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RESEARCH ARTICLE

A Variable Temperature Study of the π - π Stacking Interaction in the Co-Crystal Naphthalene-Octafluoronaphthalene

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Abstract:

Introduction:

The structure of the 1:1 co-crystal of naphthalene and octafluoronaphthalene, which has been previously determined at room temperature, was determined at 100, 150, 200 and 250 K.

Results:

Reductions in intermolecular distances and unit cell dimensions are observed on cooling. DFT calculations reveal that the energies of interaction between pairs of molecules vary little with temperature.

Conclusion:

The strongest interaction is the π - π stacking between virtually parallel naphthalene and octafluoronaphthalene molecules and this displays less change with temperature than the other, weaker, interactions, which have much shallower energy minima.

Keywords: π - π stacking, DFT calculations, X-ray crystal structure, Naphthalene, Octafluoronaphthalene, Intermolecular interactions.

Article History

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1. INTRODUCTION

The π - π stacking interaction between arenes and polyfluoroarenes is being increasingly used in crystal engineering [1 - 13]. A number of studies have indicated its geometric properties, in particular a separation of ca. 3.35 Å between the planes of the virtually parallel arene and polyfluoroarene, and an offset of ca. 1.7 Å [1 - 29], and strength, which has been calculated as 36 and 47 kJ mol⁻¹ for that between toluene and hexafluorobenzene [30], and that between naphthalene and octafluoronaphthalene [31] respectively. The majority of crystal structures of arene-polyfluoroarene co-crystals and molecules which display π - π stacking have been determined either at room temperature [14 - 18, 32] or low temperature [19 - 23], but rarely both [24 - 29], and to our knowledge only one variable temperature structural study has been undertaken, that for the crystal structure of 1,2,3,4-tetrafluoronaphthalene (CCDC reference CAXNUL) [33, 34]. However, although theoretical lattice energies were

calculated, changes in the π - π stacking geometry and the energy of interaction were not reported.

In order to address this deficiency, we decided to perform a variable temperature structural study on a suitable co-crystal containing infinite columns of π - π stacked alternating arene and polyfluoroarene molecules. For the study, it would be desirable if the columns, and consequently the π - π stacking interaction, occurs along one crystallographic axis, so that any changes in this direction can be related directly to the interaction. For simplicity it would also be desirable if the interactions were symmetric about each molecule, *i.e.* the midpoint of each molecule lies on a crystallographic centre of inversion. The crystal structure of naphthalene-octafluoronaphthalene, **1**, which has been determined at room temperature [32] (CCDC reference NPOFNP) satisfies both criteria. Here, we report the results of the study.

2. RESULTS AND DISCUSSION

The crystal structure of naphthalene-octafluoronaphthalene co-crystal, **1**, was determined at 100, 150, 200 and 250 K, all of which are consistent with that previously reported for room temperature [32] (CCDC reference NPOFNP). Co-crystal **1**

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crystallizes in the $P2_1/c$ space group, with columns of alternating parallel naphthalene and octafluoronaphthalene molecules, parallel to the a axis (Fig. 1), with the midpoints of all the molecules lying on centres of inversion. The crystal data

are presented in Table 1, selected bond distances and angles in Table 2, and selected intermolecular distances and angles in Table 3. The molecular structure of **1** at 100 K and the atom numbering scheme are shown in Fig. (2).

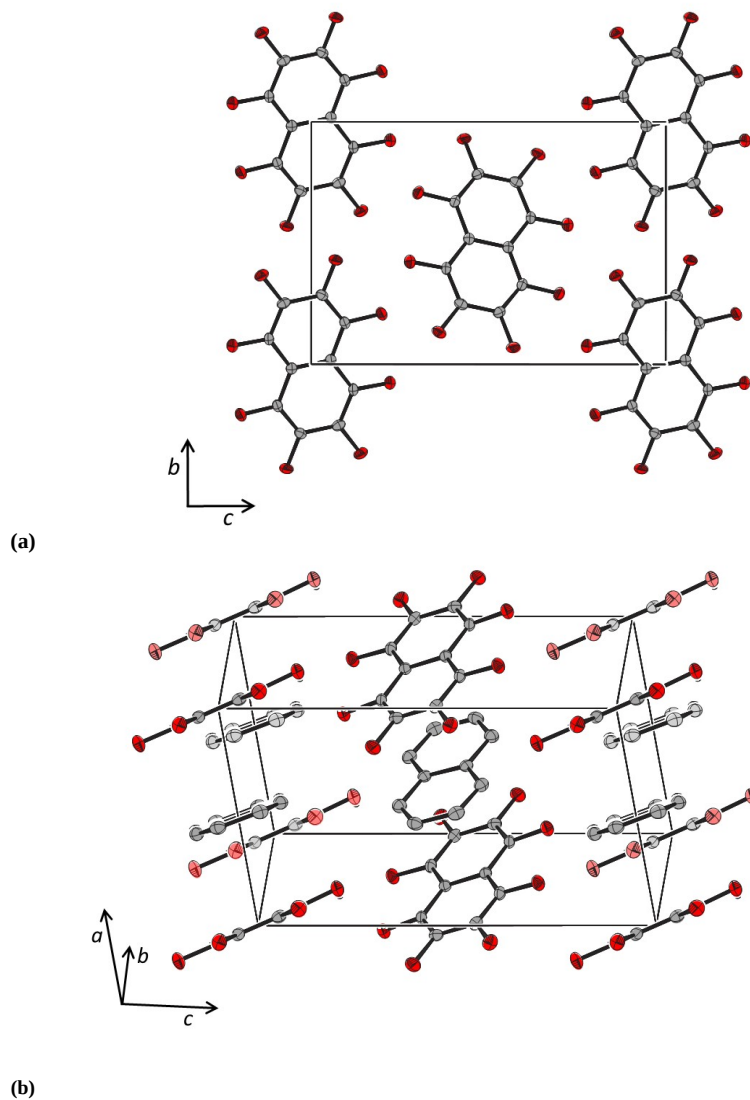


Fig. (1). The crystal structure of **1** 100 K viewed (a) parallel to the a axis and (b) parallel to the planes of the molecules of the columns at the edges of the unit cell. Hydrogen atoms are omitted for clarity. (Red = fluorine, grey = carbon).

Table 1. Crystallographic Data and Refinement Parameters for naphthalene-octafluoronaphthalene, **1**.^a

	100 K	150 K	200 K	250 K
T , K	100.0(2)	150.0(1)	200.0(1)	250.0(1)
a , Å	7.3124(5)	7.3492(4)	7.3825(4)	7.4226(3)
b , Å	8.4324(5)	8.4440(3)	8.4651(4)	8.4850(3)
c , Å	12.4637(8)	12.5125(5)	12.5621(6)	12.6258(5)
β , °	98.529(7)	98.694(4)	98.888(5)	99.102(4)
V , Å ³	760.03(9)	767.56(6)	775.63(7)	785.16(5)
D_c , g cm ⁻³	1.749	1.732	1.714	1.693
μ , mm ⁻¹	1.523	1.508	1.492	1.474
θ range, °	6.12 - 74.03	6.04 - 73.55	6.07 - 73.90	6.04 - 73.86

(Table 3) contd.....

Total reflections	4286	4364	4233	4385
Unique reflections (R_{int})	1502 (0.0414)	1510 (0.0448)	1504 (0.0412)	1529 (0.0399)
Observed reflections [$I > 2\sigma(I)$]	1192	1196	1129	1174
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0445$ $wR_2 = 0.1187$	$R_1 = 0.0437$ $wR_2 = 0.1127$	$R_1 = 0.0462$ $wR_2 = 0.1121$	$R_1 = 0.0639$ $wR_2 = 0.1494$
R indices (all data)	$R_1 = 0.0597$ $wR_2 = 0.1298$	$R_1 = 0.0600$ $wR_2 = 0.1278$	$R_1 = 0.0730$ $wR_2 = 0.1306$	$R_1 = 0.0792$ $wR_2 = 0.1649$
Weighting scheme $^b A, B$	0.0784, 0.1209	0.0712, 0	0.0646, 0.1336	0.1177, 0
Max., min. $\Delta\rho$ ($e \text{ \AA}^{-3}$)	0.316, -0.416	0.296, -0.443	0.417, -0.424	0.505, -0.764
Goodness of fit on F^2	1.0372	1.0934	1.1089	1.0132

^a Estimated standard deviations are given in parentheses. The data were collected using graphite monochromated Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$). C₂₀H₈F₈ ($M = 400.27 \text{ g mol}^{-1}$): monoclinic, space group $P2_1/c$ (no. 14), $Z = 2$, $Z' = 0.5$.

^b $w = 1/[\sigma^2(F_o^2) + \{A(F_o^2 + 2F_c^2)/3\}^2 + B(F_o^2 + 2F_c^2)/3]$

Table 2. Selected bond distances (\AA) and angles ($^\circ$) for naphthalene-octafluoronaphthalene, 1.^a

	100 K	150 K	200 K	250 K	294 [32]
C(1)—C(1)	1.431(4)	1.433(3)	1.427(4)	1.433(4)	1.423(6)
C(1)—C(2)	1.415(3)	1.412(3)	1.412(3)	1.409(3)	1.415(6)
C(2)—C(3)	1.359(3)	1.360(3)	1.356(3)	1.357(3)	1.358(5)
C(3)—C(4)	1.393(3)	1.392(3)	1.390(3)	1.392(3)	1.374(6)
C(4)—C(5)	1.359(3)	1.361(2)	1.358(3)	1.355(3)	1.343(6)
C(5)—C(1)	1.414(3)	1.411(3)	1.413(3)	1.415(3)	1.419(6)
C(2)—F(2)	1.338(2)	1.341(2)	1.338(2)	1.337(2)	1.336(5)
C(3)—F(3)	1.342(2)	1.337(2)	1.342(2)	1.338(2)	1.342(5)
C(4)—F(4)	1.338(2)	1.343(2)	1.339(2)	1.339(2)	1.344(5)
C(5)—F(5)	1.344(2)	1.339(2)	1.341(2)	1.340(2)	1.336(4)
C(11)—C(11)	1.426(4)	1.428(4)	1.418(4)	1.418(4)	1.405(7)
C(11)—C(12)	1.423(3)	1.418(3)	1.420(3)	1.417(3)	1.423(7)
C(12)—C(13)	1.371(3)	1.364(3)	1.364(3)	1.362(3)	1.357(7)
C(13)—C(14)	1.408(3)	1.407(3)	1.397(3)	1.401(4)	1.390(6)
C(14)—C(15)	1.368(3)	1.367(3)	1.368(3)	1.362(3)	1.359(6)
C(15)—C(11)	1.421(3)	1.418(3)	1.418(3)	1.418(3)	1.421(6)
C(1)—C(1)—C(2)	118.3(2)	118.3(2)	118.5(2)	118.5(2)	118.4
C(1)—C(2)—C(3)	121.1(2)	121.3(2)	121.1(2)	121.3(2)	120.7
C(2)—C(3)—C(4)	120.7(2)	120.4(2)	120.6(2)	120.4(2)	120.5
C(3)—C(4)—C(5)	120.3(2)	120.5(2)	120.4(2)	120.5(2)	121.5
C(4)—C(5)—C(1)	121.4(2)	121.3(2)	121.3(2)	121.4(2)	120.9
C(5)—C(1)—C(1)	118.2(2)	118.3(2)	118.1(2)	117.9(2)	118.0
C(2)—C(1)—C(5)	123.4(2)	123.4(2)	123.4(2)	123.6(2)	123.6
C(11)—C(11)—C(12)	118.8(2)	118.6(2)	118.8(2)	119.0(2)	119.6
C(11)—C(12)—C(13)	120.5(2)	121.0(2)	120.5(2)	120.7(2)	119.8
C(12)—C(13)—C(14)	120.6(2)	120.4(2)	120.7(2)	120.9(2)	120.6
C(13)—C(14)—C(15)	120.5(2)	120.4(2)	120.6(2)	120.5(2)	121.4
C(14)—C(15)—C(11)	120.6(2)	120.8(2)	120.4(2)	120.9(2)	119.6
C(15)—C(11)—C(11)	119.0(2)	118.8(2)	119.0(2)	118.4(2)	119.1
C(12)—C(11)—C(15)	122.2(2)	122.6(2)	122.2(2)	122.5(2)	121.4

^a Estimated standard deviations are given in parentheses.

Table 3. Selected intermolecular distances (\AA) and angles ($^\circ$) for naphthalene-octafluoronaphthalene, 1.^a

	100 K	150 K	200 K	250 K	294 [32]
$\langle C_{10}F_{8(\text{plane})} \rangle \alpha$ axis	66.5(4)	66.6(4)	66.5(4)	66.6(4)	66.7
$\langle C_{10}H_{8(\text{plane})} \rangle \alpha$ axis	70.3(4)	70.2(4)	70.2(4)	70.1(4)	69.9
$\langle C_{10}F_{8(\text{plane})} \rangle bc$ plane	30.05(4)	30.03(5)	30.2(1)	30.2(1)	30.5

(Table 5) contd....

	100 K	150 K	200 K	250 K	294 [32]
$\langle C_{10}H_{8(\text{plane})}bc \text{ plane}$	25.85(6)	26.0(1)	26.2(1)	26.4(1)	26.7
$\langle C_{10}F_{8(\text{plane})} C_{10}F_{8(\text{plane})}^b$	33.51(8)	33.63(7)	33.9(1)	34.1(1)	34.1
$\langle C_{10}H_{8(\text{plane})} C_{10}H_{8(\text{plane})}^b$	30.54(6)	30.7(1)	30.9(1)	31.2(1)	31.5
$C_{10}F_{8(\text{plane})} \cdots C_{10}F_{8(\text{plane})}$	6.704(3)	6.743(3)	6.771(3)	6.813(3)	6.847
offset $C_{10}F_{8} \cdots C_{10}F_{8}$	2.919(3)	2.922(3)	2.941(3)	2.949(3)	2.954
$C_{10}H_{8(\text{plane})} \cdots C_{10}H_{8(\text{plane})}$	6.885(3)	6.916(3)	6.947(3)	6.979(3)	7.004
Offset $C_{10}H_{8} \cdots C_{10}H_{8}$	2.462(3)	2.485(3)	2.497(3)	2.529(3)	2.559
$\langle C_{10}F_{8(\text{plane})} C_{10}H_{8(\text{plane})}$	4.30(8)	4.08(6)	4.1(1)	3.9(1)	3.7
$C_{10}H_{8(\text{centre})} \cdots C_{10}F_{8(\text{centre})}$	3.656(3)	3.675(3)	3.691(3)	3.711(3)	3.728
$C_{10}H_{8(\text{centre})} \cdots C_{10}F_{8(\text{plane})}$	3.352(3)	3.372(3)	3.385(3)	3.407(3)	3.424
offset	1.460(3)	1.461(3)	1.471(3)	1.471(3)	1.475
$C_{10}F_{8(\text{centre})} \cdots C_{10}H_{8(\text{plane})}$	3.442(3)	3.458(3)	3.473(3)	3.490(3)	3.502
offset	1.232(3)	1.244(3)	1.250(3)	1.262(3)	1.278
C(13)···F(4)	3.258(2)	3.282(2)	3.309(3)	3.334(3)	3.360
C(14)···F(3)	3.587(2)	3.602(2)	3.629(2)	3.648(2)	3.681
F(3)···F(4)	3.053(2)	3.067(2)	3.081(2)	3.097(2)	3.114
F(4)···F(4)	2.757(2)	2.776(2)	2.801(2)	2.828(2)	2.865
C(14)···C(14)	3.852(3)	3.876(3)	3.909(3)	3.941(3)	3.987
C(13)···C(14)	4.124(2)	4.144(2)	4.168(3)	4.193(3)	4.225
C(12)···F(5)	3.326(2)	3.349(2)	3.370(3)	3.393(3)	3.410
C(13)···F(5)	3.260(2)	3.281(2)	3.310(3)	3.331(3)	3.360
C(13)···F(2)	3.725(2)	3.751(2)	3.784(3)	3.813(3)	3.856
F(2)···F(4)	2.792(2)	2.814(2)	2.832(2)	2.857(2)	2.891
F(5)···F(4)	2.988(2)	3.005(2)	3.024(2)	3.050(2)	3.079
F(3)···F(5)	3.292(2)	3.321(2)	3.347(2)	3.382(2)	3.420

^a Estimated standard deviations are given in parentheses. ^b The angle between the planes of the molecules of different columns.

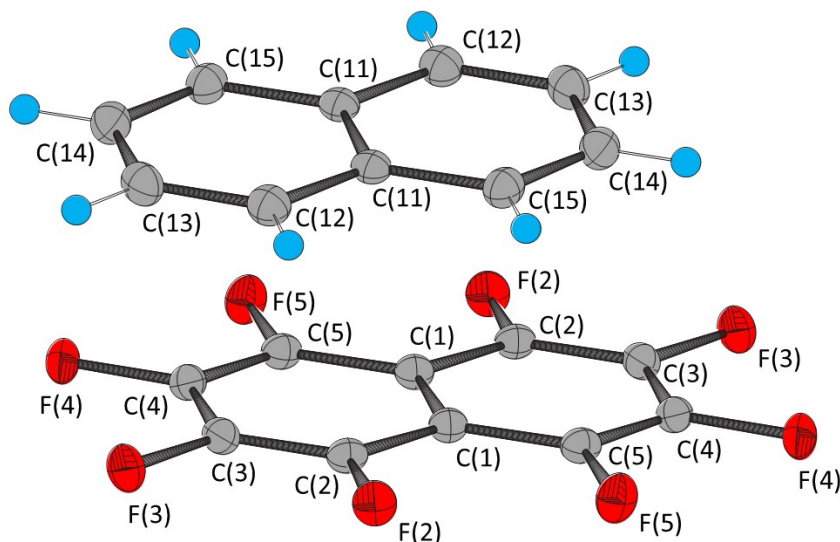


Fig. (2). The molecular structure of **1** at 100 K showing the atom numbering scheme. Thermal ellipsoids are at the 50% level. (Red = fluorine, grey = carbon, blue = hydrogen).

The planes defined by the carbon atoms of octafluoronaphthalene and naphthalene subtend angles with the *a* axis of 66.7 and 69.9° respectively. The molecules of the column at

the centre of the unit cell are tilted oppositely to those centred at the vertices. The planes defined by the carbon atoms of octafluoronaphthalene and naphthalene are at 34.1 and 31.5°

respectively to those of analogous differently tilted molecules.

As expected, the unit cell contracts as the temperature is lowered with a greater contraction along the *a* and *c* axes, 0.110 Å (1.5%) and 0.162 Å (1.3%) respectively, than along the *b* axis, 0.053 Å (0.6%), on decreasing the temperature from 250 to 100 K. The coefficients of linear expansion, α_L , are 1.0×10^{-4} , 0.4×10^{-4} and $0.9 \times 10^{-4} \text{ K}^{-1}$ along the *a*, *b* and *c* axes respectively. There is a commensurate decrease in β of ca. 0.6° (by ca. $4 \times 10^{-3} \text{ }^\circ \text{K}^{-1}$). The values of α_L are similar to those observed for 1,2,3,4-tetrafluoronaphthalene [31] (1.0×10^{-4} , 0.3×10^{-4} and $0.7 \times 10^{-4} \text{ K}^{-1}$), but the change in β , although of similar magnitude, is of opposite sign.

The bond distances and angles are invariant with temperature within experimental error, but the intermolecular distances increase with temperature (Table 3). The distance between the parallel rings is reduced by ca. 1.2% and the offset by ca. 2% on cooling from 250 to 100 K. The change in the intermolecular distance is smaller than those between other adjacent molecules (Fig. 3) which are ca. 2%. The energies of

the interactions were calculated for isolated pairs molecules in the gas phase by the long-range corrected functional ωB97xD [35] method using the 6-311G++(2d,2p) basis set. The values for the structure at 100 K are -59 kJ mol^{-1} for the π - π stacking interaction, -10 , -8 and -6 kJ mol^{-1} for the $\text{C}_{10}\text{F}_8 \cdots \text{C}_{10}\text{F}_8$, $\text{C}_{10}\text{H}_8 \cdots \text{C}_{10}\text{H}_8$ and $\text{C}_{10}\text{F}_8 \cdots \text{C}_{10}\text{H}_8$ interactions shown in Fig. (3a), and -9 and -7 kJ mol^{-1} for the $\text{C}_{10}\text{F}_8 \cdots \text{C}_{10}\text{F}_8$ and $\text{C}_{10}\text{F}_8 \cdots \text{C}_{10}\text{H}_8$ shown in Fig. (3b). There is little variation in the energies with temperature; a decrease of $< 2 \text{ kJ mol}^{-1}$ on going from 100 to 250 K.

Calculations reveal that the energy of the π - π stacking interaction has a much steeper minimum than the other interactions (Fig. 4), which are presumably van der Waals in nature. The π - π stacking interaction energy increases by ca. 8 kJ mol^{-1} as the distance between the two planes is increased or decreased by 0.3 Å, whereas for the other interactions the energies vary by only ca. 2 kJ mol^{-1} over 1 Å. Thus, the π - π stacking interaction is expected to show much less variability in geometry than the other intermolecular interactions. Experimental observation is consistent with this expectation.

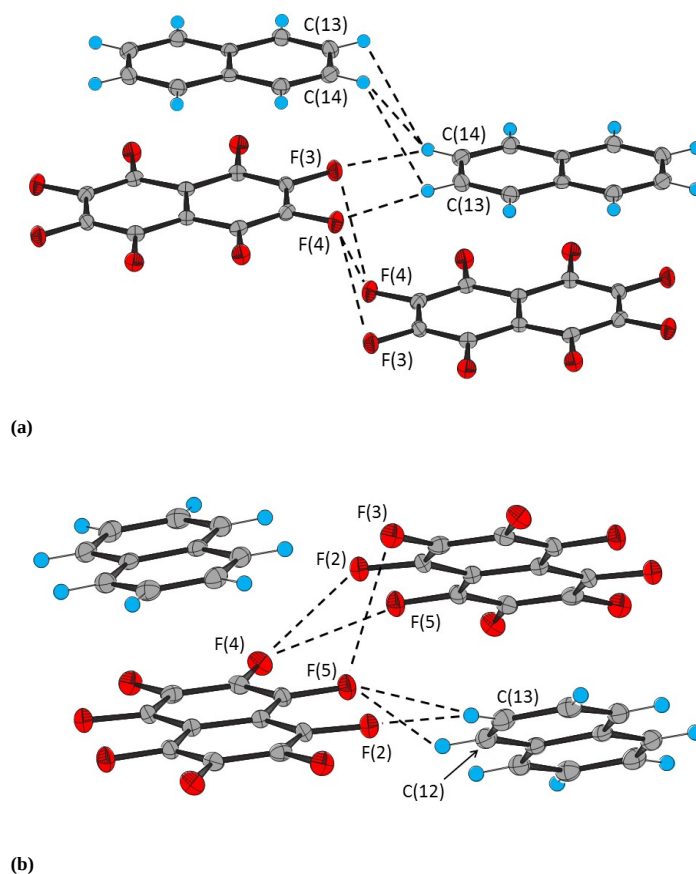


Fig. (3). Short intermolecular distances between adjacent molecules of different stacks in the crystal structure of **1** at 100 K viewed (a) parallel to the *c* axis and (b) parallel to the *b* axis. Thermal ellipsoids are at the 50% level. (Red = fluorine, grey = carbon, blue = hydrogen).

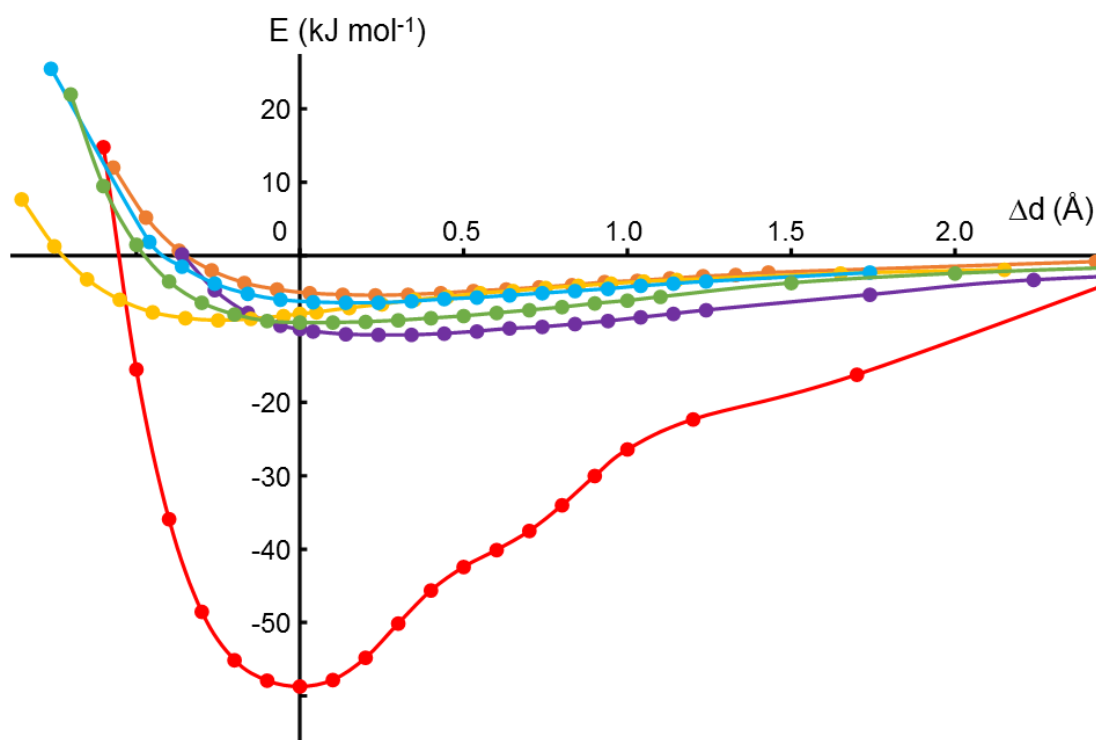


Fig. (4). Variation of interaction energy with distance relative to that found experimentally at 100 K for the π - π stacking interaction along the C(2)···C(11) axis (red) and the interactions along the F(4)···H(13) (orange), F(4)···F(4) (violet), C(14)···F(14) (yellow), C(1)···H(13) (blue) and C(2)···C(4) (green) axes.

3. MATERIALS AND METHODS

Naphthalene-octafluoronaphthalene, **1**, was prepared by mixing and melting the two reagents as previously described [36]. A crystal suitable for single crystal X-ray diffraction was grown from acetone. The same crystal ($0.177 \times 0.059 \times 0.034$ mm) was used to determine the structure at the four different temperatures. Diffraction data were collected on an Agilent SuperNova, single source at offset, Atlas diffractometer with graphite-monochromated Cu- K_{α} radiation. The structures were solved using Olex2 [37] structure solution programme using Charge Flipping and refined with the olex2.refine [38] refinement package using Gauss-Newton minimization. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were added in idealized positions and a riding model with fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded (1.5 for CH_3)) was used for subsequent refinements. The function minimized was $\Sigma[w(|F_o|^2 - |F_c|^2)^2]$ with reflection weights $w^{-1} = [\sigma^2 |F_o|^2 + (g1P)^2 + (g2P)^2]$ where $P = [\max |F_o|^2 + 2|F_c|^2]/3$. The crystal data are presented in Table 1. CCDC 1947799 - 1947802 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. DFT calculations using the long-range corrected functional ω B97XD [35] method with the 6-311G++(2d,2p) basis sets were performed using Gaussian 09 [39]. The energies of interaction were calculated as the

difference between the energy of the species and the sum of those of its components. The C-H bonds of the experimental structures were normalized to 1.083 Å [40] before single point energy calculations were performed.

CONCLUSION

The crystal structure of naphthalene-octafluoronaphthalene, **1**, has been determined at a range of temperatures. The molecular structures are invariant with temperature. The π - π stacking between the virtually parallel naphthalene and octafluoronaphthalene molecules, which is the strongest interaction, undergoes less variation than the other intermolecular interactions, which are weaker. Calculations reveal that this is to be expected since the latter possess shallower minima.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

Not applicable.

FUNDING

None.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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