

Three new fluorinated *N*-phenyl-substituted pentacyclic ethanoanthracenedicarboximides

Anke Schwarzer^a and Edwin Weber^{b*}

^aInstitut für Anorganische Chemie, TU Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg/Sachsen, Germany, and ^bInstitut für Organische Chemie, TU Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg/Sachsen, Germany
Correspondence e-mail: edwin.weber@chemie.tu-freiberg.de

Received 14 September 2011

Accepted 13 October 2011

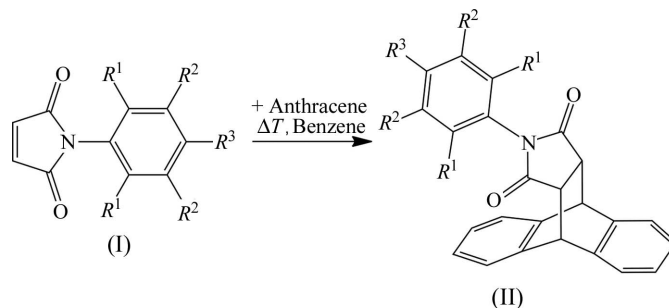
Online 25 October 2011

Diels–Alder reaction between maleimides featuring 3,5-di-, 2,4,6-tri- and pentafluorinated *N*-phenyl substituents and anthracene yields the corresponding pentacyclic ethanoanthracenedicarboximide compounds, namely *N*-(3,5-difluorophenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximide, C₂₄H₁₅F₂NO₂, (IIa), *N*-(2,4,6-trifluorophenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximide, C₂₄H₁₄F₃NO₂, (IIb), *N*-(2,3,4,5,6-pentafluorophenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximide, C₂₄H₁₂F₅NO₂, (IIc). The crystal structures of (IIa)–(IIc) reveal an expected molecular geometry with a ‘V’-shape of the anthracene-derived tricyclic moiety. The crystal packings of (IIa) and (IIb) are dominated by π – π and C–H...O/F interactions, while F...F and C–H... π contacts are absent. In contrast, (IIc) shows F...F and C–H...O/F contacts, but no π -involved contacts of relevance.

Comment

N-Phenyl-substituted ethanoanthracenedicarboximides with different substituents on the benzene ring are known to form crystalline inclusion compounds with a variety of solvents (Weber *et al.*, 1991). On the other hand, the efficiency of the photoreaction of anthracene and differently substituted maleimides as a function of the dienophile concentration has been reported (Sun *et al.*, 1999). Moreover, anthracene-2,6-dicarboxylate derivatives modified with maleimides have been used in poly(ethylene terephthalate) copolymers (Jones *et al.*, 1999). Investigations of the conformational environment of the selected derivatives were described by Csöregi *et al.* (2003), while Grossmann *et al.* (2003) reported NMR spectroscopic analysis of the geometric features of the *ortho*-substituted molecules. Verma and co-workers reported several detailed studies on the analysis of the rotation around the C_{aryl}–N bond in, for example, *o*-OMe-, *o*-Me-, *o*-Cl- and *o*-Br-substituted *N*-arylimides with dynamic and temperature-

dependent NMR spectroscopy (Verma & Singh, 1976, 1978; Srivastava *et al.*, 1991). A detailed analysis of the conformational influence of the imide ring in fluorinated *N*-phenylmaleimides has been reported recently by Schwarzer & Weber (2008).



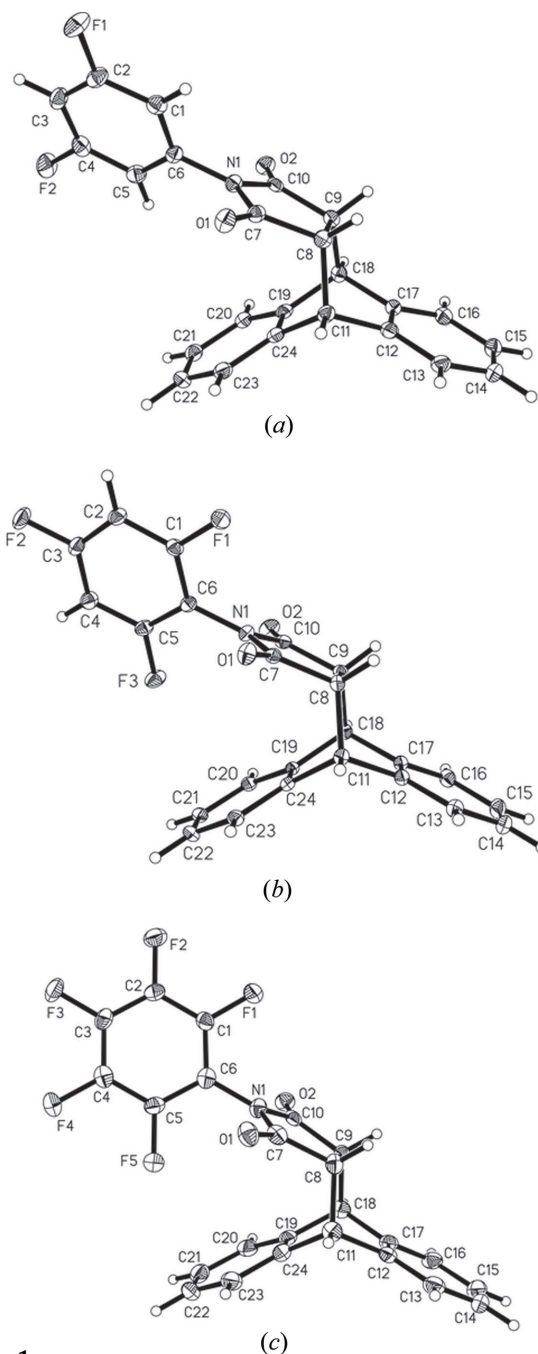
(Ia)/(IIa): R¹ = R³ = H; R² = F
(Ia)/(IIb): R¹ = R³ = F; R² = H
(Ia)/(IIc): R¹ = R² = R³ = F

We describe here the preparation of three new ethanoanthracenedicarboximides, (IIa)–(IIc), having *N*-phenyl substituents with different modes of fluorine substitution (see Scheme) and report on their single-crystal X-ray structures. These pentacyclic dicarboximides were synthesized in an analogous manner to the bridged fulvene adducts described by Schwarzer *et al.* (2010). Attempts to achieve inclusion compounds from crystallization using different solvents were unsuccessful. Single crystals suitable for X-ray crystallography in the present study were grown from benzene solutions.

Remarkably, (IIa) and (IIb) are isomorphous. Only minor differences between their packing arise due to the differences in fluorine substitution in the C1–C6 ring. Even the C–H...F contacts are comparable [C5–H5...F2 = 2.56 Å in (IIa) and C4–H4...F3 = 2.51 Å in (IIb), both along (–x + 1, –y + 1, –z + 1)]. Similar structures with related cell parameters were also reported by Kishikawa *et al.* (1997), Grossmann *et al.* (2003) and Goh & White (2009).

The semi-rigid ethanoanthracenedicarboximide moiety of the title compounds (Fig. 1) shows the typical geometry observed in earlier studies (Weber *et al.*, 1991; Csöregi *et al.*, 2003) confirming the expected bond lengths and angles. The ‘V’ shape of the dihydroanthracene moiety is a structural property best described by the angle between the phenylene rings [49.43 (8)° in (IIa), 53.24 (4)° in (IIb) and 51.47 (10)° in (IIc)]. Another feature is the angle between the imide unit and the benzene ring, describing the intramolecular attractive and repulsive forces between the carbonyl O atoms and the *ortho*-phenyl H or F atoms. While *N*-phenylmaleimides (Ia) and (Ib), as the starting compounds of the synthesis (see Scheme), show torsion angles of 52.3° in (Ia) and 66.5° in (Ib) according to Schwarzer & Weber (2008), the dihydroanthracene derivatives (IIa)–(IIc) exhibit torsion angles of 57.83 (7), 60.88 (4) and 66.25 (13)°, respectively.

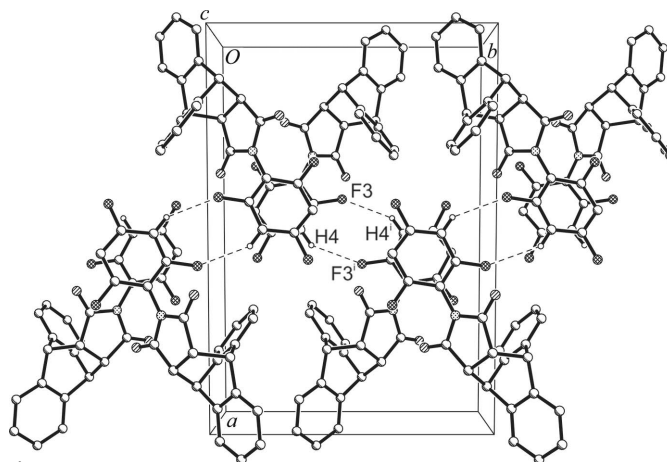
The closest centre-to-centre distance between adjacent aryl units is 4.0871 (15) Å for (IIa) and 4.0533 (8) Å for (IIb). Hence, in (IIa) and (IIb), weak stacking interactions form zigzag chains (Fig. 2) extending along the crystallographic *c*


Figure 1

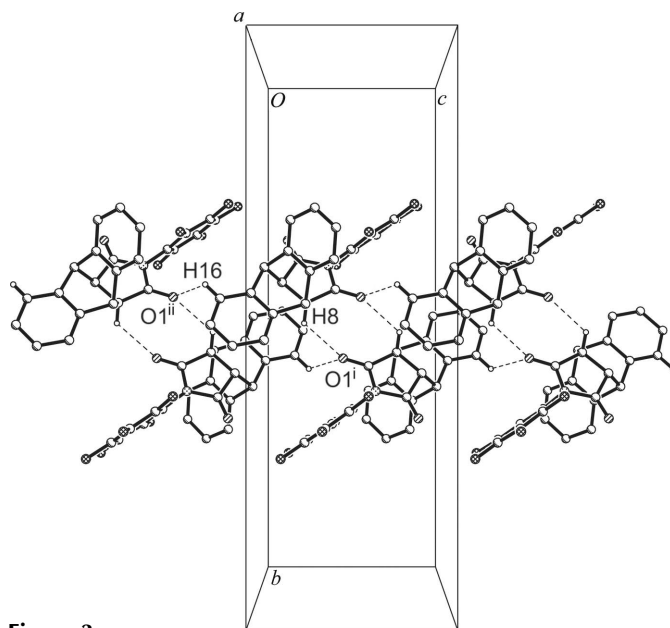
The molecular structures of (a) (IIa), (b) (IIb) and (c) (IIc), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

axis. The angles between the stacks are 25.14° in (IIa) and 24.53° in (IIb). On the other hand, a centre-to-centre distance greater than 5.1 \AA in the crystal packing of (IIc) indicates no relevant stacking interactions (Fig. 3).

Several C—H \cdots O and C—H \cdots F contacts are found in the packings. In (IIa), two C—H \cdots O contacts complete the chain generated by the π -stacking interactions, while one C—H \cdots F contact forms dimers. As in the case of (IIa), the trifluorinated derivative (IIb) also does not show F \cdots F contacts, but a bifurcated C—H \cdots O and two C—H \cdots F interactions generate


Figure 2

The packing structure of (IIb) representative for (IIa) and (IIb), viewed down the c axis, showing the stackings and the C—H \cdots F contacts connecting the zigzag chains. Dashed lines indicate C—H \cdots F contacts. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]


Figure 3

The packing structure of (IIc), viewed along the a axis. Dashed lines indicate C—H \cdots O contacts. [Symmetry codes: (i) $x, y, z - 1$; (ii) $-x + 1, -y + 1, -z + 1$.]

a network structure instead of a single or zigzag chain. In contrast, in (IIc), with the maximum number of F atoms on the phenyl ring, F \cdots F contacts occur [$2.811(3) \text{ \AA}$, $\Theta_1 = 114.9(2)^\circ$ and $\Theta_2 = 111.2(2)^\circ$], giving rise to zigzag chains. These chains are parallel to the zigzag chain along the crystallographic c axis formed by the bifurcated C—H \cdots O contact. In conclusion, (IIa) and (IIb) show a similar crystal packing, while differences are seen in the crystal packing of (IIc), owing to the perfluorinated N -phenyl ring.

Experimental

The starting N -phenylmaleimides (Ia)–(Ic) (see Scheme) were prepared as described by Schwarzer & Weber (2008). The title

compounds (IIa)–(IIc) were synthesized in a similar manner to the fulvene adducts described by Schwarzer *et al.* (2010). To a stirred solution of the respective *N*-phenylmaleimide (Ia)–(Ic) (10 mmol) in benzene (25 ml), a solution of anthracene (10 mmol) in benzene (25 ml) was added. The mixture was heated under reflux for 5 h and then allowed to cool to room temperature. The solid precipitate that formed was collected and dried in a vacuum. Recrystallization of the crude products from acetone yielded the pure compounds as colourless solids. Single crystals of compounds (IIa)–(IIc) were obtained from benzene solutions. Spectroscopic data for all three compounds are available in the archived CIF.

Compound (IIa)

Crystal data

$C_{24}H_{15}F_2NO_2$	$V = 1743.9 (4) \text{ \AA}^3$
$M_r = 387.37$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 18.229 (2) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$b = 11.7659 (13) \text{ \AA}$	$T = 93 \text{ K}$
$c = 8.1599 (10) \text{ \AA}$	$0.40 \times 0.23 \times 0.23 \text{ mm}$
$\beta = 94.852 (4)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	3043 independent reflections
16554 measured reflections	2714 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	262 parameters
$wR(F^2) = 0.112$	H-atom parameters constrained
$S = 1.18$	$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
3043 reflections	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$

Compound (IIb)

Crystal data

$C_{24}H_{14}F_3NO_2$	$V = 1760.1 (3) \text{ \AA}^3$
$M_r = 405.36$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 17.687 (2) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$b = 12.3369 (14) \text{ \AA}$	$T = 90 \text{ K}$
$c = 8.1066 (9) \text{ \AA}$	$0.46 \times 0.45 \times 0.23 \text{ mm}$
$\beta = 95.716 (7)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	5138 independent reflections
26961 measured reflections	4058 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	271 parameters
$wR(F^2) = 0.106$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$
5138 reflections	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

Compound (IIc)

Crystal data

$C_{24}H_{12}F_5NO_2$	$V = 3710.1 (14) \text{ \AA}^3$
$M_r = 441.35$	$Z = 8$
Orthorhombic, $Pccn$	Mo $K\alpha$ radiation
$a = 18.259 (4) \text{ \AA}$	$\mu = 0.14 \text{ mm}^{-1}$
$b = 24.104 (6) \text{ \AA}$	$T = 93 \text{ K}$
$c = 8.4301 (18) \text{ \AA}$	$0.49 \times 0.07 \times 0.05 \text{ mm}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$) for (IIa).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C22-H22\cdots O2^i$	0.95	2.65	3.552 (3)	160
$C5-H5\cdots F2^{ii}$	0.95	2.56	3.458 (3)	157
$C9-H9\cdots O1^{iii}$	1.00	2.60	3.084 (3)	110

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (IIb).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C4-H4\cdots F3^i$	0.95	2.51	3.2030 (15)	130
$C21-H21\cdots F2^{ii}$	0.95	2.62	3.3051 (14)	129
$C14-H14\cdots O1^{iii}$	0.95	2.70	3.5544 (15)	150

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

Table 3

Hydrogen-bond geometry (\AA , $^\circ$) for (IIc).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C16-H16\cdots O1^i$	0.95	2.46	3.070 (5)	122
$C8-H8\cdots O1^{ii}$	1.00	2.40	3.091 (5)	126

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

Data collection

Bruker SMART CCD area-detector diffractometer	3652 independent reflections
20727 measured reflections	1997 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.152$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$	290 parameters
$wR(F^2) = 0.174$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.45 \text{ e \AA}^{-3}$
3652 reflections	$\Delta\rho_{\text{min}} = -0.45 \text{ e \AA}^{-3}$

For compounds (IIa)–(IIc), H atoms were positioned geometrically and allowed to ride on their parent atoms, with $C-H = 0.95-1.00 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2-1.5U_{\text{eq}}(\text{parent atom})$. The inferior crystal quality for compound (IIc) is reflected in a high R_{int} value.

For all compounds, data collection: *SMART* (Bruker, 2007); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3076). Services for accessing these data are described at the back of the journal.

References

- Bruker (2007). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Csöregi, I., Finge, S. & Weber, E. (2003). *Struct. Chem.* **14**, 241–246.
- Goh, Y. W. & White, J. M. (2009). *Aust. J. Chem.* **62**, 419–424.
- Grossmann, G., Potrzebowski, M. J., Olejniczak, S., Ziółkowska, N. E., Bujacz, G. D., Ciesielski, W., Prezdo, W., Nazarov, V. & Golovko, V. (2003). *New J. Chem.* **27**, 1095–1101.

- Jones, J. R., Liotta, C. L., Collard, D. M. & Schiraldi, D. A. (1999). *Macromolecules*, **32**, 5786–5792.
- Kishikawa, K., Yoshizaki, K., Kohmoto, S., Yamamoto, M., Yamaguchi, K. & Yamada, K. (1997). *J. Chem. Soc. Perkin Trans. 1*, pp. 1233–1239.
- Schwarzer, A., Bombicz, P. & Weber, E. (2010). *J. Fluorine Chem.* **131**, 345–356.
- Schwarzer, A. & Weber, E. (2008). *Cryst. Growth Des.* **8**, 2862–2874.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Srivastava, N., Srivastava, V. & Verma, S. M. (1991). *Indian J. Chem. Sect. B*, **30**, 1080–1082.
- Sun, D., Hubig, S. M. & Kochi, J. K. (1999). *J. Photochem. Photobiol. A*, **122**, 87–94.
- Verma, S. M. & Singh, N. B. (1976). *Aust. J. Chem.* **29**, 295–300.
- Verma, S. M. & Singh, N. B. (1978). *Bull. Chem. Soc. Jpn.* **51**, 520–523.
- Weber, E., Finge, S. & Csöregi, I. (1991). *J. Org. Chem.* **56**, 7281–7288.