	C·· π	H·· π	C–H·· π	φ
C2–H2·· π^v	4.4207 (14)	3.44 (2)	177.6 (15)	61.3 (16)
C5–H5·· π^v	4.0164 (19)	3.15 (2)	145.1 (16)	76.3 (18)
C6–H6·· π^{vi}	3.926 (2)	3.34 (2)	122.3 (15)	66.4 (16)
C7–H7·· π^{vi}	3.836 (2)	3.13 (2)	132.5 (16)	71.0 (18)

Symmetry codes: (v) y, -x, -z + 1; (vi) y + $\frac{1}{2}$, x - $\frac{1}{2}$, z + $\frac{1}{2}$.

For (II), the Friedel-related reflections were merged. For both structures, all the H atoms were found in intermediate difference Fourier maps and were refined fully with isotropic displacement parameters [for (I), phenyl C–H = 0.957 (16)–0.986 (15) Å and aliphatic C–H = 1.006 (14)–1.034 (14) Å; for (II), phenyl C–H = 0.94 (2)–1.00 (2) Å and aliphatic C–H = 0.984 (19)–1.009 (18) Å].

For (I), data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-NT* (Bruker, 1999); data reduction: *SAINT-NT*. For (II), data collection: *IPDS Software* (Stoe & Cie, 2000); cell refinement: *IPDS Software*; data reduction: *IPDS Software*. For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3104). Services for accessing these data are described at the back of the journal.

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