organic compounds

The effect of Cl···π interactions on the conformations of 4-chloro-5-(2-phenoxyethoxy)phthalonitrile and 4-chloro-5-[2-(pentafluoro-phenoxy)ethoxy]phthalonitrile

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4-Chloro-5-(2-phenoxyethoxy)phthalonitrile, $C_{16}H_{11}ClN_2O_2$, (I), and 4-chloro-5-[2-(pentafluorophenoxy)ethoxy]phthalonitrile, $C_{16}H_6ClF_5N_2O_2$, (II), show different types of electrostatic interaction. In (I), the phenoxy and phthalonitrile (benzene-1,2-dicarbonitrile) moieties are well separated in an open conformation and intermolecular C—H···π interactions are observed in the crystal packing. On the other hand, in (II), the pentafluorophenoxy moiety interacts closely with the Cl atom to form a folded conformation containing an intramolecular halogen–π interaction.

Comment

The anion–π interaction has been found and discussed as one of the most interesting topics regarding electrostatic interactions in the last decade. The provocative title of a paper, 'Anion–π interactions: do they exist?', which was a theoretical study of the interaction reported by Quiñonero et al. (2002), attracted the interest of many chemists (Schottel et al., 2008). Since π-conjugated molecules show remarkable electrostatic interactions because of their quadrupole moments (i.e. negative charge of the aromatic centre), benzene molecules show cation–π, C—H···π and the sliding conformation of π–π interactions (Doerksenm & Thakkar, 1999). On the other hand, fluorinated compounds such as hexafluorobenzene have the opposite quadrupole moment (i.e. positive charge of the aromatic centre induced by the surrounding F atoms) and show the opposite electrostatic interactions, e.g. anion···C_6F_6 (anion–π), CF···C_6F_6 (CF–π) and the sliding conformation of C_6F_6···C_6F_6 (π–π) interactions. Several papers then demonstrated the existence of anion–π interactions between anion sources and aromatic moieties (Demeshko et al., 2004; de Hoog et al., 2004; Berryman et al., 2006; Dawson et al., 2010),

which includes noncovalent π-interactions between lone-pair electrons of electronegative atoms (F, Cl, Br, O, S and N) and perfluorobenzene derivatives (Quiñonero et al., 2002). These studies of quadrupole moments and electrostatic interactions prompted us to compare them with the crystal structures of fluorinated compounds, which also show several unique electrostatic interactions in the crystalline state (Hori et al., 2007; Hori & Naganuma, 2010), e.g. the arene–perfluoroarene interaction (Patrick & Prosser, 1960; Williams, 1993) and C—H···F interactions (Desiraju, 1996; Thalladi et al., 1998). In this paper, we discuss the halogen–π interaction, classified as an anion–π interaction, between the pentafluorophenoxy group and Cl atoms in 4-chloro-5-[2-(pentafluorophenoxy)-ethoxy]phthalonitrile, (II), in order to understand fluorine-substitution effects, given that no halogen–π interactions are observed in the nonfluorinated compound 4-chloro-5-(2-phenoxyethoxy)phthalonitrile, (I).
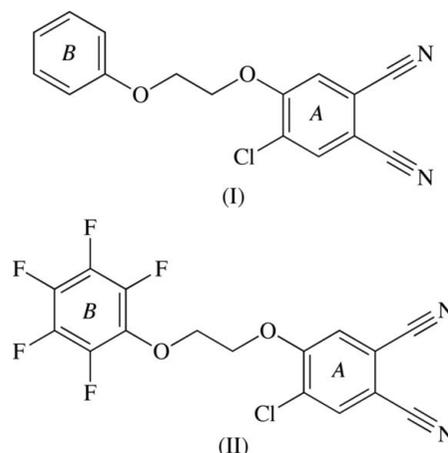
The molecular conformations of (I) and (II) are different (Fig. 1), viz. open in (I) and folded in (II), and the folded structure of (II) shows an apparently attractive interaction between atom Cl1 and the pentafluorophenoxy moiety (ring B). The Cl1···CgB distance in (II) is 3.7253 (12) Å, where CgB is the centroid of ring B. The aromatic rings (A and B) in each compound are linked by the ethane-1,2-diyldioxy group, and significant conformational differences of trans–gauche–trans and trans–gauche–gauche conformations are observed in the C5—O1—C9—C10—O2—C11 groups of (I) and (II), respectively. The C9—C10—O2—C11 torsion angles in (I) and (II) are trans [−173.89 (10)°] and gauche [−77.06 (18)°], respectively. The thermodynamically unfavourable gauche–gauche conformation is realised in (II) because of the intramolecular interaction between atom Cl1 and ring B. The O1—C9—C10—O2 torsion angles have the same gauche configuration, viz. 75.96 (13)° in (I) and 71.99 (17)° in (II), and the C5—O1—C9—C10 torsion angles are trans, viz. 171.51 (11)° in (I) and −179.93 (13)° in (II). The dihedral angle between the aromatic rings (A and B) of (II) is 68.75 (4)°, which is smaller than the corresponding angle in (I) [70.89 (5)°]. The C4—Cl1 bond distance of 1.7256 (16) Å in (II) is slightly longer than that of 1.7168 (14) Å in (I), although the C10—O2 bond in (II) is longer than that in (I) [1.454 (2) versus 1.4309 (16) Å]. The C≡N bond distances in (I) and (II) are
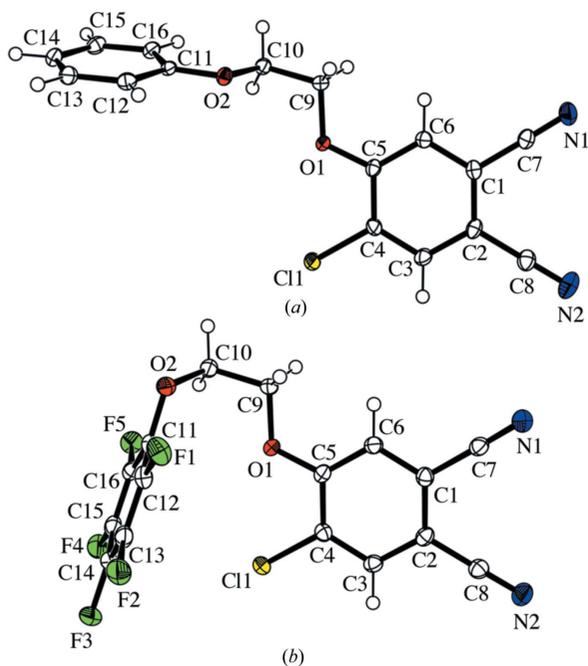
Figure 1
The molecular structures of (*a*) (I) and (*b*) (II), both at 100 K, showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level.

almost the same [C7$\equiv$N1 = 1.1458 (19) Å and C8$\equiv$N2 = 1.144 (2) Å for (I), and C7$\equiv$N1 = 1.144 (2) Å and C8$\equiv$N2 = 1.149 (2) Å for (II)]. The C5—O1 bond distances are also the same, *i.e.* 1.3535 (16) and 1.3524 (18) Å for (I) and (II), respectively.

In the crystal structure of (I), no π–π stacking is observed, but inversion-related pairs of molecules are linked by a C—H$\cdots\pi$ interaction (Fig. 2); atom H3 of ring *A* at (*x*, *y*, *z*) interacts closely with a phenoxy group at ($-x + 2$, $-y + 1$, $-z + 1$) [symmetry code (i)]. The intermolecular Cl1$\cdots$Cl1^{i} distance in the pair is short, at 3.274 (1) Å. The formation of the pair allows stabilization of the *gauche* configuration of O1—C9—C10—O2 to give a *trans–gauche–trans* conformation in (I). Further, the H atoms in C10—H10*A* and C10—H10*B* interact with rings *B*^{ii} [symmetry code: (ii) $-x + 1$, $-y$, $-z + 1$] and *A*^{iii} [symmetry code: (iii) *x*, *y* − 1, *z*], respectively, through C—H$\cdots\pi$ interactions; H10*A*$\cdots$*CgB*^{ii} = 2.59 Å [C10$\cdots$*CgB*^{ii} = 3.477 (2) Å] and H10*B*$\cdots$*CgA*^{iii} = 2.71 Å [C10$\cdots$*CgA*^{iii} = 3.492 (2) Å]. Accordingly, the molecules are in a head-to-tail arrangement along the *a* axis and, further, they form zigzag arrangements along the *c* axis.

In (II), the molecules are aligned parallel to the *a* axis. In this direction, atom F5 in the pentafluorophenoxy group interacts with ethoxy atom H9*B* of a neighbouring molecule through a weak C—H$\cdots$F contact (Howard *et al.*, 1996), with F5$\cdots$H9*B*^{iv} = 2.51 Å [symmetry code: (iv) *x* − 1, *y*, *z*]. The F5$\cdots$C5^{iv} distance is also short, at 2.950 (2) Å. Because the pentafluorophenoxy groups are aligned in the same direction, the F substituents are located close to one another, with F1$\cdots$F5^{v} = 2.8625 (15) Å and F2$\cdots$F4^{v} = 2.8914 (17) Å [symmetry code: (v) *x* + 1, *y*, *z*]. Similarly, the molecules are
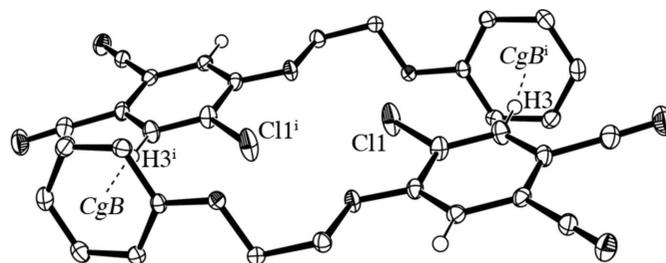
Figure 2
A centrosymmetric pair of molecules of (I) linked through C—H$\cdots\pi$ interactions. The unit-cell outline and H atoms not involved in the motif shown have been omitted for clarity. [Symmetry code: (i) $-x + 2$, $-y + 1$, $-z + 1$.]

aligned along the *b* axis and the F3$\cdots$F4^{vi} distance is short, at 2.7756 (17) Å [symmetry code: (vi) $-x$, $-y$, $-z + 1$]. No π–π stacking is observed in the crystal packing of (II).

In conclusion, the structures of (I) and (II) demonstrate that ring fluorination is associated with the folded structure of (II) through the halogen–π interaction. Since no strong intermolecular interactions are observed between the molecules in either structure, the halogen–π interaction may be the dominant driving force for the folding in (II).

Experimental

Compounds (I) and (II) were prepared in one step using a general procedure (Durmuş *et al.*, 2009). Typically, K$_2$CO$_3$ (11 g, 81 mmol) was added in portions over a period of 2 h to a dry dimethyl-formamide solution (60 ml) of 4,5-dichlorophthalonitrile (4.0 g, 20 mmol) and 2-phenoxyethanol (5.1 ml, 40 mmol) under an N$_2$ atmosphere. The reaction mixture was then stirred at 333 K for 2 d. The mixture was evaporated to remove the solvent and the residue was extracted with CHCl$_3$. The product was further purified by column chromatography (silica gel, CHCl$_3$/MeOH) and recycled gas-phase chromatography (CHCl$_3$) to give (I) as a white powder. Compound (II) was obtained from 2-(pentafluorophenoxy)ethanol using the same procedure as for (I). Both compounds were crystallized from CHCl$_3$ by the vapour diffusion of MeOH to give colourless crystals. Data for (I): yield 23%, m.p. 397–398 K; ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 7.79 (*s*, Ar), 7.41 (*s*, Ar), 7.32 (*t*, *J* = 7.8 Hz, Ar), 7.01 (*t*, *J* = 7.8 Hz, Ar), 6.93 (*d*, *J* = 7.8 Hz, Ar), 4.54–4.51 (*m*, CH$_2$), 4.44–4.41 (*m*, CH$_2$); EI–MS: 298 *m/z* (*M*$^+$); elemental analysis calculated for C$_{16}$H$_{11}$ClN$_2$O$_2$: C 64.3, H 3.7, N 9.4%; found: C 64.2, H 3.7, N 9.4%. Data for (II): yield 32%, m.p. 405–407 K; ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 7.80 (*s*, Ar), 7.31 (*s*, Ar), 4.62–4.60 (*m*, CH$_2$), 4.49–4.47 (*m*, CH$_2$); EI–MS: 388 *m/z* (*M*$^+$); elemental analysis calculated for C$_{16}$H$_6$ClF$_5$N$_2$O$_2$: C 49.4, H 1.6, N 7.2%; found: C 49.4, H 1.5, N 7.1%.

Compound (I)

Crystal data

C$_{16}$H$_{11}$ClN$_2$O$_2$	$V = 1413.2$ (10) Å^3
$M_r = 298.72$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.808$ (4) Å	$\mu = 0.28$ mm^{-1}
$b = 6.555$ (3) Å	$T = 100$ K
$c = 22.018$ (9) Å	$0.20 \times 0.10 \times 0.10$ mm
$\beta = 93.259$ (4)°	

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Data collection

Bruker APEXII CCD
  diffractometer
Absorption correction: empirical
  (using intensity measurements)
  (*SADABS*; Sheldrick, 1996)
  $T_{min} = 0.947$, $T_{max} = 0.973$

15329 measured reflections
3228 independent reflections
2744 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.087$
$S = 1.04$
3228 reflections

190 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}

Compound (II)

Crystal data

$C_{16}H_6ClF_5N_2O_2$
$M_r = 388.68$
Monoclinic, $P2_1/c$
$a = 5.8272\ (13)$ Å
$b = 13.319\ (3)$ Å
$c = 19.380\ (4)$ Å
$\beta = 96.544\ (2)°$

$V = 1494.3\ (6)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.33$ mm^{-1}
$T = 100$ K
$0.24 \times 0.10 \times 0.08$ mm

Data collection

Bruker APEXII CCD
  diffractometer
Absorption correction: empirical
  (using intensity measurements)
  (*SADABS*; Sheldrick, 1996)
  $T_{min} = 0.925$, $T_{max} = 0.974$

16533 measured reflections
3408 independent reflections
2890 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.088$
$S = 1.03$
3408 reflections

235 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

All H atoms were placed in geometrically idealized positions and refined as riding, with aromatic C—H = 0.95 Å and aliphatic C—H = 0.99 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

For both compounds, data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; 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*.

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