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## Structure Reports

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# *N,N'*-Bis(2,2,3,3,4,4,4-heptafluorobutyl)-naphthalene-1,4:5,8-tetracarboximide

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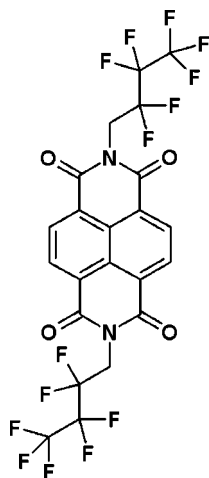
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 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.008$  Å;  $R$  factor = 0.067;  $wR$  factor = 0.223; data-to-parameter ratio = 11.0.

The title molecule,  $\text{C}_{22}\text{H}_8\text{F}_{14}\text{N}_2\text{O}_4$ , lies across a crystallographic inversion center with the naphthalene diimide core essentially planar (mean deviation from plane is 0.0583 Å). The  $\text{CF}_2$  groups in the perfluorobutyl chains are in an energetically favorable all *trans* conformation. In the crystal structure, molecules are packed in slightly displaced layers so that the side chains overlap the aromatic naphthalene diimide rings, thus minimizing any possible  $\pi$ - $\pi$  overlap.

## Related literature

For general background on the semiconducting properties and use of this class of materials in organic thin-film transistor applications, see: Chesterfield *et al.* (2004a,b); Facceti *et al.* (2008); Jones *et al.* (2004); Katz *et al.* (2000a,b); Kazmaier & Hoffmann (1994); Klebe *et al.* (1989); Shukla *et al.* (2008); Wurthner (2004).



## Experimental

## Crystal data

$\text{C}_{22}\text{H}_8\text{F}_{14}\text{N}_2\text{O}_4$	$\gamma = 89.115$ (7)°
$M_r = 630.30$	$V = 549.64$ (11) Å <sup>3</sup>
Triclinic, $P\bar{1}$	$Z = 1$
$a = 5.1910$ (5) Å	Mo $K\alpha$ radiation
$b = 10.1459$ (12) Å	$\mu = 0.21$ mm <sup>-1</sup>
$c = 11.5988$ (15) Å	$T = 293$ (2) K
$\alpha = 66.693$ (4)°	$0.15 \times 0.10 \times 0.05$ mm
$\beta = 79.064$ (4)°	

## Data collection

Nonius KappaCCD diffractometer	2094 independent reflections
Absorption correction: none	909 reflections with $I > 2\sigma(I)$
3049 measured reflections	$R_{\text{int}} = 0.057$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.067$	190 parameters
$wR(F^2) = 0.223$	H-atom parameters constrained
$S = 0.93$	$\Delta\rho_{\text{max}} = 0.23$ e Å <sup>-3</sup>
2094 reflections	$\Delta\rho_{\text{min}} = -0.23$ e Å <sup>-3</sup>

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *Materials Studio* (Accelrys, 2002); software used to prepare material for publication: *publCIF* (Westrip, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2728).

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**supplementary materials**

*Acta Cryst.* (2008). E64, o2327 [ doi:10.1107/S1600536808036738 ]

## *N,N'*-Bis(2,2,3,3,4,4,4-heptafluorobutyl)naphthalene-1,4:5,8-tetracarboximide

D. Shukla, M. Rajeswaran, W. G. Ahearn and D. M. Meyer

### Comment

Amongst n-type semiconductors used in organic thin film transistors, perylene diimides (PDIs) and naphthalene diimides (NDIs) have attracted considerable attention. The  $\pi$ -orbital wavefunctions in these systems form nodes at the two nitrogen positions in the imide rings. Indeed, it has been shown that semiconducting properties and device performance of these materials is very sensitive to the nature of substituents on the diimide nitrogen atoms. The title compound *N,N'*-Bis(1*H*,1*H*-perfluorobutyl) naphthalene-1,4,5,8-tetracarboxylic acid diimide(I) has been shown to exhibit good n-type semiconducting behavior and OTFTs made incorporating I can be operated in air. The latter property has been ascribed to the denser packing of fluorinated alkyl chains in thin film.

Naphthalene diimide (NDI) and perylene diimide (PDI) based systems have been studied extensively (Chesterfield, *et al.*, 2004*a*; Chesterfield *et al.*, 2004*b*; Facceti *et al.*, 2008; Jones, *et al.*, 2004; Katz, *et al.*, 2000*a*; Katz, *et al.*, 2000*b*). We report here the structure of the title diimide molecule (I) (Fig. 1 and Fig 2). In the crystal structure, molecules are packed in slightly displaced layers so that the side chains overlap the aromatic naphthalene diimide rings, thus resulting in minimizing any possible  $\pi$ - $\pi$  overlap (Fig. 3).

### Experimental

The method described in Katz *et al.*, 2000*a*, was followed for preparation of the title compound (I). Crystals of title (I) appeared during powder X-ray diffraction data collection of the dry lot sample. The crystals were weakly diffracting, but we were unable to get better quality crystals. Diffraction data were collected on various crystals, and the results of structure determination using best data set results are reported here.

### Refinement

All H-atoms were positioned geometrically and refined using a riding model with  $d(\text{C}-\text{H}) = 0.93 \text{ \AA}$ ,  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$  for aromatic  $0.97 \text{ \AA}$ ,  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$  for  $\text{CH}_2$  atoms.

### Figures

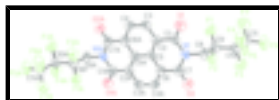


Fig. 1. Molecular structure of the title compound, with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

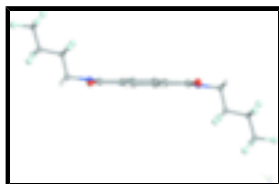


Fig. 2. A diagram illustrating planar naphthalene diimide core and *trans* configuration of perfluorobutyl chains on diimide N atoms.

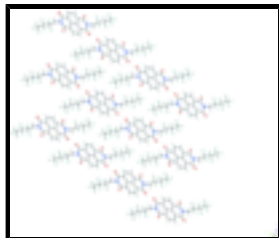


Fig. 3. Unit cell packing showing layered structure.

## *N,N'*-Bis(2,2,3,3,4,4,4-heptafluorobutyl)naphthalene-1,4:5,8-tetracarboximide

### Crystal data

$C_{22}H_8F_{14}N_2O_4$

$M_r = 630.30$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$a = 5.1910$  (5) Å

$b = 10.1459$  (12) Å

$c = 11.5988$  (15) Å

$\alpha = 66.693$  (4)°

$\beta = 79.064$  (4)°

$\gamma = 89.115$  (7)°

$V = 549.64$  (11) Å<sup>3</sup>

$Z = 1$

$F_{000} = 312$

$D_x = 1.904$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 4558 reflections

$\theta = 1.0$ – $26.7^\circ$

$\mu = 0.21$  mm<sup>-1</sup>

$T = 293$  (2) K

Needle, pink

$0.15 \times 0.10 \times 0.05$  mm

### Data collection

Nonius KappaCCD  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 9 pixels mm<sup>-1</sup>

$T = 293$ (2) K

$\varphi$  and  $\omega$  scans

Absorption correction: none

3049 measured reflections

2094 independent reflections

909 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.057$

$\theta_{max} = 26.6^\circ$

$\theta_{min} = 4.1^\circ$

$h = -6 \rightarrow 6$

$k = -12 \rightarrow 11$

$l = -14 \rightarrow 12$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.067$

$wR(F^2) = 0.223$

$S = 0.93$

2094 reflections

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.3623P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.23$  e Å<sup>-3</sup>

190 parameters

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$$

Primary atom site location: structure-invariant direct methods

Extinction correction: none

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
F1	0.1050 (6)	0.4145 (3)	0.7561 (3)	0.0814 (11)
F2	0.1713 (6)	0.5174 (3)	0.8788 (3)	0.0828 (12)
F3	0.5849 (6)	0.3623 (4)	0.9393 (3)	0.0873 (12)
F4	0.5572 (7)	0.2684 (3)	0.8049 (3)	0.0883 (12)
F5	0.3622 (7)	0.0974 (4)	1.0537 (3)	0.0931 (12)
F6	0.0806 (7)	0.2472 (4)	1.0654 (4)	0.1050 (15)
F7	0.0800 (9)	0.1477 (4)	0.9346 (4)	0.1234 (17)
O1	0.2493 (8)	0.6081 (4)	0.4924 (4)	0.0742 (12)
O2	0.5194 (8)	0.8024 (4)	0.7439 (4)	0.0725 (12)
N1	0.3566 (7)	0.6967 (4)	0.6298 (4)	0.0484 (11)
C1	0.2325 (10)	0.7037 (5)	0.5308 (5)	0.0528 (14)
C2	0.0799 (9)	0.8305 (5)	0.4790 (5)	0.0467 (12)
C3	-0.0607 (10)	0.8401 (5)	0.3865 (5)	0.0562 (14)
H3	-0.0557	0.7679	0.3559	0.067*
C4	-0.2109 (10)	0.9584 (5)	0.3386 (5)	0.0541 (14)
H4	-0.3058	0.9637	0.2767	0.065*
C5	0.0752 (9)	0.9387 (5)	0.5243 (4)	0.0440 (12)
C6	0.2199 (9)	0.9345 (5)	0.6184 (5)	0.0482 (13)
C7	0.3779 (10)	0.8079 (5)	0.6691 (5)	0.0523 (14)
C8	0.4892 (9)	0.5658 (5)	0.6912 (5)	0.0537 (14)
H8A	0.6355	0.5891	0.7224	0.064*
H8B	0.5580	0.5257	0.6292	0.064*
C9	0.2958 (10)	0.4562 (6)	0.8023 (5)	0.0544 (14)
C10	0.4188 (10)	0.3238 (5)	0.8827 (5)	0.0550 (14)
C11	0.2281 (13)	0.2022 (6)	0.9871 (6)	0.0676 (16)

### Atomic displacement parameters ( $\text{\AA}^2$ )

$U^{11}$        $U^{22}$        $U^{33}$        $U^{12}$        $U^{13}$        $U^{23}$

## supplementary materials

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F1	0.061 (2)	0.082 (2)	0.086 (2)	-0.0057 (16)	-0.0279 (18)	-0.0114 (19)
F2	0.091 (2)	0.063 (2)	0.074 (2)	0.0213 (17)	0.0167 (18)	-0.0222 (18)
F3	0.074 (2)	0.098 (3)	0.083 (3)	-0.0005 (18)	-0.0340 (18)	-0.021 (2)
F4	0.108 (3)	0.077 (2)	0.070 (2)	0.0396 (19)	-0.0012 (19)	-0.0278 (19)
F5	0.107 (3)	0.071 (2)	0.078 (2)	0.025 (2)	-0.018 (2)	-0.0064 (19)
F6	0.101 (3)	0.087 (3)	0.082 (3)	0.023 (2)	0.026 (2)	-0.007 (2)
F7	0.147 (4)	0.081 (3)	0.125 (4)	-0.039 (3)	-0.057 (3)	-0.008 (3)
O1	0.095 (3)	0.070 (3)	0.073 (3)	0.031 (2)	-0.024 (2)	-0.042 (2)
O2	0.079 (3)	0.067 (3)	0.080 (3)	0.0131 (19)	-0.038 (2)	-0.029 (2)
N1	0.054 (2)	0.040 (2)	0.051 (3)	0.0061 (18)	-0.010 (2)	-0.018 (2)
C1	0.059 (3)	0.046 (3)	0.052 (3)	0.009 (3)	-0.006 (3)	-0.021 (3)
C2	0.049 (3)	0.048 (3)	0.044 (3)	0.003 (2)	-0.002 (2)	-0.023 (3)
C3	0.068 (3)	0.051 (3)	0.057 (3)	0.006 (3)	-0.015 (3)	-0.028 (3)
C4	0.064 (3)	0.058 (3)	0.047 (3)	0.005 (3)	-0.016 (2)	-0.026 (3)
C5	0.045 (3)	0.044 (3)	0.038 (3)	0.001 (2)	-0.002 (2)	-0.014 (2)
C6	0.046 (3)	0.051 (3)	0.041 (3)	0.003 (2)	-0.003 (2)	-0.014 (3)
C7	0.051 (3)	0.052 (3)	0.044 (3)	0.000 (2)	-0.004 (3)	-0.012 (3)
C8	0.050 (3)	0.055 (3)	0.051 (3)	0.009 (2)	-0.010 (2)	-0.017 (3)
C9	0.053 (3)	0.056 (3)	0.057 (4)	0.010 (3)	-0.010 (3)	-0.026 (3)
C10	0.060 (3)	0.058 (3)	0.054 (3)	0.014 (3)	-0.011 (3)	-0.031 (3)
C11	0.085 (4)	0.056 (4)	0.058 (4)	0.003 (3)	-0.024 (4)	-0.015 (3)

### *Geometric parameters (Å, °)*

F1—C9	1.357 (6)	C2—C5	1.389 (6)
F2—C9	1.341 (6)	C3—C4	1.402 (7)
F3—C10	1.325 (6)	C3—H3	0.9300
F4—C10	1.338 (6)	C4—C6 <sup>i</sup>	1.360 (7)
F5—C11	1.321 (6)	C4—H4	0.9300
F6—C11	1.294 (7)	C5—C6	1.425 (6)
F7—C11	1.314 (6)	C5—C5 <sup>i</sup>	1.435 (9)
O1—C1	1.213 (6)	C6—C4 <sup>i</sup>	1.360 (7)
O2—C7	1.223 (6)	C6—C7	1.491 (7)
N1—C7	1.387 (6)	C8—C9	1.522 (7)
N1—C1	1.398 (6)	C8—H8A	0.9700
N1—C8	1.467 (6)	C8—H8B	0.9700
C1—C2	1.477 (7)	C9—C10	1.513 (7)
C2—C3	1.380 (7)	C10—C11	1.539 (8)
C7—N1—C1	124.8 (4)	N1—C8—C9	109.7 (4)
C7—N1—C8	117.3 (5)	N1—C8—H8A	109.7
C1—N1—C8	117.8 (4)	C9—C8—H8A	109.7
O1—C1—N1	120.4 (5)	N1—C8—H8B	109.7
O1—C1—C2	123.0 (5)	C9—C8—H8B	109.7
N1—C1—C2	116.6 (5)	H8A—C8—H8B	108.2
C3—C2—C5	120.2 (5)	F2—C9—F1	105.5 (4)
C3—C2—C1	119.6 (5)	F2—C9—C10	108.6 (4)
C5—C2—C1	120.2 (5)	F1—C9—C10	108.7 (4)
C2—C3—C4	120.1 (5)	F2—C9—C8	110.1 (4)

C2—C3—H3	119.9	F1—C9—C8	109.2 (4)
C4—C3—H3	119.9	C10—C9—C8	114.3 (4)
C6 <sup>i</sup> —C4—C3	120.9 (5)	F3—C10—F4	107.7 (4)
C6 <sup>i</sup> —C4—H4	119.6	F3—C10—C9	109.0 (4)
C3—C4—H4	119.6	F4—C10—C9	108.5 (4)
C2—C5—C6	122.3 (5)	F3—C10—C11	107.7 (5)
C2—C5—C5 <sup>i</sup>	120.6 (6)	F4—C10—C11	107.2 (5)
C6—C5—C5 <sup>i</sup>	117.2 (6)	C9—C10—C11	116.4 (5)
C4 <sup>i</sup> —C6—C5	121.0 (5)	F6—C11—F7	109.6 (6)
C4 <sup>i</sup> —C6—C7	121.4 (5)	F6—C11—F5	108.2 (5)
C5—C6—C7	117.7 (5)	F7—C11—F5	107.3 (5)
O2—C7—N1	121.5 (5)	F6—C11—C10	111.6 (5)
O2—C7—C6	120.7 (5)	F7—C11—C10	110.2 (5)
N1—C7—C6	117.8 (5)	F5—C11—C10	109.8 (5)
C7—N1—C1—O1	171.2 (4)	C4 <sup>i</sup> —C6—C7—N1	173.8 (4)
C8—N1—C1—O1	-4.5 (7)	C5—C6—C7—N1	-5.4 (6)
C7—N1—C1—C2	-9.8 (7)	C7—N1—C8—C9	95.1 (5)
C8—N1—C1—C2	174.5 (4)	C1—N1—C8—C9	-88.9 (5)
O1—C1—C2—C3	2.8 (8)	N1—C8—C9—F2	-50.4 (6)
N1—C1—C2—C3	-176.1 (4)	N1—C8—C9—F1	65.0 (6)
O1—C1—C2—C5	-178.0 (5)	N1—C8—C9—C10	-173.0 (5)
N1—C1—C2—C5	3.1 (7)	F2—C9—C10—F3	-59.0 (5)
C5—C2—C3—C4	-0.6 (7)	F1—C9—C10—F3	-173.3 (4)
C1—C2—C3—C4	178.6 (4)	C8—C9—C10—F3	64.4 (6)
C2—C3—C4—C6 <sup>i</sup>	0.4 (8)	F2—C9—C10—F4	-176.0 (4)
C3—C2—C5—C6	-179.1 (4)	F1—C9—C10—F4	69.7 (5)
C1—C2—C5—C6	1.7 (7)	C8—C9—C10—F4	-52.6 (6)
C3—C2—C5—C5 <sup>i</sup>	0.0 (8)	F2—C9—C10—C11	63.0 (6)
C1—C2—C5—C5 <sup>i</sup>	-179.2 (5)	F1—C9—C10—C11	-51.3 (7)
C2—C5—C6—C4 <sup>i</sup>	-179.8 (4)	C8—C9—C10—C11	-173.5 (5)
C5 <sup>i</sup> —C5—C6—C4 <sup>i</sup>	1.1 (8)	F3—C10—C11—F6	65.9 (6)
C2—C5—C6—C7	-0.6 (7)	F4—C10—C11—F6	-178.4 (5)
C5 <sup>i</sup> —C5—C6—C7	-179.7 (5)	C9—C10—C11—F6	-56.8 (7)
C1—N1—C7—O2	-169.7 (5)	F3—C10—C11—F7	-172.1 (5)
C8—N1—C7—O2	6.0 (7)	F4—C10—C11—F7	-56.4 (6)
C1—N1—C7—C6	11.0 (7)	C9—C10—C11—F7	65.2 (7)
C8—N1—C7—C6	-173.3 (4)	F3—C10—C11—F5	-54.1 (7)
C4 <sup>i</sup> —C6—C7—O2	-5.5 (7)	F4—C10—C11—F5	61.6 (6)
C5—C6—C7—O2	175.3 (4)	C9—C10—C11—F5	-176.8 (5)

Symmetry codes: (i)  $-x, -y+2, -z+1$ .

Fig. 1

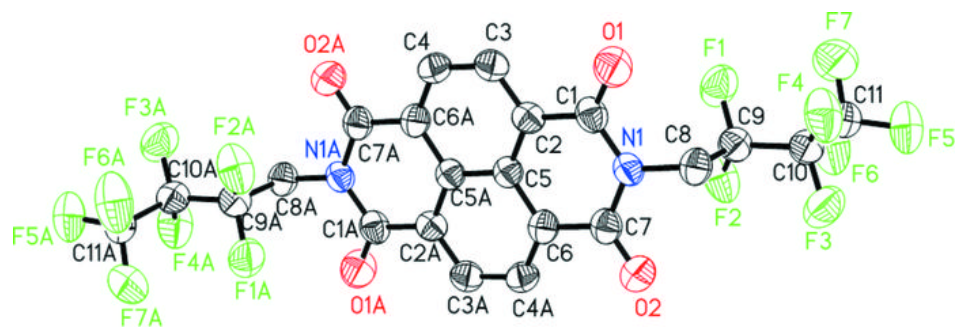


Fig. 2

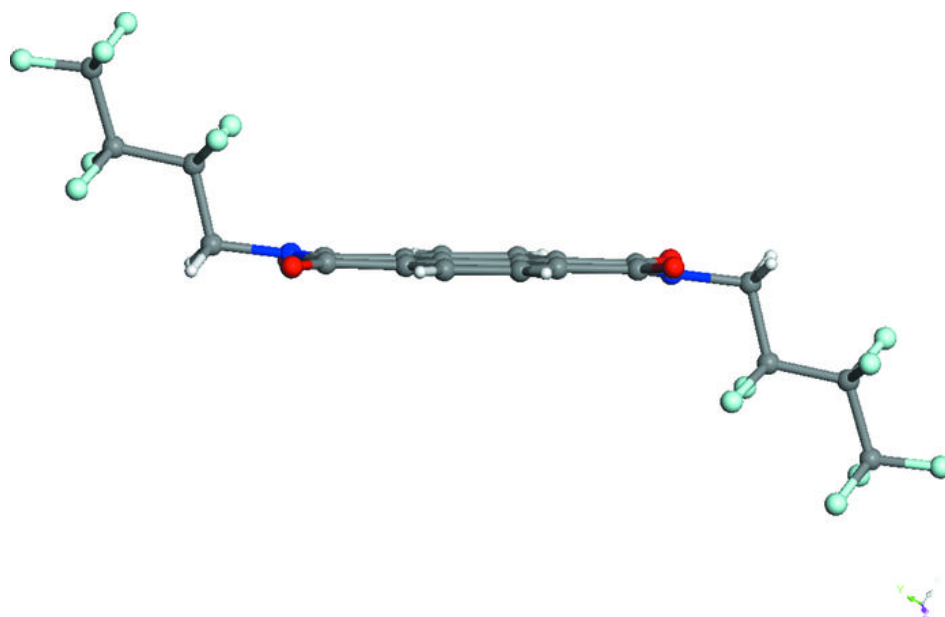


Fig. 3

