Molecular complexes of fullerene C_{60} with aromatic hydrocarbons containing flexible phenyl substituents

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New C_{60} molecular complexes with aromatic hydrocarbons containing flexible phenyl substituents 2TPE·C_{60} (**1**) (TPE = tetraphenylethylene), TPB·C_{60} (**2**) (TPB = 1,3,5-triphenylbenzene), 2TPB·C_{60}·C_6H_5Cl (**3**), DPA·C_{60} (**4**) (DPA = 9,10-diphenylanthracene), and PA·C_{60}·C_6H_6 (**5**) (PA = 9-phenylanthracene) have been synthesized. Crystal structures of **1**–**4** have been studied. It has been shown that in the structures of **1**, **2** and **4** the layers of the C_{60} molecules alternate with the layers composed of the hydrocarbon ones. The phenyl substituents of hydrocarbons occupy the cavities formed in the layers of the C_{60} molecules. In the structure of **3** the C_{60} molecules form columns, which are separated by the pairs of stacked TPB ones. The IR spectra indicate a neutral ground state of the complexes. The charge transfer band (CTB) with its maximum at 630 nm has been found only in the UV-visible spectrum of **4** indicating the π-interaction of DPA and C_{60} in the complex.

Introduction

Neutral complexes of fullerenes may be interesting due to their further modification (doping in the gaseous phase[1]), and photoinduced electron transfer[2] can result in the appearance of interesting conducting and magnetic properties. The modes of fullerene molecule packing and the distances between them in a crystal can be varied using different types of donor molecules. By now fullerene complexes with various types of donors have been studied.[3–13] Among them there are only several C_{60} complexes with aromatic hydrocarbons.[8–16] Aromatic solvents such as benzene,[6,7] toluene,[8] xylene[9] and methyl-substituted naphthalenes[10] comprising one or two condensed six-membered rings form crystalline solvates. Non-planar hydrocarbons like dianthracene and triptycene also form complexes with fullerenes due to steric conformity of their shapes to the spherical surface of the C_{60} molecule.[11–13] The donor molecules containing flexible phenyl substituents (for example, 2,2′,6,6′-tetraphenyl-4,4′-bi(4*H*-pyranylidene),[14] tetraphenylporphyrin and its metal-containing analogues[15]) also form complexes with the spherical C_{60} molecules. However, up to now the C_{60} complexes of such type with aromatic hydrocarbons have not been known. Recently we have reported preliminary data on the synthesis of several fullerene complexes with tetraphenylbutadiene (TPB·C_{60}), diphenylanthracene (DPA·C_{60}) and tetraphenylethylene (TPE·C_{60}·0.5C_6H_5Cl).[5]

This paper reports the synthesis and detailed crystal structures of the new C_{60} complexes with aromatic hydrocarbons comprising flexible phenyl substituents attached to a planar core, namely, tetraphenylethylene (TPE), 2TPE·C_{60} (**1**); 1,3,5-triphenylbenzene (TPB), TPB·C_{60} (**2**) and 2TPB·C_{60}·C_6H_5Cl (**3**); 9,10-diphenylanthracene (DPA), DPA·C_{60} (**4**); and 9-phenylanthracene (PA), PA·C_{60}·C_6H_6 (**5**) (Fig. 1). The IR-UV-visible spectra and thermodynamic stability of the complexes have been discussed.

Experimental

Synthesis

Fullerene C_{60} of 99.5% purity grade was used. Benzene was distilled over sodium in an argon atmosphere. The complexes were prepared by evaporation of a benzene solution containing C_{60} and appropriate hydrocarbon at a 1 : 3 molar ratio for a week in an argon atmosphere. The solvent was decanted from the resulting crystals before precipitation of the excess of the hydrocarbon. The crystals were washed with acetone. The data

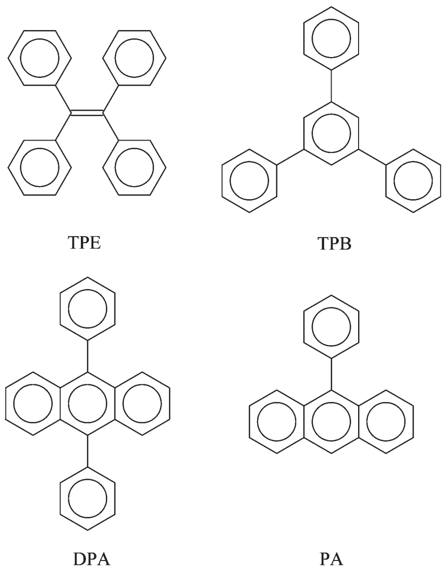

Fig. 1 Molecular structure of the aromatic hydrocarbons: tetraphenylethylene (TPE); 1,3,5-triphenylbenzene (TPB); 9,10-diphenylanthracene (DPA), and 9-phenylanthracene (PA).

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Table 1 Resulting C_{60} complexes and the data of TGA and elemental analysis

				TG analysis/°C (%)		Elemental analysis (found/calculated) (%)		
No.	Complex	C_{60} yield (%)	Crystal shape	Solvent	Hydrocarbon	C	H	Cl
1	$2TPE·C_{60}$	80	Parallelepipeds	—	277 (26.5)	97.80/97.09	3.20/2.91	—
2	$TPB·C_{60}$	60	Plates	—	330 (20.4)	97.05/98.23	2.30/1.77	—
3	$2TPB·C_{60}·C_6H_5Cl$	90	Plates	105 (3.6)	330 (20.8)	95.85/94.69	3.20/2.86	2.54/2.45
4	$DPA·C_{60}$	70	Prisms	—	450 (16.8)	98.30/98.27	2.05/1.73	—
5	$PA·C_{60}·C_6H_6$	90	Plates	150 (4.0)	390 (16.6)	98.11/98.09	1.89/1.91	—

of elemental and thermogravimetric analysis (TGA) are listed in Table 1.

General

The IR spectra were registered by a ‘Perkin Elmer 1725X’ spectrophotometer using KBr (1 : 400) pellets in the 400–7000 cm^{-1} range. Electronic absorption spectra were recorded on a ‘Perkin Elmer Lambda 19 UV-vis-NIR’ spectrophotometer in the 220–3000 nm range (KBr pellets, 1 : 2000). Thermogravimetric analysis was performed using a ‘Q-1000’ derivatograph and quartz bowls in an argon flow (10–20 ° min^{-1} rate) over 298–1273 K.

X-Ray crystal structure determination

The X-ray data for **1** and **4** were collected at 90 K using a Bruker SMART1000 CCD diffractometer installed at a rotating anode source (MoKα radiation), and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. The data were collected by the rotation method with a 0.3° frame-width (ω scan) and 20 sec exposure time per frame. They were integrated, scaled, sorted and averaged using the SMART software package of programs.[16] The X-ray data for **2** and **3** were collected at 110 K on a Bruker SMART1000 CCD diffractometer with a sealed tube source and treated with the same software.

The structures were solved by direct methods using SHELXTL NT Version 5.10.[17] Positions of hydrogen atoms were found from the difference electronic density Fourier synthesis and refined using a ‘riding model’ with fixed $U_{iso} = 1.2U_{eq}$ of the preceding carbon atom. The structures were refined by full-matrix least-squares against F^2 of all data. The ordered non-hydrogen atoms except the minor components of the disordered moieties were refined in anisotropic approximation. Crystallographic data for complexes **1**–**4** are shown in Table 2.

CCDC reference numbers 195336–195339.

See http://www.rsc.org/suppdata/ce/b2/b209875j/ for crystallographic data in CIF or other electronic format.

Results and discussion

$2TPE·C_{60}$ (1)

The asymmetric unit of **1** contains one half of the TPE molecule and a quarter of the C_{60} one. The TPE molecule resides on a 2-fold crystallographic axis, whereas the C_{60} molecule is on the 2-fold axis and in the *m*-plane. This makes the stoichiometry of the complex $2TPE·C_{60}$. The C_{60} molecules are disordered through rotation of 180° about a 2-fold axis, with the occupancy of each part being refined to 53/47%. Figs. 2 and 3 show the most populated orientation of the C_{60} molecule. The C_{60} and TPE molecules form layers in the *ac* plane (Fig. 2). Each fullerene molecule has six neighbors in a

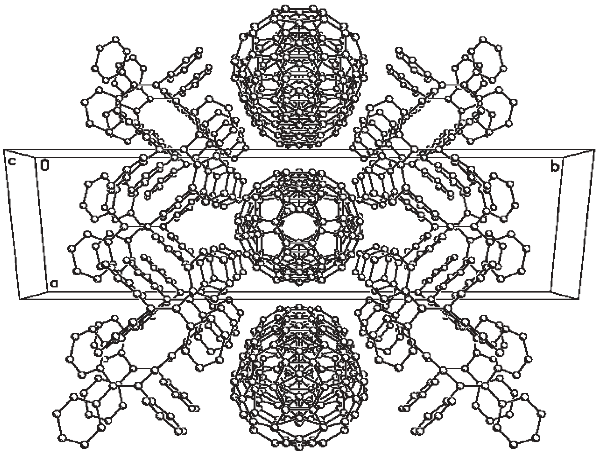

Fig. 2 Projection of the crystal structure of **1** along the *c* axis. Click here to access a 3D representation.

Table 2 Crystal data for complexes **1**–**4**

Parameter	1	2	3	4
Formula	$C_{112}H_{40}$	$C_{84}H_{18}$	$C_{114}H_{41}Cl$	$C_{86}H_{18}$
M	1385.50	1026.9	1445.9	1051.09
Crystal appearance	Black parallelepipeds	Black plates	Black plates	Black prisms
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/*m*	$P2_1/c$	$P\bar{1}$	*C*2/*c*
a/Å	10.4757(7)	13.255(3)	10.089(5)	25.207(2)
b/Å	32.920(2)	18.550(5)	12.709(5)	9.8028(6)
c/Å	10.3173(7)	18.596(4)	13.642(5)	17.461(1)
α/°	—	—	91.17(4)	—
β/°	118.224(2)	108.882(6)	91.06(4)	94.077(1)
γ/°	—	—	111.42(3)	—
$V/Å^3$	3135.0(4)	4326	1627.3	4303.7(5)
Z	8	4	1	4
$D_c/g\ cm^{-3}$	1.468	1.577	1.475	1.622
Unique reflections	4311	12 580	9328	4863
Observed reflections	2802	4881	6297	3638
$R_1\ [F > 4\sigma(F)]$	0.056	0.081	0.090	0.039
wR_2	0.147	0.220	0.272	0.097
Final GOF	0.962	0.896	1.044	1.03

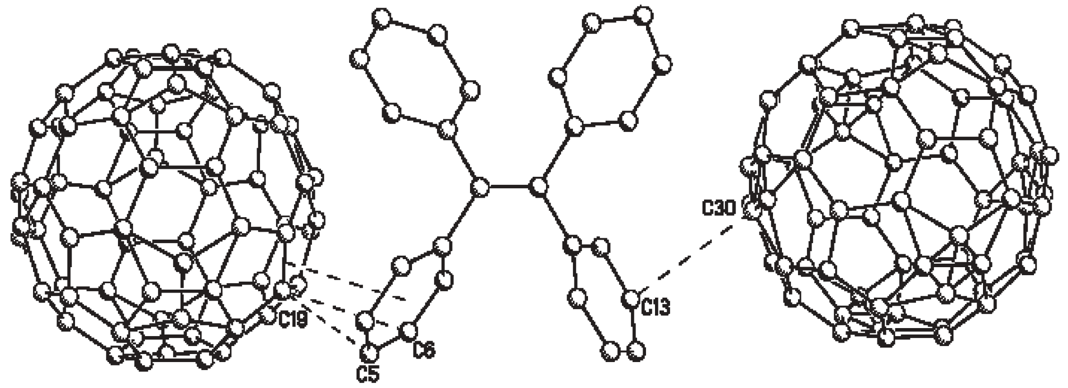

Fig. 3 Short van der Waals contacts between TPE and two C_{60} molecules from different layers in **1**. Only the major orientation of the C_{60} molecules is shown.

layer with centre-to-centre distances equal to 10.48 (×2), 10.32 (×2) and 10.67 (×2) Å. However, there are no shortened van der Waals contacts between the carbon atoms of C_{60} in the layer.

Phenyl substituents of TPE insert into the cavities formed by the C_{60} spheres in the layer. As this takes place, the phenyl substituents form several shortened van der Waals C···C contacts in the range of 3.20–3.26 Å (the sum of van der Waals radii of carbon atoms is 3.42 Å[18]). The other phenyl substituents also have shortened van der Waals contacts with another C_{60} molecule (the shortest distance is 3.42 Å) (Fig. 3). Therefore, according to crystallographic symmetry, each TPE molecule forms van der Waals contacts with four adjacent fullerene ones. There are also several shortened H(TPE)···C(C_{60}) contacts in the 2.79–2.83 Å range.

Bulky phenyl substituents in the central C=C bond of TPE make it twist with a corresponding torsion angle of 8.93(9)°. Each of the phenyl substituents rotates about the mean plane of the C=C bond with torsion angles in the 48.0(1)–58.0(1)° range.

TPB·C_{60} (2)

In **2**, both the fullerene and the hydrocarbon molecules are located in general positions. Disorder of C_{60} is aproximated by two orientations related by a 60° rotation about the non-crystallographic 3-fold axis with occupancies of 68 and 32%. Two opposite six-membered rings and adjacent atoms are common for both orientations, whereas the 'equatorial' belt of the C_{60} cage is disordered. This type of rotational disorder was observed earlier in C_{60} complexes with *catena*-cyclotriveratrylene,[19] dibenzotetrathiafulvalene[20] and tetraphenylporphyrin.[15]

The C_{60} spheres form puckered layers perpendicular to the *a* axis (Fig. 4). Each molecule has five neighbours within the layer with centre-to-centre distances of 9.86 (×2), 10.02 (×2) and 10.08 Å. The shortest intermolecular C···C distances are 3.17–3.26 Å. The minimal distance between the molecules from different layers is 13.12 Å. The C_{60} layers are separated from the TPB ones which are also puckered (Fig. 4). Phenyl rings of the TPB molecule form C···C van der Waals contacts with C_{60} in the 3.21–3.51 Å range, the shortest of them being formed with the ordered carbon atoms of C_{60}. Several shortened H(TPB)···C(C_{60}) contacts in the 2.73–2.83 Å range additionally stabilize this structure.

Phenyl groups in the TPB molecule are tilted to form the angles of 35.6, 38.6 and 40.3° with the central ring. The TPB molecule in the pristine compound attains almost the same conformation with torsion angles in the range of 35.3–39.8°.[21]

2TPB·C_{60}·C_6H_5Cl (3)

The fullerene molecule is located in an inversion centre so that only half of its atoms are independent. The TPB molecule is placed in a general position, while the molecule of chlorobenzene is disordered between two equally occupied orientations linked by the inversion centre.

In contrast to other complexes studied, **3** contains ordered C_{60} molecules. Fullerene molecules form columns along the *a* axis. Each C_{60} molecule has two neighbours in the column with a centre-to-centre distance of 10.09 Å. The shortest C···C contacts between the fullerenes in the column are 3.42 and 3.45 Å and are formed by the two atoms linked with the 5/6 bond.

The columns of the C_{60} molecules are separated from the pairs of stacked TPB molecules (Fig. 5). Two TPB molecules in

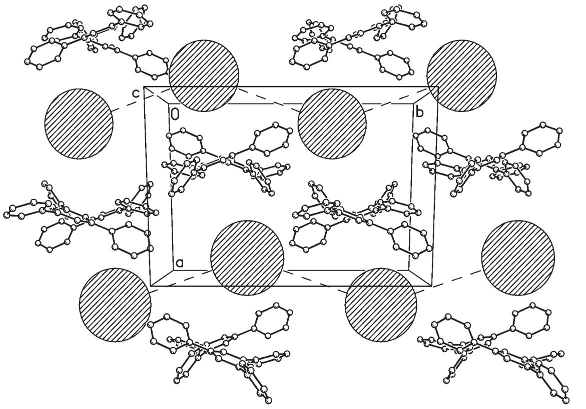

Fig. 4 Molecular packing in **2** (projection down the *c* axis). The disordered C_{60} molecules are shown as dashed spheres.

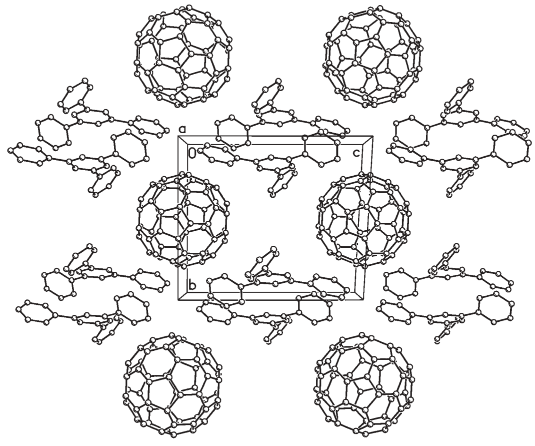

Fig. 5 Molecular packing in **3** (projection down the *a* axis). The disordered C_6H_5Cl molecules are not shown. Click here to access a 3D representation.

the pair are linked with the inversion centre, so that their central rings are parallel. The C···C distances between the stacked central rings within the pair lie in the range of 3.68–3.70 Å, which may be indicative of a weak π–π interaction. The phenyl groups of TPB form C···C and H···C contacts with the C_{60} molecule in the 3.32–3.52 and 2.76–2.89 Å ranges, respectively.

The TPB molecule has an usual propeller-like shape with phenyl groups rotated at torsion angles of 43.9, 40.7 and 46.6°, being slightly more non-planar than in the pristine hydrocarbon (possibly due to steric reasons).

DPA·C_{60} (4)

The fullerene and DPA molecules reside in special positions on the inversion centre. C_{60} is disordered between two orientations, related by a 60° rotation about the 3-fold non-crystallographic axis. The two positions were refined to 60/40% occupancy. Figs. 6 and 7 show the most populated orientation of the C_{60} molecules.

The C_{60} molecules form dense-packed hexagonal layers in the *bc* plane (Fig. 6). Inside the layer every C_{60} molecule has six neighbours with distances between the centres in the 9.80–10.01 Å range. These distances are close to that in the C_{60} crystals (9.94 Å at 153 K).[22] The shortest distance between the centres of the C_{60} molecules in adjacent layers is 13.52 Å.

The C_{60} layers alternate with those composed of the DPA molecules. Each DPA molecule forms shortened van der Waals contacts with the four C_{60} molecules (Fig. 7). Side phenylene groups of the central anthracene fragment form van der Waals contacts with hexagons of the two C_{60} molecules from the adjacent layers with the shortest C···C distances of 3.26–3.64 Å (Fig. 7). The π-interaction between DPA and C_{60} is evidenced by a small value of the dihedral angle (4.4°) between the phenylene groups of DPA and the C_{60} hexagons. The phenyl groups of the DPA molecules insert into the cavities formed in the layers by the spherical C_{60} molecules. They form shortened van der Waals C···C contacts with the hexagons of the C_{60} molecules in the range of 3.41–3.50 Å.

It is interesting to note that the distances and the dihedral angles between the phenyl substituents of DPA and the C_{60} hexagons are essentially larger than those for the phenylene groups of DPA. Nevertheless, namely the formation of van der Waals contacts with the phenyl substituents of DPA results in the ordering of two hexagons in C_{60} and the formation of a six-fold rotation axis along which fullerene molecules are disordered. There are several shortened H(DPA)···C(C_{60}) contacts in the 2.74–2.90 Å range.

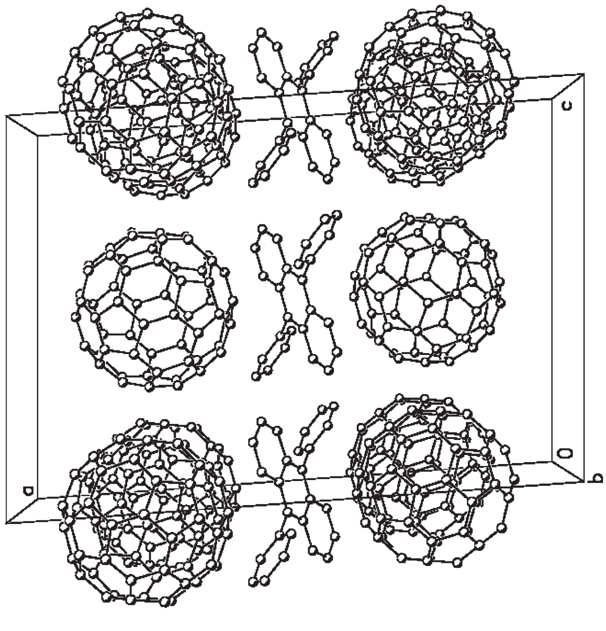

Fig. 6 Projection of the crystal structure of **4** along the *b* axis. Only the major occupied orientation of C_{60} is shown. Click here to access a 3D representation.

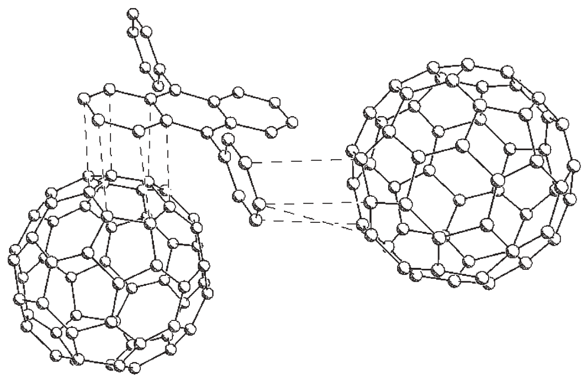

Fig. 7 Shortened van der Waals contacts within one layer between DPA and C_{60} molecules in **4**. Only the major occupied orientation of C_{60} is shown.

The geometry of DPA does not change considerably upon insertion into the complex with C_{60} as compared with the geometry of DPA in neat crystals.[23]

According to TGA results the complexes start to decompose only at temperatures higher than 277 °C for **1**, 330 °C for **2**, and 450 °C for **4**, due to an aromatic hydrocarbon decomposition indicating high thermal stability. However, **3** and **5** start to decompose even at 105 and 150 °C, respectively, because of elimination of solvent from the crystals.

The IR spectra of **1**–**5** show absorption bands of the parent hydrocarbons, fullerene C_{60} and the solvent (solvent is involved in **3** and **5** only). The bands of the hydrocarbons remain almost unchanged upon complex formation (the maximum shifts do not exceed 2 cm^{-1}). Thus, the IR spectra, together with the X-ray data, indicate the retention of the initial geometry of the hydrocarbons in the complexes with fullerenes. The band of C_{60} at 1429 cm^{-1}, sensitive to charge transfer to the fullerene molecule,[24] is not shifted (± 1 cm^{-1}) in the complexes with respect to the parent C_{60}. Thus, the resulting compounds can be attributed to complexes with a neutral ground state.

The UV-visible spectra of **1**–**5** are a superposition of the spectra of the starting C_{60} and the corresponding hydrocarbons. Only the spectrum of **4** exhibits a wide weak band in the visible range (Fig. 8a) which is absent in the spectra of the starting DPA (Fig. 8c) and C_{60} (Fig. 8b). To differentiate this band

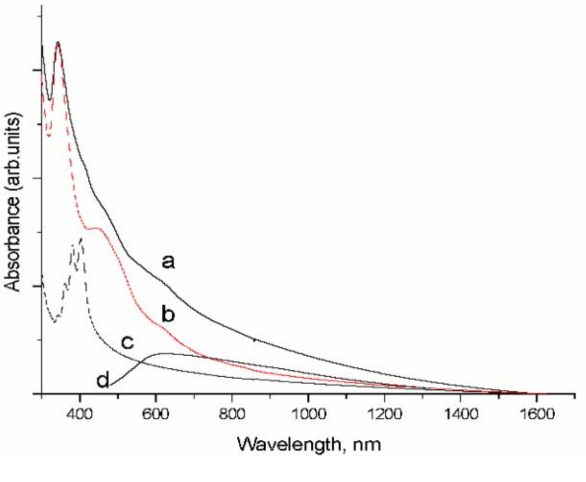

Fig. 8 UV-visible spectra of (a) DPA·C_{60}, (b) C_{60}, (c) DPA, and (d) the deconvoluted charge transfer band.

correctly we subtracted the normalized spectra of DPA and C_{60} from that of **4** (Fig. 8d). This band can be attributed to charge transfer from DPA to C_{60} (CTB: charge transfer band). The presence of this band in the spectrum of the complex may be evidence of the π-interaction of DPA and C_{60} (this is really observed from the X-ray diffraction data). However, the energy of charge transfer corresponding to the maximum of the CTB is rather high (630 nm, 1.97 eV). This can be attributed to the weak hydrocarbon properties of DPA (the ionization potential is equal to 7.05 eV[25]). The absence of CTB in the spectra of **1**–**3**, and **5** is probably associated with a shift of these bands to the UV-range relative to that in the spectrum of **4**. As a result, the CTB is shadowed by the intense absorption of C_{60} in this range.

Conclusions

New C_{60} complexes (**1**–**5**) with aromatic hydrocarbons containing flexible phenyl substituents have been obtained. The complexes have a large variety of packing motifs of the fullerene molecules in a crystal ranging from one-dimensional chains to layered structures with dense and loose packing of the fullerenes. The formation of complexes with C_{60} is attained due to the flexibility of the phenyl substituents of the hydrocarbon molecules. In **1**, **2** and **4** the phenyl substituents insert into the cavities formed in the layers by the spherical C_{60} molecules. Such packing allows van der Waals contacts with the spherical C_{60} molecules with relatively short C(hydrocarbon)···C(C_{60}) distances in the range of 3.20–3.32 Å. These contacts are comparable with the similar C···C distances in the C_{60} complexes with concave aromatic hydrocarbons. For example, the C_{60} complexes with triptycene and dianthracene have the shortest C···C distances, in the 3.27–3.35 Å range.[14,15] The interaction between the aromatic hydrocarbons and C_{60} molecules is rather weak and this results in the disorder of fullerene molecules in **1**, **2** and **4**.

Unexpectedly, **4** is isostructural with the three-component $(ET\cdot I_3)C_{60}$ complex, where ET is bis(ethylenedithiotetrathiafulvalene).[26] In $(ET\cdot I_3)C_{60}$ the flat ET^+ cations and the linear I_3^- anions also occupy the cavities in the C_{60} layer. Therefore, this type of packing is evidently characteristic of C_{60} complexes comprising flat enough donor molecules. Initially flat donor molecules are usually distorted in the C_{60} complexes.[3,5,20]

According to the optical and X-ray diffraction data the complexes have a neutral ground state as a result of the weak donor properties of the hydrocarbons used relative to fullerene C_{60}.

The fullerene complexes with aromatic hydrocarbons have various structures, neutral ground states and some of them are thermally stable and, therefore, these complexes can be promising in intercalation by alkali metals.[1] Intercalation of such complexes by alkali metals can result in fullerene or aromatic hydrocarbon reduction[27] accompanied by the formation of $(D^{-\bullet}C_{60}{}^{-\bullet}nM^+)$ compounds containing both hydrocarbon and fullerene radical anions. Thermal stability of the solvent-free C_{60} complexes with aromatic hydrocarbons can provide higher intercalation temperatures and more homogeneous samples.

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References

1 A. Otsuka, G. Saito, S. Hirate, S. Pac, T. Ishida, A. A. Zakhidov and K. Yakushi, *Mater. Res. Soc. Symp. Proc.*, 1998, **488**, 495.

2 D. V. Konarev, G. Zerza, M. Sharber, N. S. Sariciftci and R. N. Lyubovskaya, *Synth. Met.*, 2001, **121**, 1127.

3 A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito and H. Shinohara, *J. Chem. Soc., Chem. Commun.*, 1992, 1472.

4 G. Saito, T. Teramoto, A. Otsuka, Y. Sugita, T. Ban, M. Kusunoki and K.-I. Sakaguchi, *Synth. Met.*, 1994, **64**, 359.

5 D. V. Konarev, R. N. Lyubovskaya, N. V. Drichko, E. I. Yudanova, Yu. M. Shul’ga, A. L. Litvinov, V. N. Semkin and B. P. Tarasov, *J. Mater. Chem.*, 2000, **10**, 803.

6 A. L. Balch, J. W. Lee, B. C. Noll and M. M. Olmstead, *J. Chem. Soc., Chem. Commun.*, 1993, 56.

7 M. F. Meidine, P. B. Hitchcock, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 1534.

8 M. P. Luger, D. Zobel, W. Duczek and J. C. A. Boeyens, *Cryst. Res. Technol.*, 1996, **31**, 43.

9 J. Sworakowski, K. Palewska and M. Bertault, *Synth. Met.*, 1994, **64**, 323.

10 P. Byszewski, E. Kowalska and J. Mieczkowski, *Synth. Met.*, 1998, **94**, 87.

11 D. V. Konarev, E. F. Valeev, Yu. L. Slovokhotov, Yu. M. Shul’ga and R. N. Lyubovskaya, *J. Chem. Res. (S)*, 1997, 442.

12 D. V. Konarev, Yu. V. Zubavichus, E. F. Valeev, Yu. L. Slovokhotov, Yu. M. Shul’ga and R. N. Lyubovskaya, *Synth. Met.*, 1999, **103**, 2364.

13 E. M. Veen, P. M. Postma, H. T. Jonkman, A. L. Spek and B. L. Feringa, *Chem. Commun*, 1999, 1709.

14 D. V. Konarev, R. N. Lyubovskaya, O. S. Roschupkina and Yu. M. Shul’ga, *Russ. Chem. Bull.*, 1995, **44**, 1985.

15 D. V. Konarev, I. S. Neretin, Yu. L. Slovokhotov, E. I. Yudanova, N. V. Drichko, Yu. M. Shul’ga, B. P. Tarasov, L. L. Gumanov, A. S. Batsanov, J. A. K. Howard and R. N. Lyubovskaya, *Chem. Eur. J.*, 2001, **7**, 2605.

16 SMART and SAINTPLUS, Area Detector Control and Integration Software, Ver. 6. 01, Bruker Analytical X-Ray Systems, Madison, WI, USA, 1999.

17 G. M. Sheldrick, SHELXTL NT Version 5.10, Program for Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

18 Yu. V. Zefirov and P. M. Zorkii, *Russ. Chem. Rev.*, 1989, **58**, 713.

19 J. L. Atwood, M. J. Barnes, M. G. Gardiner and C. L. Raston, *Chem. Commun.*, 1996, 1449.

20 D. V. Konarev, Y. V. Zubavichus, Yu. L. Slovokhotov, Yu. M. Shul’ga, V. N. Semkin, N. V. Drichko and R. N. Lyubovskaya, *Synth. Met.*, 1998, **92**, 1.

21 Y. C. Lin and D. E. Willams, *Acta Crystallogr., Sect. B*, 1975, **31**, 318.

22 H.-B. Burgi, E. Blanc, D. Schwarzenbach, S. Liu, Y.-j. Lu, M. M. Kappes and J. A. Ibers, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 640.

23 V. Langer and H.-D. Becker, *Z. Kristallogr.*, 1992, **199**, 313.

24 T. Picher, R. Winkler and H. Kuzmany, *Phys. Rev. B*, 1994, **49**, 15 879.

25 R. Boschi, E. Clar and W. Schmidt, *J. Chem. Phys.*, 1974, **60**, 4406.

26 D. V. Konarev, A. Yu. Kovalevsky, P. Coppens and R. N. Lyubovskaya, *Chem. Commun.*, 2000, 2357.

27 E. Clar, *Polycyclic Hydrocarbons*, Khimiya, Moscow, 1971, p. 282 (in Russian).