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 δ -Hexabromocyclododecane

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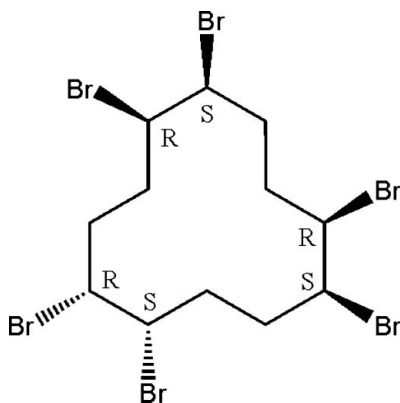
Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.013$ Å; R factor = 0.045; wR factor = 0.107; data-to-parameter ratio = 24.5.

(1*R*,2*S*,5*R*,6*S*,9*S*,10*R*)-Hexabromocyclododecane ($\text{C}_{12}\text{H}_{18}\text{Br}_6$, δ -HBCD) was crystallized from acetonitrile. The C—Br distances range from 1.962 (8) to 1.982 (8) Å and intermolecular Br \cdots Br contacts contribute to the formation of layers.

Related literature

The corresponding α -, β - and γ -stereoisomers of HBCD form comparable Br \cdots Br contacts (Koeppen *et al.*, 2007).

For related literature, see: Arsenault *et al.* (2007); BSEF (2007); Becher (2005); Covaci *et al.* (2006); Dodder *et al.* (2006); Groweiss *et al.* (1991); Heeb *et al.* (2005, 2007); Law *et al.* (2005); Pedireddi *et al.* (1994); Vos *et al.* (2003).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{18}\text{Br}_6$
 $M_r = 641.72$
 Triclinic, $P\bar{1}$
 $a = 9.218$ (6) Å

$b = 10.664$ (7) Å
 $c = 10.807$ (7) Å
 $\alpha = 116.807$ (8)°
 $\beta = 96.310$ (9)°

$\gamma = 104.703$ (9)°
 $V = 885.6$ (10) Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 13.58$ mm⁻¹
 $T = 294$ (2) K
 $0.12 \times 0.11 \times 0.1$ mm

Data collection

Bruker APEX CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
 $T_{\min} = 0.194$, $T_{\max} = 0.257$

6072 measured reflections
 4046 independent reflections
 2183 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.107$
 $S = 0.87$
 4046 reflections

165 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.66$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.79$ e Å⁻³

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXTL* (Bruker, 2001).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2387).

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supplementary materials

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δ -Hexabromocyclododecane

R. Köppen, F. Emmerling, A. Kohl and R. Becker

Comment

1,2,5,6,9,10-Hexabromocyclododecane (HBCD) is a widely used brominated flame retardant with a complex stereochemistry (Heeb *et al.*, 2005; Law *et al.*, 2005). The commercial HBCD mixture consists largely of a mixture of three diastereomeric pairs of enantiomers, termed (\pm) α , β , and γ -HBCD with the γ -isomers as main component (Groweiss *et al.*, 1991; Becher, 2005). Recently the presence of small amounts of δ - and ϵ -HBCD diastereomers in both technical mixture and environmental samples has been reported (Heeb *et al.*, 2005; Dodder *et al.*, 2006). HBCD has been subject of intensive studies (*i.e.* Heeb *et al.*, 2007) as a result of its persistence in the environment, its potential bioactivity and increasing levels in the biosphere (Vos *et al.*, 2003; Covaci *et al.*, 2006; BSEF, 2007). After elucidation of the crystal structure of the six main stereoisomers of the technical mixture (Koeppen *et al.*, 2007), we directed our attention to the two minor diastereomers. Recently both minor diastereomers were characterized by NMR and their order of elution on a C18 stationary phase was determined (Arsenault *et al.*, 2007). Furthermore, no attempt was made to confirm absolute configurations of δ - and ϵ -HBCD using single-crystal X-ray crystallography. The knowledge of the three-dimensional structures of all HBCD diastereomers occurring in the environment is necessary for the understanding of the bioaccumulation and the potentially bioisomerization of HBCD. The average C—Br distance in the title compound (Fig. 1) [1.972 (8) Å] is in good agreement with those in the other stereoisomers ($d_{\text{av}}(\text{C—Br})=1.962$ (10)–1.974 (13) Å, Koeppen *et al.*, 2007). The average C—C distance of 1.520 (12) Å is also in good agreement with the distances observed in the other HBCD compounds.

The packing of the molecules is mainly influenced by Br \cdots Br interactions. The observed Br \cdots Br contacts range from 3.611 (3) to 3.664 (3) Å and can be classified both as type I (Br5 \cdots Br10, $d=3.611$ (3) Å, $\theta_1=136.69^\circ$, $\theta_2=154.01^\circ$) and II (Br2 \cdots Br9, $d=3.664$ (3) Å, $\theta_1=83.75^\circ$, $\theta_2=162.48^\circ$) contacts, whereas the latter is polarization-induced and contributes actively to crystal structure stabilization (Pedireddi *et al.*, 1994). These contacts lead to the formation of layers parallel to the b-c plane, stacked along the a direction (Fig. 2). The shortest centroid to centroid distances between two HBCD molecules of different layers amount to 5.864 (8) and 5.985 (9) Å, respectively.

Experimental

1*R*,2*S*,5*R*,6*S*,9*S*,10*R*-Hexabromocyclododecane (δ -HBCD) was obtained by bromination of *trans,trans,trans*-cyclododeca-1,5,9-triene (t,t,t-CDT), as illustrated in the reaction scheme (Fig. 3). δ -HBCD was isolated from the reaction mixture by preparative HPLC (C-18 column). For single-crystal x-ray crystallography colourless crystals of δ -HBCD were grown by solvent evaporation from acetonitrile at ambient temperature. LC—MS/MS-experiments ($[\text{M—H}]^-$ (m/z 640.6) \rightarrow $[\text{Br}]^-$ (m/z 79.0)) using a combination of a Zorbax XBD-C18 (Agilent Technologies, Waldbronn, Germany) and a chiral NUCLEODEX β -PM (Macherey- Nagel GmbH & Co, Düren, Germany) analytical column shows that δ -HBCD elute between ($-$) α - and ($+$) α -HBCD. This corresponds to the results reported in literature (*i.e.* Arsenault *et al.*, 2007). Spectroscopic Analysis, IR (microscope, cm^{-1}): 2960, 2937, 2924, 2890, 2862, 2848, 1736, 1459, 1441, 1421, 1373, 1335, 1297, 1278, 1260, 1239, 1157, 1105, 1056, 1037, 1021, 1003, 985, 907, 863, 787, 751, 742, 735, 672, 645, 602.

Refinement

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in difference maps but positioned with idealized geometry and refined using the riding model, with C—H = 0.93–0.97 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

Figures

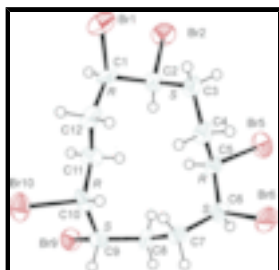


Fig. 1. The structure of HBCD with labelling and displacement ellipsoids drawn at the 50% probability level.

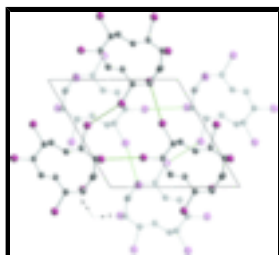


Fig. 2. The crystal packing, showing the layers of HBCD molecules parallel to the b-c plane, connected by Br...Br contacts (green lines).

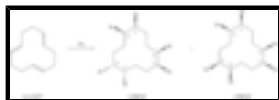


Fig. 3. General reaction scheme of synthesis of δ - and ϵ -HBCD.

(1*R*,2*S*,5*R*,6*S*,9*S*,10*R*)-Hexabromocyclododecane

Crystal data

$\text{C}_{12}\text{H}_{18}\text{Br}_6$

$M_r = 641.72$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 9.218$ (6) Å

$b = 10.664$ (7) Å

$c = 10.807$ (7) Å

$\alpha = 116.807$ (8)°

$\beta = 96.310$ (9)°

$\gamma = 104.703$ (9)°

$V = 885.6$ (10) Å³

$Z = 2$

$F_{000} = 600$

$D_x = 2.407$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 102 reflections

$\theta = 3.5$ – 28°

$\mu = 13.58$ mm⁻¹

$T = 294$ (2) K

Block, colourless

$0.12 \times 0.11 \times 0.1$ mm

Data collection

Bruker APEX CCD area-detector diffractometer	4046 independent reflections
Radiation source: fine-focus sealed tube	2183 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.060$
$T = 273(2)$ K	$\theta_{\text{max}} = 27.6^\circ$
ω scans	$\theta_{\text{min}} = 2.2^\circ$
Absorption correction: ψ scan (SAINT; Bruker, 2001)	$h = -11 \rightarrow 9$
$T_{\text{min}} = 0.194$, $T_{\text{max}} = 0.257$	$k = -10 \rightarrow 13$
6072 measured reflections	$l = -13 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.045$	H-atom parameters constrained
$wR(F^2) = 0.107$	$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2]$
$S = 0.87$	where $P = (F_o^2 + 2F_c^2)/3$
4046 reflections	$(\Delta/\sigma)_{\text{max}} = 0.007$
165 parameters	$\Delta\rho_{\text{max}} = 0.66 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.79 \text{ e } \text{\AA}^{-3}$
	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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.15295 (11)	0.27503 (12)	0.38667 (10)	0.0522 (3)
Br2	0.42537 (11)	0.58963 (12)	0.68589 (11)	0.0527 (3)
Br5	0.29225 (11)	0.57767 (11)	1.09885 (10)	0.0509 (3)
Br6	-0.01545 (11)	0.26237 (13)	1.05275 (11)	0.0550 (3)
Br9	0.56301 (10)	-0.01812 (12)	0.77553 (10)	0.0475 (3)

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Br10	0.25800 (11)	-0.22121 (11)	0.46069 (10)	0.0530 (3)
C1	0.2920 (9)	0.2702 (10)	0.5343 (8)	0.040 (2)
H1	0.3929	0.2794	0.5117	0.048*
C2	0.3175 (9)	0.4033 (9)	0.6823 (9)	0.035 (2)
H2	0.3891	0.3946	0.7496	0.043*
C3	0.1755 (10)	0.4198 (10)	0.7442 (9)	0.042 (2)
H3A	0.1991	0.5251	0.8116	0.051*
H3B	0.0889	0.3912	0.6659	0.051*
C4	0.1214 (9)	0.3341 (10)	0.8186 (8)	0.038 (2)
H4A	0.0892	0.2283	0.7492	0.045*
H4B	0.0303	0.3543	0.8479	0.045*
C5	0.2374 (9)	0.3656 (10)	0.9492 (8)	0.036 (2)
H5	0.3321	0.3535	0.9199	0.043*
C6	0.1904 (9)	0.2662 (10)	1.0140 (9)	0.036 (2)
H6	0.2665	0.3100	1.1059	0.044*
C7	0.1842 (9)	0.1070 (10)	0.9223 (9)	0.039 (2)
H7A	0.1171	0.0652	0.8275	0.047*
H7B	0.1387	0.0480	0.9642	0.047*
C8	0.3428 (9)	0.0945 (10)	0.9078 (8)	0.042 (2)
H8A	0.3892	0.0860	0.9874	0.050*
H8B	0.4083	0.1864	0.9163	0.050*
C9	0.3434 (9)	-0.0364 (10)	0.7682 (9)	0.037 (2)
H9	0.2894	-0.1299	0.7656	0.044*
C10	0.2658 (9)	-0.0404 (9)	0.6350 (8)	0.034 (2)
H10	0.1581	-0.0482	0.6380	0.041*
C11	0.3370 (9)	0.0978 (9)	0.6213 (8)	0.034 (2)
H11A	0.3692	0.1860	0.7157	0.041*
H11B	0.4293	0.0907	0.5871	0.041*
C12	0.2291 (9)	0.1175 (10)	0.5215 (8)	0.037 (2)
H12A	0.1289	0.1050	0.5433	0.044*
H12B	0.2139	0.0407	0.4233	0.044*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0463 (6)	0.0689 (8)	0.0452 (6)	0.0099 (5)	0.0026 (4)	0.0388 (6)
Br2	0.0551 (7)	0.0439 (7)	0.0621 (7)	0.0064 (5)	0.0154 (5)	0.0341 (6)
Br5	0.0488 (6)	0.0401 (7)	0.0510 (6)	0.0162 (5)	0.0066 (5)	0.0134 (5)
Br6	0.0478 (6)	0.0791 (9)	0.0723 (7)	0.0349 (5)	0.0385 (5)	0.0532 (7)
Br9	0.0394 (6)	0.0548 (7)	0.0606 (6)	0.0240 (5)	0.0189 (5)	0.0333 (6)
Br10	0.0492 (6)	0.0407 (7)	0.0491 (6)	0.0092 (5)	0.0144 (5)	0.0092 (5)
C1	0.033 (5)	0.049 (7)	0.033 (5)	0.007 (4)	0.009 (4)	0.021 (5)
C2	0.031 (5)	0.038 (6)	0.040 (5)	0.007 (4)	0.008 (4)	0.024 (5)
C3	0.045 (6)	0.043 (6)	0.050 (6)	0.019 (5)	0.023 (5)	0.028 (5)
C4	0.029 (5)	0.053 (7)	0.033 (5)	0.011 (4)	0.009 (4)	0.025 (5)
C5	0.033 (5)	0.042 (6)	0.023 (5)	0.009 (4)	0.006 (4)	0.010 (4)
C6	0.038 (5)	0.032 (6)	0.033 (5)	0.009 (4)	0.014 (4)	0.012 (5)
C7	0.044 (6)	0.033 (6)	0.045 (6)	0.016 (4)	0.020 (4)	0.019 (5)

C8	0.035 (6)	0.048 (7)	0.037 (5)	0.019 (4)	0.009 (4)	0.015 (5)
C9	0.032 (5)	0.039 (6)	0.054 (6)	0.014 (4)	0.019 (4)	0.032 (5)
C10	0.032 (5)	0.035 (6)	0.032 (5)	0.013 (4)	0.009 (4)	0.014 (4)
C11	0.027 (5)	0.030 (6)	0.035 (5)	0.008 (4)	0.006 (4)	0.008 (4)
C12	0.036 (5)	0.043 (6)	0.027 (5)	0.009 (4)	0.003 (4)	0.017 (4)

Geometric parameters (Å, °)

Br1—C1	1.962 (8)	C5—H5	0.9800
Br2—C2	1.964 (8)	C6—C7	1.512 (11)
Br5—C5	1.981 (8)	C6—H6	0.9800
Br6—C6	1.982 (8)	C7—C8	1.520 (10)
Br9—C9	1.973 (8)	C7—H7A	0.9700
Br10—C10	1.973 (8)	C7—H7B	0.9700
C1—C12	1.518 (12)	C8—C9	1.526 (11)
C1—C2	1.526 (11)	C8—H8A	0.9700
C1—H1	0.9800	C8—H8B	0.9700
C2—C3	1.548 (10)	C9—C10	1.513 (10)
C2—H2	0.9800	C9—H9	0.9800
C3—C4	1.501 (11)	C10—C11	1.534 (11)
C3—H3A	0.9700	C10—H10	0.9800
C3—H3B	0.9700	C11—C12	1.508 (11)
C4—C5	1.519 (10)	C11—H11A	0.9700
C4—H4A	0.9700	C11—H11B	0.9700
C4—H4B	0.9700	C12—H12A	0.9700
C5—C6	1.518 (12)	C12—H12B	0.9700
C12—C1—C2	115.5 (7)	C6—C7—C8	113.2 (7)
C12—C1—Br1	108.2 (5)	C6—C7—H7A	108.9
C2—C1—Br1	110.9 (6)	C8—C7—H7A	108.9
C12—C1—H1	107.3	C6—C7—H7B	108.9
C2—C1—H1	107.3	C8—C7—H7B	108.9
Br1—C1—H1	107.3	H7A—C7—H7B	107.8
C1—C2—C3	118.6 (7)	C7—C8—C9	115.6 (6)
C1—C2—Br2	109.7 (5)	C7—C8—H8A	108.4
C3—C2—Br2	108.8 (6)	C9—C8—H8A	108.4
C1—C2—H2	106.4	C7—C8—H8B	108.4
C3—C2—H2	106.4	C9—C8—H8B	108.4
Br2—C2—H2	106.4	H8A—C8—H8B	107.4
C4—C3—C2	118.6 (8)	C10—C9—C8	113.5 (7)
C4—C3—H3A	107.7	C10—C9—Br9	110.7 (5)
C2—C3—H3A	107.7	C8—C9—Br9	106.5 (5)
C4—C3—H3B	107.7	C10—C9—H9	108.7
C2—C3—H3B	107.7	C8—C9—H9	108.7
H3A—C3—H3B	107.1	Br9—C9—H9	108.7
C3—C4—C5	116.8 (7)	C9—C10—C11	115.6 (7)
C3—C4—H4A	108.1	C9—C10—Br10	110.5 (6)
C5—C4—H4A	108.1	C11—C10—Br10	109.4 (5)
C3—C4—H4B	108.1	C9—C10—H10	107.0
C5—C4—H4B	108.1	C11—C10—H10	107.0

supplementary materials

H4A—C4—H4B	107.3	Br10—C10—H10	107.0
C6—C5—C4	117.0 (7)	C12—C11—C10	114.2 (6)
C6—C5—Br5	109.5 (5)	C12—C11—H11A	108.7
C4—C5—Br5	108.9 (6)	C10—C11—H11A	108.7
C6—C5—H5	107.0	C12—C11—H11B	108.7
C4—C5—H5	107.0	C10—C11—H11B	108.7
Br5—C5—H5	107.0	H11A—C11—H11B	107.6
C7—C6—C5	114.4 (7)	C11—C12—C1	112.1 (6)
C7—C6—Br6	108.6 (5)	C11—C12—H12A	109.2
C5—C6—Br6	109.9 (6)	C1—C12—H12A	109.2
C7—C6—H6	107.9	C11—C12—H12B	109.2
C5—C6—H6	107.9	C1—C12—H12B	109.2
Br6—C6—H6	107.9	H12A—C12—H12B	107.9

Fig. 1

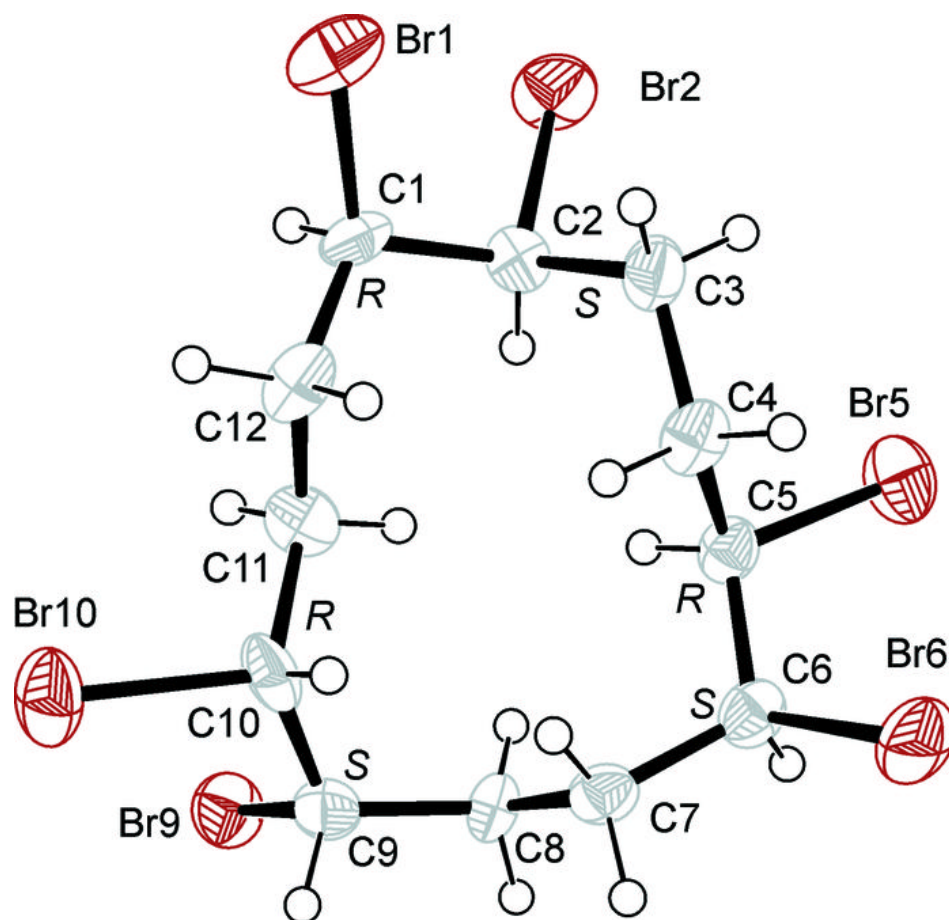


Fig. 2

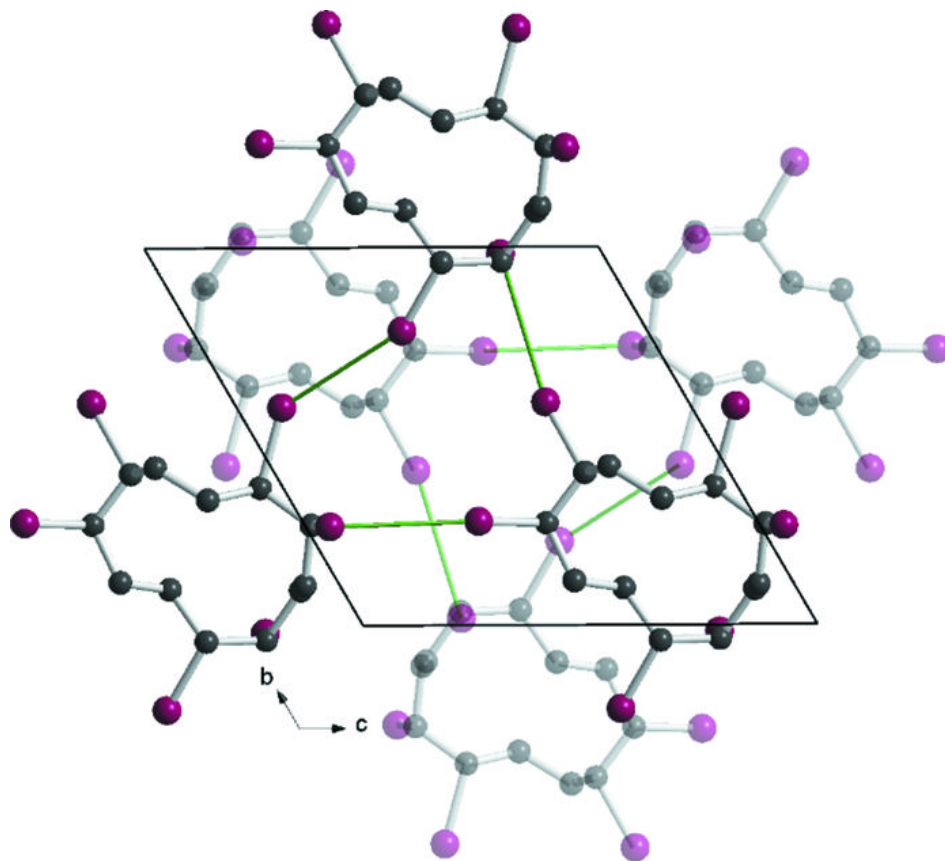


Fig. 3

