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# 1,2-Dimethyl-4,5-diphenylbenzene determined on a Bruker SMART X2S benchtop crystallographic system

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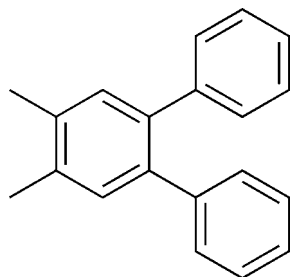
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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.046;  $wR$  factor = 0.166; data-to-parameter ratio = 14.9.

The title compound,  $\text{C}_{20}\text{H}_{18}$ , has two crystallographically independent molecules in the asymmetric unit. The phenyl substituents of molecule *A* are twisted away from the plane defined by the central benzene ring by  $131.8$  (2) and  $-52.7$  (3)°. The phenyl substituents of molecule *B* are twisted by  $-133.3$  (2) and  $50.9$  (3)°. Each molecule is stabilized by a pair of intramolecular  $\text{C}(\text{aryl}, sp^2)-\text{H}\cdots\pi$  interactions, as well as by several intermolecular  $\text{C}(\text{methyl}, sp^3)-\text{H}\cdots\pi$  interactions.

## Related literature

For potential applications and utility of the title compound as a synthetic intermediate, see: Kharasch *et al.* (1965); Horiuchi *et al.* (2008); Amine & Chen (2008); Eaton (2008); Peters & Friedrichsen (1995); Segura & Martín (1999). For the synthesis and related crystal structures, see: Maier *et al.*, (1969); Maeyama & Yonezawa (2003); Brown & Levy (1979).



## Experimental

### Crystal data

$\text{C}_{20}\text{H}_{18}$   
 $M_r = 258.34$   
 Triclinic,  $P\bar{1}$   
 $a = 9.3033$  (7) Å  
 $b = 10.7546$  (9) Å

$c = 16.3322$  (12) Å  
 $\alpha = 93.793$  (3)°  
 $\beta = 98.934$  (3)°  
 $\gamma = 106.549$  (2)°  
 $V = 1536.8$  (2) Å<sup>3</sup>

$Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.06$  mm<sup>-1</sup>

$T = 296$  K  
 $0.50 \times 0.50 \times 0.05$  mm

### Data collection

Bruker SMART X2S diffractometer  
 Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2007)  
 $T_{\text{min}} = 0.969$ ,  $T_{\text{max}} = 0.997$

15460 measured reflections  
 5450 independent reflections  
 3881 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.031$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.166$   
 $S = 0.87$   
 5450 reflections

365 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.32$  e Å<sup>-3</sup>

**Table 1**

C—H $\cdots\pi$  interaction geometry (Å, °).

| C—H $\cdots\pi$         | C—H  | H $\cdots\pi$ | C $\cdots\pi$ | C—H $\cdots\pi$ |
|-------------------------|------|---------------|---------------|-----------------|
| C7A—H7A2 $\cdots$ C5A   | 0.96 | 2.892         | 3.780         | 154.41          |
| C7A—H7A3 $\cdots$ C12A  | 0.96 | 2.920         | 3.824         | 157.38          |
| C8A—H8A1 $\cdots$ C16B  | 0.96 | 3.014         | 3.924         | 158.82          |
| C14A—H14A $\cdots$ C15A | 0.93 | 2.811         | 3.126         | 101.09          |
| C16A—H16A $\cdots$ C9A  | 0.93 | 2.881         | 3.167         | 99.24           |
| C7B—H7B1 $\cdots$ C11B  | 0.96 | 2.991         | 3.666         | 128.53          |
| C8B—H8B1 $\cdots$ C12B  | 0.96 | 2.943         | 3.809         | 150.67          |
| C14B—H14B $\cdots$ C15B | 0.93 | 2.784         | 3.129         | 103.11          |
| C16B—H16B $\cdots$ C9B  | 0.93 | 2.823         | 3.138         | 101.13          |

Data collection: *GIS* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE*; 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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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2245).

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**supplementary materials**

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## 1,2-Dimethyl-4,5-diphenylbenzene determined on a Bruker SMART X2S benchtop crystallographic system

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### Comment

*o*-Terphenyl has been utilized as a photochemical precursor to triphenylene (Kharasch *et al.*, (1965)), as part of a cathode active material layer in battery applications (Horiuchi *et al.*, (2008)), as a stabilizing additive in non-aqueous electrolytes (Amine & Chen, (2008)), and as a voltage stabilizer within the insulating layer of power cables (Eaton, (2008)). The title compound, an *o*-terphenyl derivative, is a potentially interesting synthetic intermediate leading to novel isobenzofuran (Peters & Friedrichsen, (1995)) and/or quinodimethane (Segura & Martín, (1999)) species and was first prepared in 1969 (Maier *et al.*, (1969)). The synthesis of *o*-terphenyl derivatives was recently reviewed (Maeyama & Yonezawa, (2003)). A crystal structure of unsubstituted *o*-terphenyl has been published (Brown & Levy, (1979)).

The asymmetric unit of (I) contains two molecules (Fig. 1). The relative rotations of the phenyl substituents at C4 and C5 are influenced by a pair of stabilizing intramolecular  $C(\text{aryl}, sp^2)\text{-H}\cdots\pi$  interactions involving one *ortho* hydrogen atom on each phenyl substituent and one  $\pi$  bond associated with the *ipso* carbon of the other phenyl substituent (Fig. 2). The atoms of closest contact ( $H_{ortho}\text{-}C_{ipso}$ ) are separated by 2.784 Å (Table 1). An MM2 force field minimization for a single molecule in a vacuum places the same two atoms 2.80 Å apart indicating that the molecular conformation within the crystal lattice is little influenced by packing forces. There are, *e.g.*, no significant  $\pi\text{-}\pi$  interactions in the crystal structure.

Weaker intermolecular  $\text{CH}\cdots\pi$  interactions involving both methyl substituents and  $\pi$  bonds on adjacent molecules help to define the spacing between molecules in the crystal structure (Table 1, Figs. 3–4). There are a total of five unique intermolecular  $\text{CH}\cdots\pi$  interactions. Within the asymmetric unit, there is one intermolecular  $\text{CH}\cdots\pi$  interaction ( $H8A1_{methyl}\cdots C16B_{ortho}$ , 3.014 Å) involving one molecule A and one molecule B (A—B). Additionally, each molecule A and molecule B within the asymmetric unit has two unique  $\text{CH}\cdots\pi$  interactions involving other molecules of the same type (2 A—A; 2 B—B). The two type A—A intermolecular  $\text{CH}\cdots\pi$  interactions can be described as  $H7A2_{methyl}\text{-}C5A_{central\ ring}$  (2.892 Å) and  $H7A3_{methyl}\text{-}C12A_{para}$  (2.920 Å). The two type B—B intermolecular  $\text{CH}\cdots\pi$  interactions can be described as  $H7B1_{methyl}\text{-}C11B_{meta}$  (2.991 Å) and  $H8B1_{methyl}\text{-}C12B_{para}$  (2.943 Å). Figure 3 illustrates the one unique type A—B intermolecular  $\text{CH}\cdots\pi$  interaction as well as one type A—A and one type B—B  $\text{CH}\cdots\pi$  interaction.

### Experimental

The title compound was prepared as illustrated in Fig. 5. An oven-dried glass pressure vessel containing a magnetic stir bar was charged with palladium(II) acetate (0.034 g, 0.152 mmol), 1,2-dibromo-4,5-dimethylbenzene (2 g, 7.58 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.124 g, 0.303 mmol), phenylboronic acid (2.77 g, 22.7 mmol) and powdered, anhydrous potassium phosphate (11.26 g, 53.0 mmol). Dry THF (20 ml) was added and  $N_2$  gas was bubbled through the resulting mixture for 15 min. The glass pressure vessel was sealed with a Teflon cap and heated at 75 °C for 20 h with stirring. The reaction mixture was allowed to cool to room temperature after which the mixture was diluted with diethyl ether (30 ml) and washed with water three times. The organic layer was dried over magnesium sulfate and concentrated at

## supplementary materials

reduced pressure. The crude product was purified by flash column chromatography on silica gel using hexane-chloroform (80/20 v/v) as eluent. The title compound, 1,2-dimethyl-4,5-diphenylbenzene, was obtained in 76% isolated yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.35 (s, 6H), 7.11–7.21 (m, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  19.6 (CH<sub>3</sub>), 126.4 (CH), 128.0 (CH), 130.1 (CH), 132.1 (CH), 136.0 (C), 138.2 (C), 141.7 (C). An X-ray grade crystal was obtained by slow evaporation of a dichloromethane solution.

### Figures

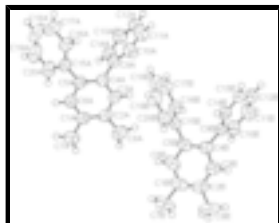


Fig. 1. The molecular structure showing the crystallographic labelling scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

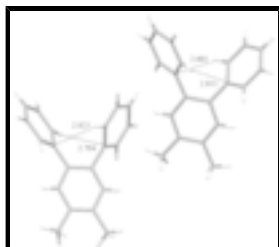


Fig. 2. Perspective view of the title molecule showing the two pairs of stabilizing intramolecular  $C(\text{aryl}, sp^2)\text{-H}\cdots\pi$  interactions involving one *ortho* hydrogen atom on each phenyl substituent and one  $\pi$  bond associated with the *ipso* carbon of the other phenyl substituent.

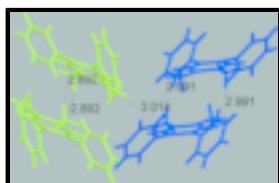


Fig. 3. Perspective view of the title molecule showing stabilizing intermolecular  $C(\text{methyl}, sp^3)\text{-H}\cdots\pi$  interactions involving methyl substituents and  $\pi$  bonds associated with carbons of neighboring phenyl substituents. Molecule A is colored in green and molecule B is colored in blue. One unique type A—B as well as one type A—A and one type B—B  $\text{CH}\cdots\pi$  interaction is shown.



Fig. 4. Perspective view of long range packing in the crystal structure.

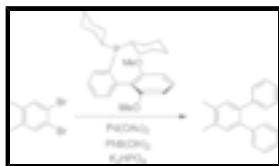


Fig. 5. Synthesis of the title compound, 1,2-dimethyl-4,5-diphenylbenzene.

### 1,2-Dimethyl-4,5-diphenylbenzene

#### Crystal data

$\text{C}_{20}\text{H}_{18}$

$M_r = 258.34$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$Z = 4$

$F_{000} = 552$

$D_x = 1.117 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

$a = 9.3033$  (7) Å  
 $b = 10.7546$  (9) Å  
 $c = 16.3322$  (12) Å  
 $\alpha = 93.793$  (3)°  
 $\beta = 98.934$  (3)°  
 $\gamma = 106.549$  (2)°  
 $V = 1536.8$  (2) Å<sup>3</sup>

Cell parameters from 5281 reflections

$\theta = 1.3$ – $25.2$ °  
 $\mu = 0.06$  mm<sup>-1</sup>  
 $T = 296$  K  
 Plate, clear colourless  
 $0.50 \times 0.50 \times 0.05$  mm

### Data collection

Bruker SMART X2S  
 diffractometer

5450 independent reflections

Radiation source: micro-focus sealed tube

3881 reflections with  $I > 2\sigma(I)$

Monochromator: doubly curved silicon crystal

$R_{\text{int}} = 0.031$

$T = 296$  K

$\theta_{\text{max}} = 25.2$ °

$\omega$  scans

$\theta_{\text{min}} = 1.3$ °

Absorption correction: multi-scan  
 (SADABS; Bruker, 2007)

$h = -11 \rightarrow 11$

$T_{\text{min}} = 0.969$ ,  $T_{\text{max}} = 0.997$

$k = -12 \rightarrow 12$

15460 measured reflections

$l = -19 \rightarrow 19$

### Refinement

Refinement on  $F^2$

Secondary atom site location: difference Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.046$

H-atom parameters constrained

$wR(F^2) = 0.166$

$$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.5P]$$

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

$S = 0.87$

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

5450 reflections

$\Delta\rho_{\text{max}} = 0.25$  e Å<sup>-3</sup>

365 parameters

$\Delta\rho_{\text{min}} = -0.32$  e Å<sup>-3</sup>

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.

## supplementary materials

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

|      | <i>x</i>   | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|------------|--------------|--------------|----------------------------------|
| C1A  | 0.6791 (2) | 1.08007 (18) | 0.97275 (13) | 0.0567 (5)                       |
| C2A  | 0.6269 (2) | 1.01769 (19) | 0.89127 (13) | 0.0602 (5)                       |
| C3A  | 0.6488 (2) | 0.89721 (19) | 0.87258 (12) | 0.0595 (5)                       |
| H3A  | 0.6152     | 0.8566       | 0.8181       | 0.071*                           |
| C4A  | 0.7186 (2) | 0.83381 (17) | 0.93120 (11) | 0.0527 (4)                       |
| C5A  | 0.7660 (2) | 0.89453 (17) | 1.01371 (11) | 0.0507 (4)                       |
| C6A  | 0.7463 (2) | 1.01665 (18) | 1.03178 (12) | 0.0555 (5)                       |
| H6A  | 0.7800     | 1.0577       | 1.0862       | 0.067*                           |
| C7A  | 0.6614 (3) | 1.2118 (2)   | 0.99848 (16) | 0.0750 (6)                       |
| H7A1 | 0.6947     | 1.2338       | 1.0577       | 0.112*                           |
| H7A2 | 0.5562     | 1.2084       | 0.9840       | 0.112*                           |
| H7A3 | 0.7221     | 1.2768       | 0.9701       | 0.112*                           |
| C8A  | 0.5478 (3) | 1.0778 (2)   | 0.82374 (16) | 0.0822 (7)                       |
| H8A1 | 0.5130     | 1.0175       | 0.7737       | 0.123*                           |
| H8A2 | 0.6180     | 1.1570       | 0.8129       | 0.123*                           |
| H8A3 | 0.4623     | 1.0970       | 0.8418       | 0.123*                           |
| C9A  | 0.7423 (2) | 0.70697 (18) | 0.90456 (11) | 0.0547 (5)                       |
| C10A | 0.6240 (3) | 0.6064 (2)   | 0.85743 (14) | 0.0714 (6)                       |
| H10A | 0.5287     | 0.6184       | 0.8425       | 0.086*                           |
| C11A | 0.6455 (3) | 0.4888 (2)   | 0.83227 (16) | 0.0858 (7)                       |
| H11A | 0.5645     | 0.4221       | 0.8013       | 0.103*                           |
| C12A | 0.7859 (3) | 0.4703 (2)   | 0.85288 (15) | 0.0788 (7)                       |
| H12A | 0.8006     | 0.3915       | 0.8352       | 0.095*                           |
| C13A | 0.9046 (3) | 0.5682 (2)   | 0.89956 (14) | 0.0703 (6)                       |
| H13A | 0.9996     | 0.5554       | 0.9142       | 0.084*                           |
| C14A | 0.8836 (2) | 0.6858 (2)   | 0.92493 (12) | 0.0610 (5)                       |
| H14A | 0.9652     | 0.7519       | 0.9561       | 0.073*                           |
| C15A | 0.8283 (2) | 0.83145 (19) | 1.08364 (11) | 0.0543 (5)                       |
| C16A | 0.7485 (3) | 0.7074 (2)   | 1.09899 (14) | 0.0686 (6)                       |
| H16A | 0.6561     | 0.6625       | 1.0646       | 0.082*                           |
| C17A | 0.8049 (3) | 0.6501 (3)   | 1.16471 (17) | 0.0899 (8)                       |
| H17A | 0.7512     | 0.5667       | 1.1743       | 0.108*                           |
| C18A | 0.9418 (4) | 0.7172 (4)   | 1.21634 (16) | 0.0999 (10)                      |
| H18A | 0.9797     | 0.6791       | 1.2610       | 0.120*                           |
| C19A | 1.0214 (3) | 0.8393 (3)   | 1.20186 (15) | 0.0925 (8)                       |
| H19A | 1.1137     | 0.8837       | 1.2365       | 0.111*                           |
| C20A | 0.9653 (3) | 0.8970 (2)   | 1.13604 (13) | 0.0712 (6)                       |
| H20A | 1.0197     | 0.9803       | 1.1269       | 0.085*                           |
| C1B  | 0.2893 (2) | 1.2264 (2)   | 0.56098 (18) | 0.0736 (6)                       |
| C2B  | 0.3057 (3) | 1.2009 (2)   | 0.47854 (18) | 0.0767 (7)                       |
| C3B  | 0.2838 (2) | 1.0722 (2)   | 0.44640 (15) | 0.0670 (6)                       |
| H3B  | 0.2929     | 1.0554       | 0.3912       | 0.080*                           |
| C4B  | 0.2488 (2) | 0.96758 (17) | 0.49331 (12) | 0.0534 (4)                       |
| C5B  | 0.2360 (2) | 0.99418 (17) | 0.57707 (13) | 0.0549 (5)                       |
| C6B  | 0.2545 (2) | 1.12292 (19) | 0.60791 (15) | 0.0670 (6)                       |

|      |            |              |              |             |
|------|------------|--------------|--------------|-------------|
| H6B  | 0.2429     | 1.1400       | 0.6627       | 0.080*      |
| C7B  | 0.3143 (3) | 1.3648 (2)   | 0.6001 (2)   | 0.1030 (10) |
| H7B1 | 0.4207     | 1.4124       | 0.6084       | 0.155*      |
| H7B2 | 0.2808     | 1.3622       | 0.6528       | 0.155*      |
| H7B3 | 0.2570     | 1.4073       | 0.5637       | 0.155*      |
| C8B  | 0.3495 (4) | 1.3080 (3)   | 0.4225 (2)   | 0.1211 (12) |
| H8B1 | 0.2807     | 1.3598       | 0.4215       | 0.182*      |
| H8B2 | 0.3436     | 1.2692       | 0.3670       | 0.182*      |
| H8B3 | 0.4517     | 1.3624       | 0.4437       | 0.182*      |
| C9B  | 0.2263 (2) | 0.83396 (17) | 0.45237 (11) | 0.0508 (4)  |
| C10B | 0.3309 (2) | 0.8121 (2)   | 0.40513 (13) | 0.0646 (5)  |
| H10B | 0.4156     | 0.8809       | 0.4008       | 0.077*      |
| C11B | 0.3109 (3) | 0.6904 (3)   | 0.36479 (15) | 0.0773 (6)  |
| H11B | 0.3815     | 0.6779       | 0.3331       | 0.093*      |
| C12B | 0.1874 (3) | 0.5871 (2)   | 0.37099 (14) | 0.0756 (7)  |
| H12B | 0.1748     | 0.5049       | 0.3438       | 0.091*      |
| C13B | 0.0818 (3) | 0.6059 (2)   | 0.41787 (13) | 0.0683 (6)  |
| H13B | -0.0017    | 0.5363       | 0.4225       | 0.082*      |
| C14B | 0.1012 (2) | 0.72904 (18) | 0.45784 (12) | 0.0586 (5)  |
| H14B | 0.0295     | 0.7416       | 0.4887       | 0.070*      |
| C15B | 0.2085 (2) | 0.89099 (18) | 0.63430 (12) | 0.0569 (5)  |
| C16B | 0.2983 (3) | 0.8077 (2)   | 0.64348 (13) | 0.0652 (5)  |
| H16B | 0.3765     | 0.8157       | 0.6131       | 0.078*      |
| C17B | 0.2728 (3) | 0.7128 (2)   | 0.69743 (15) | 0.0832 (7)  |
| H17B | 0.3336     | 0.6575       | 0.7028       | 0.100*      |
| C18B | 0.1585 (4) | 0.7000 (3)   | 0.74299 (16) | 0.0958 (9)  |
| H18B | 0.1418     | 0.6360       | 0.7790       | 0.115*      |
| C19B | 0.0694 (4) | 0.7813 (3)   | 0.73542 (16) | 0.0950 (9)  |
| H19B | -0.0081    | 0.7725       | 0.7663       | 0.114*      |
| C20B | 0.0939 (3) | 0.8768 (2)   | 0.68189 (14) | 0.0762 (6)  |
| H20B | 0.0330     | 0.9321       | 0.6776       | 0.091*      |

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

|      | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$     | $U^{23}$     |
|------|-------------|-------------|-------------|-------------|--------------|--------------|
| C1A  | 0.0489 (10) | 0.0504 (10) | 0.0671 (12) | 0.0102 (8)  | 0.0060 (9)   | 0.0126 (9)   |
| C2A  | 0.0538 (11) | 0.0589 (11) | 0.0632 (12) | 0.0116 (9)  | 0.0017 (9)   | 0.0185 (9)   |
| C3A  | 0.0609 (12) | 0.0608 (12) | 0.0490 (10) | 0.0114 (9)  | -0.0011 (9)  | 0.0083 (9)   |
| C4A  | 0.0492 (10) | 0.0530 (10) | 0.0511 (10) | 0.0094 (8)  | 0.0043 (8)   | 0.0095 (8)   |
| C5A  | 0.0452 (9)  | 0.0532 (10) | 0.0506 (10) | 0.0110 (8)  | 0.0045 (8)   | 0.0102 (8)   |
| C6A  | 0.0526 (10) | 0.0544 (11) | 0.0526 (10) | 0.0096 (8)  | 0.0024 (8)   | 0.0044 (8)   |
| C7A  | 0.0728 (14) | 0.0597 (13) | 0.0910 (16) | 0.0206 (11) | 0.0075 (12)  | 0.0120 (11)  |
| C8A  | 0.0858 (16) | 0.0770 (15) | 0.0801 (15) | 0.0267 (13) | -0.0071 (13) | 0.0244 (12)  |
| C9A  | 0.0594 (11) | 0.0552 (11) | 0.0475 (10) | 0.0132 (9)  | 0.0098 (8)   | 0.0100 (8)   |
| C10A | 0.0699 (13) | 0.0681 (13) | 0.0691 (13) | 0.0176 (11) | 0.0023 (11)  | -0.0036 (11) |
| C11A | 0.0900 (18) | 0.0720 (15) | 0.0832 (16) | 0.0149 (13) | 0.0075 (13)  | -0.0150 (12) |
| C12A | 0.1027 (19) | 0.0640 (14) | 0.0766 (15) | 0.0291 (13) | 0.0306 (14)  | 0.0039 (11)  |
| C13A | 0.0769 (14) | 0.0765 (14) | 0.0696 (13) | 0.0319 (12) | 0.0289 (12)  | 0.0176 (11)  |

## supplementary materials

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|      |             |             |             |             |              |              |
|------|-------------|-------------|-------------|-------------|--------------|--------------|
| C14A | 0.0615 (12) | 0.0629 (12) | 0.0588 (11) | 0.0156 (9)  | 0.0157 (9)   | 0.0114 (9)   |
| C15A | 0.0542 (11) | 0.0673 (12) | 0.0469 (10) | 0.0264 (9)  | 0.0088 (8)   | 0.0091 (9)   |
| C16A | 0.0686 (13) | 0.0759 (14) | 0.0676 (13) | 0.0271 (11) | 0.0139 (10)  | 0.0252 (11)  |
| C17A | 0.101 (2)   | 0.107 (2)   | 0.0881 (18) | 0.0555 (17) | 0.0322 (16)  | 0.0513 (16)  |
| C18A | 0.113 (2)   | 0.161 (3)   | 0.0649 (15) | 0.090 (2)   | 0.0245 (16)  | 0.0473 (18)  |
| C19A | 0.0822 (17) | 0.145 (3)   | 0.0585 (14) | 0.0564 (18) | -0.0049 (12) | 0.0087 (16)  |
| C20A | 0.0644 (13) | 0.0904 (16) | 0.0576 (12) | 0.0285 (12) | -0.0011 (10) | 0.0046 (11)  |
| C1B  | 0.0521 (12) | 0.0495 (11) | 0.119 (2)   | 0.0181 (9)  | 0.0116 (12)  | 0.0077 (12)  |
| C2B  | 0.0601 (13) | 0.0559 (12) | 0.115 (2)   | 0.0187 (10) | 0.0071 (13)  | 0.0307 (13)  |
| C3B  | 0.0625 (12) | 0.0623 (13) | 0.0765 (14) | 0.0185 (10) | 0.0085 (10)  | 0.0205 (10)  |
| C4B  | 0.0445 (10) | 0.0502 (10) | 0.0649 (12) | 0.0148 (8)  | 0.0052 (8)   | 0.0111 (9)   |
| C5B  | 0.0465 (10) | 0.0493 (10) | 0.0678 (12) | 0.0137 (8)  | 0.0096 (9)   | 0.0032 (9)   |
| C6B  | 0.0566 (12) | 0.0540 (12) | 0.0895 (15) | 0.0153 (9)  | 0.0173 (11)  | -0.0022 (11) |
| C7B  | 0.0788 (16) | 0.0497 (13) | 0.178 (3)   | 0.0202 (12) | 0.0189 (18)  | -0.0019 (15) |
| C8B  | 0.133 (3)   | 0.0742 (17) | 0.164 (3)   | 0.0323 (17) | 0.028 (2)    | 0.0610 (19)  |
| C9B  | 0.0499 (10) | 0.0542 (10) | 0.0473 (10) | 0.0179 (8)  | 0.0008 (8)   | 0.0089 (8)   |
| C10B | 0.0574 (12) | 0.0755 (14) | 0.0597 (12) | 0.0216 (10) | 0.0056 (9)   | 0.0042 (10)  |
| C11B | 0.0712 (15) | 0.0945 (17) | 0.0694 (14) | 0.0399 (14) | 0.0012 (11)  | -0.0092 (12) |
| C12B | 0.0977 (18) | 0.0681 (14) | 0.0625 (13) | 0.0447 (14) | -0.0140 (12) | -0.0042 (11) |
| C13B | 0.0821 (15) | 0.0544 (12) | 0.0576 (12) | 0.0139 (10) | -0.0080 (11) | 0.0087 (9)   |
| C14B | 0.0613 (12) | 0.0579 (11) | 0.0529 (11) | 0.0146 (9)  | 0.0049 (9)   | 0.0074 (9)   |
| C15B | 0.0603 (11) | 0.0493 (10) | 0.0524 (10) | 0.0073 (9)  | 0.0053 (9)   | -0.0031 (8)  |
| C16B | 0.0709 (13) | 0.0606 (12) | 0.0592 (12) | 0.0185 (10) | 0.0007 (10)  | 0.0040 (10)  |
| C17B | 0.109 (2)   | 0.0675 (14) | 0.0639 (14) | 0.0247 (13) | -0.0077 (14) | 0.0088 (11)  |
| C18B | 0.134 (3)   | 0.0789 (17) | 0.0597 (14) | 0.0105 (17) | 0.0105 (16)  | 0.0154 (12)  |
| C19B | 0.115 (2)   | 0.0932 (19) | 0.0661 (15) | 0.0049 (17) | 0.0355 (15)  | 0.0097 (14)  |
| C20B | 0.0830 (15) | 0.0723 (14) | 0.0707 (14) | 0.0155 (12) | 0.0243 (12)  | -0.0002 (11) |

### *Geometric parameters (Å, °)*

|          |           |          |           |
|----------|-----------|----------|-----------|
| C1A—C6A  | 1.389 (3) | C1B—C6B  | 1.384 (3) |
| C1A—C2A  | 1.397 (3) | C1B—C2B  | 1.397 (4) |
| C1A—C7A  | 1.512 (3) | C1B—C7B  | 1.519 (3) |
| C2A—C3A  | 1.390 (3) | C2B—C3B  | 1.394 (3) |
| C2A—C8A  | 1.513 (3) | C2B—C8B  | 1.522 (3) |
| C3A—C4A  | 1.396 (3) | C3B—C4B  | 1.394 (3) |
| C3A—H3A  | 0.9300    | C3B—H3B  | 0.9300    |
| C4A—C5A  | 1.404 (3) | C4B—C5B  | 1.409 (3) |
| C4A—C9A  | 1.491 (3) | C4B—C9B  | 1.488 (3) |
| C5A—C6A  | 1.396 (3) | C5B—C6B  | 1.395 (3) |
| C5A—C15A | 1.491 (3) | C5B—C15B | 1.490 (3) |
| C6A—H6A  | 0.9300    | C6B—H6B  | 0.9300    |
| C7A—H7A1 | 0.9600    | C7B—H7B1 | 0.9600    |
| C7A—H7A2 | 0.9600    | C7B—H7B2 | 0.9600    |
| C7A—H7A3 | 0.9600    | C7B—H7B3 | 0.9600    |
| C8A—H8A1 | 0.9600    | C8B—H8B1 | 0.9600    |
| C8A—H8A2 | 0.9600    | C8B—H8B2 | 0.9600    |
| C8A—H8A3 | 0.9600    | C8B—H8B3 | 0.9600    |
| C9A—C10A | 1.386 (3) | C9B—C14B | 1.391 (3) |



|               |             |               |             |
|---------------|-------------|---------------|-------------|
| C9A—C14A      | 1.391 (3)   | C9B—C10B      | 1.391 (3)   |
| C10A—C11A     | 1.382 (3)   | C10B—C11B     | 1.375 (3)   |
| C10A—H10A     | 0.9300      | C10B—H10B     | 0.9300      |
| C11A—C12A     | 1.371 (4)   | C11B—C12B     | 1.374 (3)   |
| C11A—H11A     | 0.9300      | C11B—H11B     | 0.9300      |
| C12A—C13A     | 1.371 (3)   | C12B—C13B     | 1.385 (3)   |
| C12A—H12A     | 0.9300      | C12B—H12B     | 0.9300      |
| C13A—C14A     | 1.381 (3)   | C13B—C14B     | 1.388 (3)   |
| C13A—H13A     | 0.9300      | C13B—H13B     | 0.9300      |
| C14A—H14A     | 0.9300      | C14B—H14B     | 0.9300      |
| C15A—C20A     | 1.386 (3)   | C15B—C16B     | 1.389 (3)   |
| C15A—C16A     | 1.390 (3)   | C15B—C20B     | 1.394 (3)   |
| C16A—C17A     | 1.380 (3)   | C16B—C17B     | 1.386 (3)   |
| C16A—H16A     | 0.9300      | C16B—H16B     | 0.9300      |
| C17A—C18A     | 1.384 (4)   | C17B—C18B     | 1.371 (4)   |
| C17A—H17A     | 0.9300      | C17B—H17B     | 0.9300      |
| C18A—C19A     | 1.367 (4)   | C18B—C19B     | 1.364 (4)   |
| C18A—H18A     | 0.9300      | C18B—H18B     | 0.9300      |
| C19A—C20A     | 1.383 (3)   | C19B—C20B     | 1.385 (3)   |
| C19A—H19A     | 0.9300      | C19B—H19B     | 0.9300      |
| C20A—H20A     | 0.9300      | C20B—H20B     | 0.9300      |
| C6A—C1A—C2A   | 118.28 (18) | C6B—C1B—C2B   | 118.5 (2)   |
| C6A—C1A—C7A   | 119.56 (18) | C6B—C1B—C7B   | 120.1 (3)   |
| C2A—C1A—C7A   | 122.15 (18) | C2B—C1B—C7B   | 121.3 (2)   |
| C3A—C2A—C1A   | 118.55 (17) | C3B—C2B—C1B   | 118.8 (2)   |
| C3A—C2A—C8A   | 119.69 (19) | C3B—C2B—C8B   | 118.4 (3)   |
| C1A—C2A—C8A   | 121.76 (19) | C1B—C2B—C8B   | 122.8 (2)   |
| C2A—C3A—C4A   | 123.52 (18) | C2B—C3B—C4B   | 123.0 (2)   |
| C2A—C3A—H3A   | 118.2       | C2B—C3B—H3B   | 118.5       |
| C4A—C3A—H3A   | 118.2       | C4B—C3B—H3B   | 118.5       |
| C3A—C4A—C5A   | 117.80 (17) | C3B—C4B—C5B   | 118.06 (18) |
| C3A—C4A—C9A   | 119.66 (17) | C3B—C4B—C9B   | 118.42 (18) |
| C5A—C4A—C9A   | 122.53 (16) | C5B—C4B—C9B   | 123.52 (16) |
| C6A—C5A—C4A   | 118.40 (16) | C6B—C5B—C4B   | 118.42 (18) |
| C6A—C5A—C15A  | 118.50 (16) | C6B—C5B—C15B  | 119.01 (18) |
| C4A—C5A—C15A  | 123.02 (16) | C4B—C5B—C15B  | 122.54 (16) |
| C1A—C6A—C5A   | 123.39 (18) | C1B—C6B—C5B   | 123.2 (2)   |
| C1A—C6A—H6A   | 118.3       | C1B—C6B—H6B   | 118.4       |
| C5A—C6A—H6A   | 118.3       | C5B—C6B—H6B   | 118.4       |
| C1A—C7A—H7A1  | 109.5       | C1B—C7B—H7B1  | 109.5       |
| C1A—C7A—H7A2  | 109.5       | C1B—C7B—H7B2  | 109.5       |
| H7A1—C7A—H7A2 | 109.5       | H7B1—C7B—H7B2 | 109.5       |
| C1A—C7A—H7A3  | 109.5       | C1B—C7B—H7B3  | 109.5       |
| H7A1—C7A—H7A3 | 109.5       | H7B1—C7B—H7B3 | 109.5       |
| H7A2—C7A—H7A3 | 109.5       | H7B2—C7B—H7B3 | 109.5       |
| C2A—C8A—H8A1  | 109.5       | C2B—C8B—H8B1  | 109.5       |
| C2A—C8A—H8A2  | 109.5       | C2B—C8B—H8B2  | 109.5       |
| H8A1—C8A—H8A2 | 109.5       | H8B1—C8B—H8B2 | 109.5       |
| C2A—C8A—H8A3  | 109.5       | C2B—C8B—H8B3  | 109.5       |

## supplementary materials

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|                  |              |                  |              |
|------------------|--------------|------------------|--------------|
| H8A1—C8A—H8A3    | 109.5        | H8B1—C8B—H8B3    | 109.5        |
| H8A2—C8A—H8A3    | 109.5        | H8B2—C8B—H8B3    | 109.5        |
| C10A—C9A—C14A    | 117.72 (19)  | C14B—C9B—C10B    | 118.09 (18)  |
| C10A—C9A—C4A     | 120.83 (18)  | C14B—C9B—C4B     | 122.16 (17)  |
| C14A—C9A—C4A     | 121.45 (17)  | C10B—C9B—C4B     | 119.72 (17)  |
| C11A—C10A—C9A    | 121.1 (2)    | C11B—C10B—C9B    | 121.0 (2)    |
| C11A—C10A—H10A   | 119.5        | C11B—C10B—H10B   | 119.5        |
| C9A—C10A—H10A    | 119.5        | C9B—C10B—H10B    | 119.5        |
| C12A—C11A—C10A   | 120.2 (2)    | C10B—C11B—C12B   | 120.5 (2)    |
| C12A—C11A—H11A   | 119.9        | C10B—C11B—H11B   | 119.7        |
| C10A—C11A—H11A   | 119.9        | C12B—C11B—H11B   | 119.7        |
| C13A—C12A—C11A   | 119.8 (2)    | C11B—C12B—C13B   | 119.7 (2)    |
| C13A—C12A—H12A   | 120.1        | C11B—C12B—H12B   | 120.1        |
| C11A—C12A—H12A   | 120.1        | C13B—C12B—H12B   | 120.1        |
| C12A—C13A—C14A   | 120.2 (2)    | C12B—C13B—C14B   | 119.7 (2)    |
| C12A—C13A—H13A   | 119.9        | C12B—C13B—H13B   | 120.1        |
| C14A—C13A—H13A   | 119.9        | C14B—C13B—H13B   | 120.1        |
| C13A—C14A—C9A    | 121.0 (2)    | C13B—C14B—C9B    | 120.9 (2)    |
| C13A—C14A—H14A   | 119.5        | C13B—C14B—H14B   | 119.5        |
| C9A—C14A—H14A    | 119.5        | C9B—C14B—H14B    | 119.5        |
| C20A—C15A—C16A   | 118.71 (19)  | C16B—C15B—C20B   | 117.8 (2)    |
| C20A—C15A—C5A    | 120.54 (18)  | C16B—C15B—C5B    | 121.12 (18)  |
| C16A—C15A—C5A    | 120.72 (18)  | C20B—C15B—C5B    | 121.11 (19)  |
| C17A—C16A—C15A   | 120.7 (2)    | C17B—C16B—C15B   | 120.7 (2)    |
| C17A—C16A—H16A   | 119.7        | C17B—C16B—H16B   | 119.6        |
| C15A—C16A—H16A   | 119.7        | C15B—C16B—H16B   | 119.6        |
| C16A—C17A—C18A   | 119.7 (3)    | C18B—C17B—C16B   | 120.4 (3)    |
| C16A—C17A—H17A   | 120.1        | C18B—C17B—H17B   | 119.8        |
| C18A—C17A—H17A   | 120.1        | C16B—C17B—H17B   | 119.8        |
| C19A—C18A—C17A   | 120.1 (2)    | C19B—C18B—C17B   | 119.9 (3)    |
| C19A—C18A—H18A   | 119.9        | C19B—C18B—H18B   | 120.0        |
| C17A—C18A—H18A   | 119.9        | C17B—C18B—H18B   | 120.0        |
| C18A—C19A—C20A   | 120.3 (3)    | C18B—C19B—C20B   | 120.3 (3)    |
| C18A—C19A—H19A   | 119.8        | C18B—C19B—H19B   | 119.8        |
| C20A—C19A—H19A   | 119.8        | C20B—C19B—H19B   | 119.8        |
| C19A—C20A—C15A   | 120.4 (2)    | C19B—C20B—C15B   | 120.9 (2)    |
| C19A—C20A—H20A   | 119.8        | C19B—C20B—H20B   | 119.6        |
| C15A—C20A—H20A   | 119.8        | C15B—C20B—H20B   | 119.6        |
| C6A—C1A—C2A—C3A  | -1.9 (3)     | C6B—C1B—C2B—C3B  | 1.2 (3)      |
| C7A—C1A—C2A—C3A  | 179.46 (18)  | C7B—C1B—C2B—C3B  | 179.0 (2)    |
| C6A—C1A—C2A—C8A  | 178.02 (19)  | C6B—C1B—C2B—C8B  | -177.7 (2)   |
| C7A—C1A—C2A—C8A  | -0.6 (3)     | C7B—C1B—C2B—C8B  | 0.1 (4)      |
| C1A—C2A—C3A—C4A  | 0.9 (3)      | C1B—C2B—C3B—C4B  | -1.2 (3)     |
| C8A—C2A—C3A—C4A  | -179.04 (19) | C8B—C2B—C3B—C4B  | 177.7 (2)    |
| C2A—C3A—C4A—C5A  | 1.3 (3)      | C2B—C3B—C4B—C5B  | -0.3 (3)     |
| C2A—C3A—C4A—C9A  | -177.72 (18) | C2B—C3B—C4B—C9B  | 179.45 (18)  |
| C3A—C4A—C5A—C6A  | -2.5 (3)     | C3B—C4B—C5B—C6B  | 1.9 (3)      |
| C9A—C4A—C5A—C6A  | 176.55 (16)  | C9B—C4B—C5B—C6B  | -177.88 (17) |
| C3A—C4A—C5A—C15A | 174.07 (17)  | C3B—C4B—C5B—C15B | -176.16 (18) |

|                     |              |                     |              |
|---------------------|--------------|---------------------|--------------|
| C9A—C4A—C5A—C15A    | -6.9 (3)     | C9B—C4B—C5B—C15B    | 4.1 (3)      |
| C2A—C1A—C6A—C5A     | 0.7 (3)      | C2B—C1B—C6B—C5B     | 0.5 (3)      |
| C7A—C1A—C6A—C5A     | 179.40 (18)  | C7B—C1B—C6B—C5B     | -177.4 (2)   |
| C4A—C5A—C6A—C1A     | 1.5 (3)      | C4B—C5B—C6B—C1B     | -2.0 (3)     |
| C15A—C5A—C6A—C1A    | -175.20 (17) | C15B—C5B—C6B—C1B    | 176.11 (19)  |
| C3A—C4A—C9A—C10A    | -49.2 (3)    | C3B—C4B—C9B—C14B    | -131.5 (2)   |
| C5A—C4A—C9A—C10A    | 131.8 (2)    | C5B—C4B—C9B—C14B    | 48.3 (3)     |
| C3A—C4A—C9A—C14A    | 129.9 (2)    | C3B—C4B—C9B—C10B    | 46.9 (2)     |
| C5A—C4A—C9A—C14A    | -49.1 (3)    | C5B—C4B—C9B—C10B    | -133.3 (2)   |
| C14A—C9A—C10A—C11A  | 0.6 (3)      | C14B—C9B—C10B—C11B  | 0.2 (3)      |
| C4A—C9A—C10A—C11A   | 179.7 (2)    | C4B—C9B—C10B—C11B   | -178.27 (18) |
| C9A—C10A—C11A—C12A  | -0.8 (4)     | C9B—C10B—C11B—C12B  | -0.6 (3)     |
| C10A—C11A—C12A—C13A | 0.9 (4)      | C10B—C11B—C12B—C13B | 0.4 (3)      |
| C11A—C12A—C13A—C14A | -0.8 (3)     | C11B—C12B—C13B—C14B | 0.3 (3)      |
| C12A—C13A—C14A—C9A  | 0.6 (3)      | C12B—C13B—C14B—C9B  | -0.8 (3)     |
| C10A—C9A—C14A—C13A  | -0.5 (3)     | C10B—C9B—C14B—C13B  | 0.5 (3)      |
| C4A—C9A—C14A—C13A   | -179.64 (17) | C4B—C9B—C14B—C13B   | 178.92 (17)  |
| C6A—C5A—C15A—C20A   | -54.4 (2)    | C6B—C5B—C15B—C16B   | -127.1 (2)   |
| C4A—C5A—C15A—C20A   | 129.1 (2)    | C4B—C5B—C15B—C16B   | 50.9 (3)     |
| C6A—C5A—C15A—C16A   | 123.8 (2)    | C6B—C5B—C15B—C20B   | 51.4 (3)     |
| C4A—C5A—C15A—C16A   | -52.7 (3)    | C4B—C5B—C15B—C20B   | -130.5 (2)   |
| C20A—C15A—C16A—C17A | -0.5 (3)     | C20B—C15B—C16B—C17B | 0.8 (3)      |
| C5A—C15A—C16A—C17A  | -178.7 (2)   | C5B—C15B—C16B—C17B  | 179.38 (18)  |
| C15A—C16A—C17A—C18A | 0.5 (4)      | C15B—C16B—C17B—C18B | -0.3 (3)     |
| C16A—C17A—C18A—C19A | -0.5 (4)     | C16B—C17B—C18B—C19B | -0.2 (4)     |
| C17A—C18A—C19A—C20A | 0.5 (4)      | C17B—C18B—C19B—C20B | 0.0 (4)      |
| C18A—C19A—C20A—C15A | -0.5 (4)     | C18B—C19B—C20B—C15B | 0.6 (4)      |
| C16A—C15A—C20A—C19A | 0.5 (3)      | C16B—C15B—C20B—C19B | -1.0 (3)     |
| C5A—C15A—C20A—C19A  | 178.7 (2)    | C5B—C15B—C20B—C19B  | -179.6 (2)   |

**Table 1**

*C—H... $\pi$  interaction geometry ( $\text{\AA}$ ,  $^\circ$ )*

| C—H... $\pi$     | C—H  | H... $\pi$ | C... $\pi$ | C—H... $\pi$ |
|------------------|------|------------|------------|--------------|
| C7A—H7A2...C5A   | 0.96 | 2.892      | 3.780      | 154.41       |
| C7A—H7A3...C12A  | 0.96 | 2.920      | 3.824      | 157.38       |
| C8A—H8A1...C16B  | 0.96 | 3.014      | 3.924      | 158.82       |
| C14A—H14A...C15A | 0.93 | 2.811      | 3.126      | 101.09       |
| C16A—H16A...C9A  | 0.93 | 2.881      | 3.167      | 99.24        |
| C7B—H7B1...C11B  | 0.96 | 2.991      | 3.666      | 128.53       |
| C8B—H8B1...C12B  | 0.96 | 2.943      | 3.809      | 150.67       |
| C14B—H14B...C15B | 0.93 | 2.784      | 3.129      | 103.11       |
| C16B—H16B...C9B  | 0.93 | 2.823      | 3.138      | 101.13       |

Fig. 1

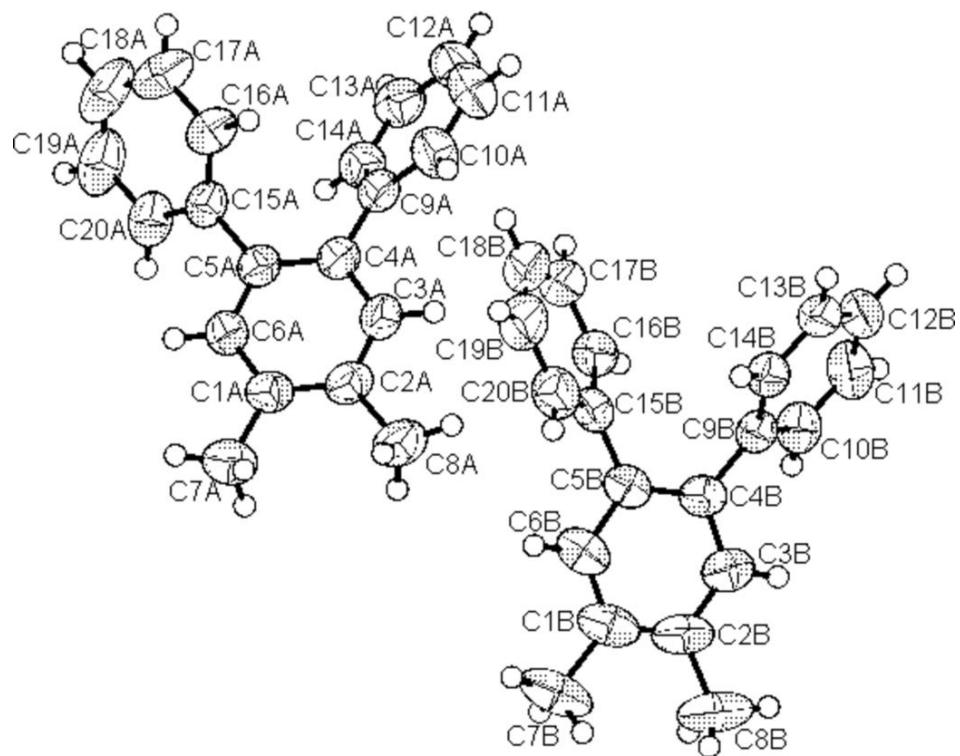


Fig. 2

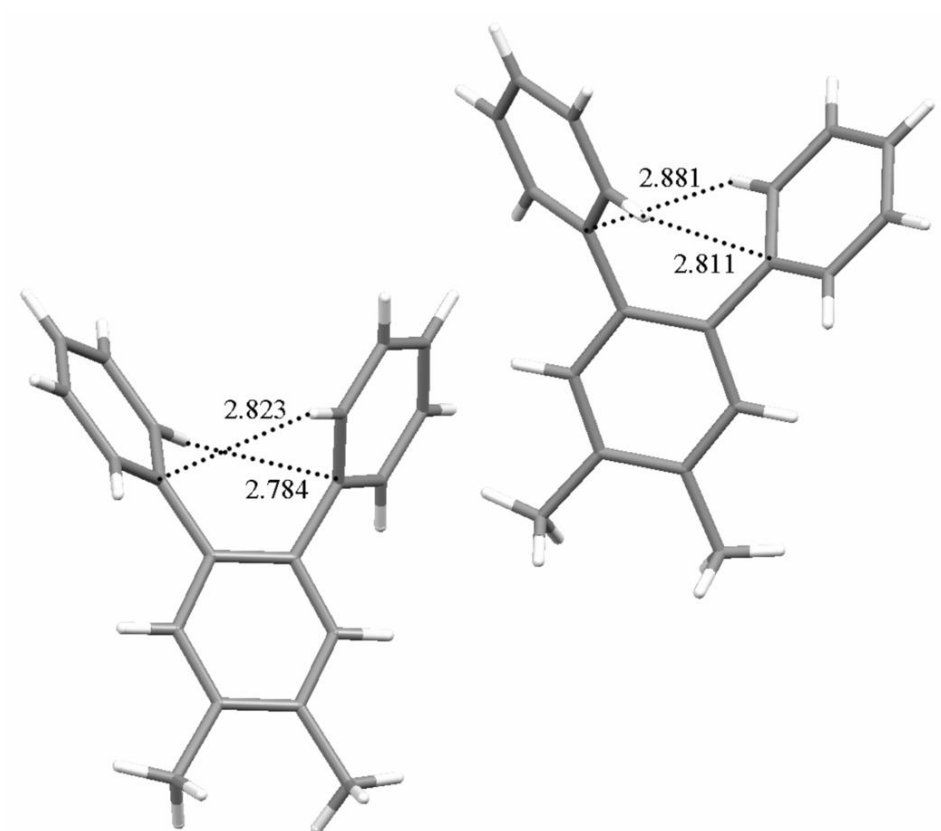


Fig. 3

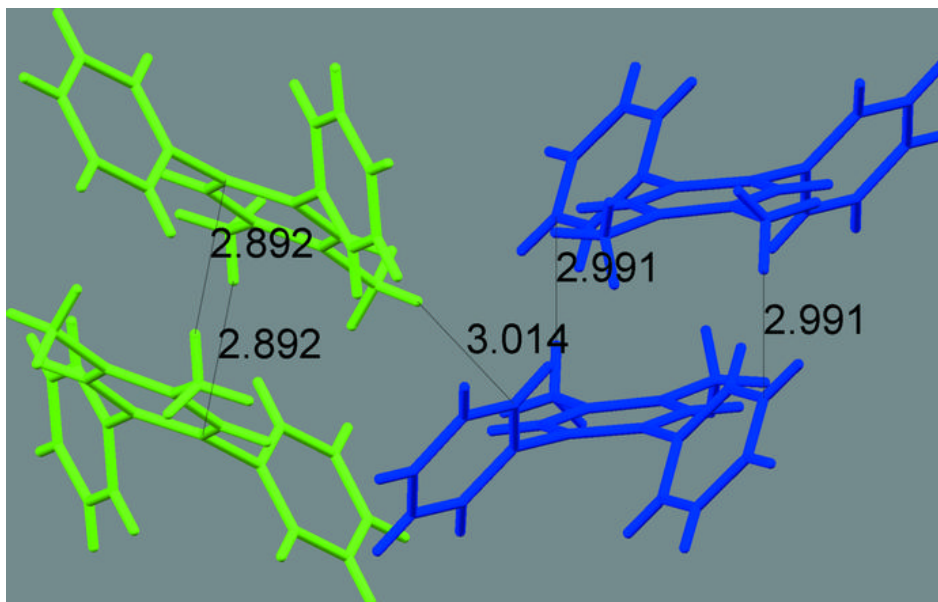


Fig. 4

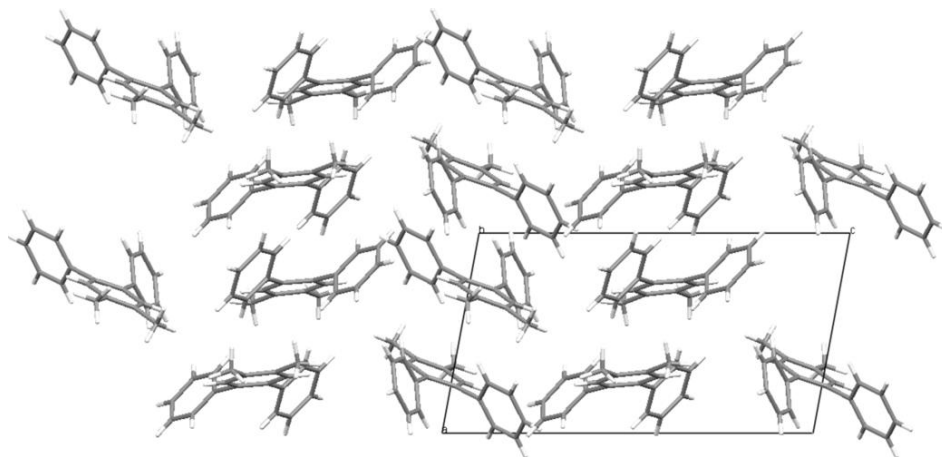


Fig. 5

