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# π-Stacking interactions in some crystalline cisoid *E*,*E*-1,4-diaryl-1,3-butadienes†

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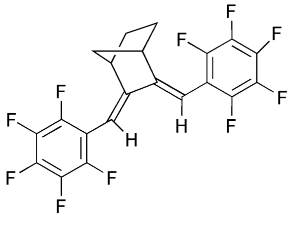
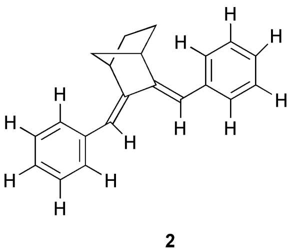
**A cisoid *E*,*E*-1,4-diperfluorophenyl-1,3-butadiene has been prepared in which offset stacking between perfluorophenyl–perfluorophenyl rings occurs, and face-to-face stacking between phenyl–perfluorophenyl rings is found in crystals of its 1 : 1 complex with a cisoid *E*,*E*-1,4-diphenyl-1,3-butadiene.**

Non-covalent π stacking interactions play an important role in many areas of chemistry, biology and material science.[1] Phenyl–phenyl rings interact in different geometries including face-to-face, edge-to-face, and offset (center-to-edge).[2] Some of theoretical studies show that the edge-to-face (T-shaped or herringbone) orientation of two phenyl rings is preferred. However, our recent study has indicated that two phenyl rings in some cases prefer the face-to-face-stacked orientation, and the intramolecular non-covalent interactions between the two stacked rings can provide a stabilizing energy for some highly crowded molecules.[3] In the past five years, there has been growing interest in intermolecular fluoroaromatic–fluoroaromatic interactions between fluorinated compounds[4] or inhibitors,[5] as well as the non-covalent interactions of anions with perfluoroaryl compounds.[6] Therefore, it would be desirable to determine whether a stacked orientation of two perfluorophenyl rings can exist in crystalline structures and to compare the orientation with that the phenyl–perfluorphenyl rings prefer using the same molecular system. Herein, we report the synthesis of a cisoid *E*,*E*-1,4-diperfluorophenyl-1,3-butadiene (**1**). The perfluorophenyl–perfluorophenyl offset stacking in its pure solid state (**1**), and the phenyl-perfluorophenyl face-to-face stacking in the 1 : 1 complex of **1** with a cisoid *E*,*E*-1,4-diphenyl-1,3-butadiene (**2**)[7] are observed.‡



**1**

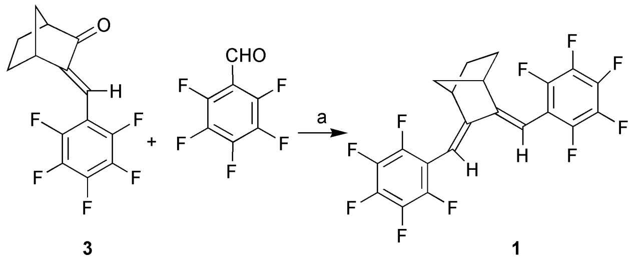


**2**

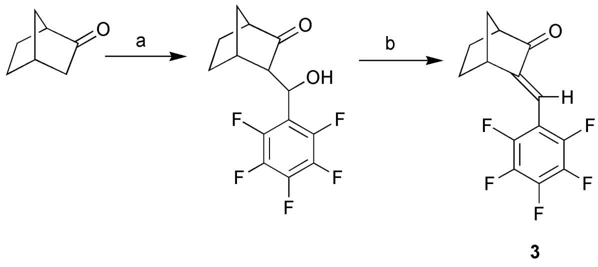
Compound **1**[8] was synthesized *via* McMurry coupling of pentafluorobenzaldehyde and a fluorinated enone (**3**), which was prepared from the nucleophilic addition of the lithium enolate of norcamphor to pentafluorobenzaldehyde, followed by dehydration (see Schemes 1 and 2). The total yield is ~10% due to the partial dimerization of pentafluorobenzaldehyde and the fluorinated enone (**3**). The $^1$H NMR spectrum of compound **1** shows a singlet at $\delta$ 6.43 for olefinic protons and a singlet at $\delta$ 2.92 for two bridgehead protons of the norbornyl moiety. At room temperature, the product (**1**) was recrystallized from ethyl acetate to afford colorless crystals. Also, colorless crystals of the 1 : 1 complex (**1:2**) were produced from a clear ethyl acetate solution, in which equivalent-molar amounts of **1** and **2** were dissolved. Furthermore, it was found that compounds **1** and **2** melted at 131–132 °C, and 130–131 °C, respectively (visual inspection). However, the melting point of complex **1:2** was 138–139 °C, which is higher than those of pure compounds.

Compound **1** was analyzed by single-crystal X-ray diffraction at 173 K, and the *E* configuration of the product was determined. The crystal structure reveals that the diene unit is almost coplanar with a torsional angle (~0.8°) and the two perfluorophenyl rings are slightly twisted from the conjugated 1,3-butadiene unit with a torsional angle (~41°). The molecules are related by an inversion center (space group: *P*1) so that only half the structure is crystallographically unique. In the crystal-packing diagram (Fig. 1), the offset-stacked orientation between the perfluorophenyl rings of the two neighboring molecules, which is caused by the intermolecular π–π interactions, is present. The closest contact between the neighboring perfluorophenyl rings is 3.18 Å, and the distance between two $C_6F_5$ ring centroids is 4.16 Å. Recent calculations of the simplest prototype of π–π interactions, the benzene dimer, have shown edge-to-face and offset orientations are isoenergetic.[9] This predication might be applicable to π stacking interactions between two perfluorophenyl rings. The crystallographic analysis of **1** was carried out and proved no significant intermolecular π–π interactions between phenyl groups. The surprising findings could indicate the intermolecular π stacking interactions between perfluorophenyl rings are stronger than those between phenyl rings.

Crystal structure of the complex **1:2** was also determined at low temperature (Fig. 2a). The structure indicates the diene unit of **1** with a torsional angle (~4°) is more bent than that of **2** in the complex, and the two perfluorophenyl rings (a torsional angle ~40°) are more twisted than the two phenyl rings with respect to its conjugated 1,3-butadiene unit. The crystal



**Scheme 1** a) $TiCl_4$, Zn in THF, reflux.



**Scheme 2** a) LDA–THF, −10 °C, then pentafluorobenzaldehyde; b) i. $CH_3COCl$, pyridine in $CH_2Cl_2$, and then ii. KO$^t$Bu in HO$^t$Bu.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b301578e/

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structure of the complex reveals a face-to-face stacked orientation between one phenyl ring and one perfluorophenyl ring of the two molecules, while the other two aryl rings are separated (Fig. 2a). The packing diagram of complex **1:2** shows the neighboring complexes are joined together *via* similar phenyl–perfluorophenyl face-to-face-stacked orientations to form a zig-zag supramolecular architecture (Fig. 2b). All H$\cdots$F distances with geometrically placed hydrogens are greater than 2.46 Å. Therefore, noncovalent $\pi$ stacking interactions are mainly responsible for the higher melting point of the 1 : 1 complex (**1:2**). Moreover, the observed triclinic form (space group: $P1$) of complex **1:2** is in good agreement with the space group of most phenyl–perfluorophenyl complexes reported in recent literature[10,11] and could be a notable feature of the co-crystals of the conjugated systems containing two perfluorophenyl rings coupled with the corresponding aromatic hydrocarbons. The cisoid conformation of the conjugated systems in **1:2** has little influence on this feature.

Despite their frequent occurrence, there is no unifying picture as to the nature of the $\pi$–$\pi$ interactions. Electrostatic interactions[12] (quadrapole–quadrapole and quadrapole–dipole, and dipole–dipole), hydrophobic effects[13] and van der Waals[14] have been proposed as important factors. Because perfluorobenzene has a positive quadrupole moment, the offset-stacked geometry (Fig. 1) minimizes $\pi$-electron repulsion and maximizes the attraction between the positive central core and the negative periphery. On the other hand, benzene has a negative quadrupole moment. Thus, the quadrapole–quadrapole attraction between phenyl–perfluorophenyl rings explains the preferred face-to-face-stacked arrangement of complex **1:2** (Fig. 2b). The observed offset and face-to-face geometries suggest that the electrostatic interactions have significant effects on the observed orientations.

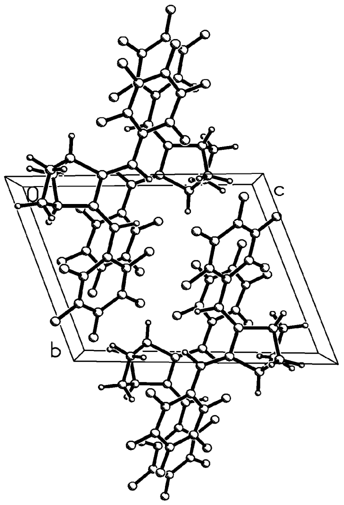

**Fig. 1** Offset stacking of the perfluorophenyl rings in the crystal structure of compound **1**.

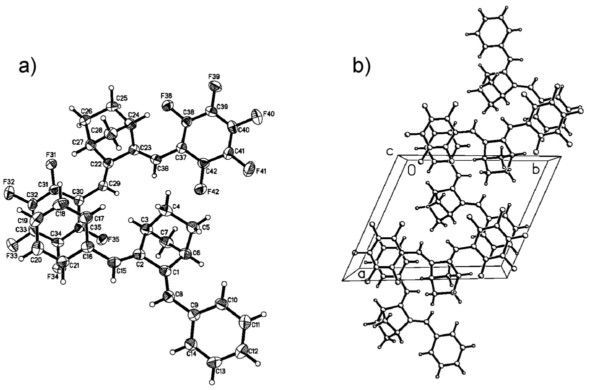

**Fig. 2** a) The X-ray structure of the 1 : 1 complex (**1:2**) at 173 K; b) Face-to-face stacking of the phenyl and perfluorophenyl rings forming a zig-zag supramolecular architecture of the complex (**1:2**).

In conclusion, we demonstrate that perfluorophenyl–perfluorophenyl rings can adopt the offset-stacked geometry, which might be preferred in energy. Compound **1**, and complex **1:2** will be utilized for the on-going molecular design of topochemical polymerization[15] of cisoid 1,3-butadienes.

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## Notes and references

‡ *Crystal_data*. Compound **1**, $C_{21}H_{10}F_{10}$, $M$ = 452.29, triclinic, space group: $P1$; $a$ = 9.1151(11), $b$ = 9.1761(16), $c$ = 11.3748(14) Å, $\alpha$ = 69.683(2), $\beta$ = 78.016(2), $\gamma$ = 84.341(2)°, $V$ = 872.40(18) Å$^3$, $Z$ = 2, $D_{calc}$ = 1.722 Mg m$^{-3}$, $\mu$ = 0.175 mm$^{-1}$, $R1$ = 0.0362 for 3253 data [$I > 2\sigma(I)$] and = 0.0449 for all 3926 data. Compound **2**, $C_{21}H_{20}$, $M$ = 272.39, monoclinic, space group: $P2_1/n$; $a$ = 6.0081(8), $b$ = 11.5316(15), $c$ = 22.082(3) Å, $\beta$= 91.343(2)°, $V$ = 1529.5(3) Å$^3$, $Z$ = 4, $D_{calc}$ = 1.183 Mg m$^{-3}$, $\mu$ = 0.066 mm$^{-1}$, $R1$ = 0.0457 for 3130 data [$I > 2\sigma(I)$] and = 0.0520 for all 3507 data. Complex **1:2**, $C_{21}H_{20}{\cdot}C_{21}H_{10}F_{10}$, $M$ = 724.68, triclinic, space group: $P1$; $a$ = 10.550(3), $b$ = 12.981(3), $c$ = 13.366(3) Å, $\alpha$ = 103.043(5), $\beta$ = 90.336(5), $\gamma$ = 113.064(5)°, $V$ = 1631.6(7) Å$^3$, $Z$ = 2, $D_{calc}$ = 1.475 Mg m$^{-3}$, $\mu$ = 0.125 mm$^{-1}$, $R1$ = 0.0431 for 3884 data [$I > 2\sigma(I)$] and = 0.0717 for all 5744 data. For all data collection, $\lambda$(MoK$\alpha$) = 0.71073 Å, $T$ = 173(2) K. Bruker SMART area diffractometer, data integration was carried out with SAINT V6.1 (Bruker Analytical X-Ray Systems, Madison, WI), corrections for absorption and decay were applied using SADABS (R. Blessing, *Acta Crystallogr. Sect. A*, 1995, **51**, 33–38). The structure was solved, by direct methods, and refined using the SHELXTL-Plus V6.1 (Bruker Analytical X-Ray Systems, Madison, WI). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed with ideal positions and refined with isotropic thermal parameters related to the parent carbon atom. CCDC 203757–203759. See http://www.rsc.org/suppdata/cc/b3/b301578e/ for crystallographic data in .cif or other electronic format.

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