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Trifluoromethyl Groups in Crystal Design of 1,4-Diphenyl-1,3-butadienes for Topochemical [2 + 2] Photodimerization

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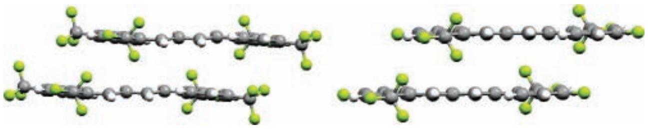
ABSTRACT



UV irradiation of the powdered crystalline sample of each of three (*E*,*E*)-1,4-di(trifluoromethyl-substituted)phenyl-1,3-butadienes (1–3) was found to yield a single [2 + 2] cycloaddition product in the solid state. Moreover, upon irradiation, the crystalline samples of two (*E*,*E*)-1,4-di(trifluoromethyl- and fluorine-substituted)phenyl-1,3-butadienes (4, 5) undergo a similar conversion to afford a [2 + 2] cycloaddition product, respectively. Our observations suggest that trifluoromethyl groups can be used to direct 1,4-diphenyl-1,3-butadiene molecules to form a parallel, offset-stacked orientation suitable for topochemical [2 + 2] cycloaddition.

Noncovalent π stacking interactions play an important role in many areas of chemistry, biology, and material science.[1] In particular, noncovalent π stacking interactions formed by fluorine atoms are extremely versatile. Studies of π stacking interactions between phenyl and perfluorophenyl rings[2] or between two perfluorophenyl rings[3] have been reported in the literature. Although the face-to-face stacking interactions have been successfully used to construct an ideal architecture for [2 + 2] photodimerization or photopolymerization,[4] a few studies were focused on stacking arrangements influenced by trifluoromethyl groups.[5] Our recent study has indicated that the self-assembling of (*E*,*E*)-1,4-di(*o*-trifluoromethyl)phenyl-1,3-butadiene, (*E*,*E*)-1,4-di(*m*-trifluoromethyl)phenyl-1,3-butadiene, and (*E*,*E*)-1,4-di(*p*-trifluoromethyl)phenyl-1,3-butadiene is suitable for topochemical [2 + 2] photodimerization in the solid state.[6] Therefore, it has occurred to us that trifluoromethyl groups could be used as directing groups in crystal engineering of (*E*,*E*)-1,4-diphenyl-1,3-butadienes (DPB).[7] To further explore the scope of trifluoromethyl groups as the new directing groups,[8] it will be interesting to know the effects of the number of trifluoromethyl groups attached to each phenyl ring on the formation of the parallel, offset-stacked orientation of DPBs. Also, questions regarding the compatibility of a trifluoromethyl group with a fluorine atom as substituents in the self-assembling of substituted DPBs need to be addressed. Herein, we report our recent study of topochemical [2 + 2] photodimerization of six trifluoromethyl-substituted DPBs.

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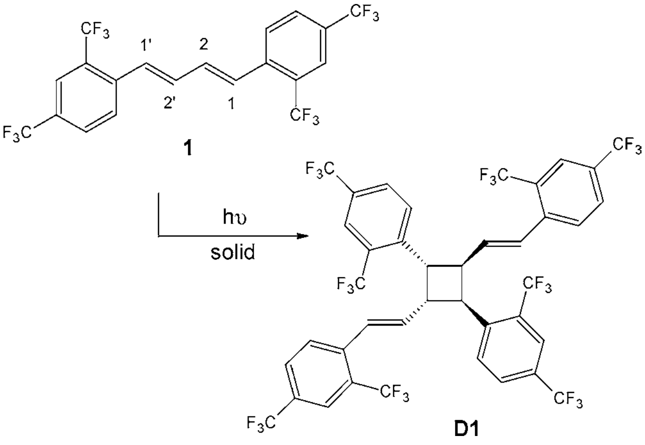
First, we decided to examine the crystal packing of (*E*,*E*)-1,4-di(*o*,*p*-bistrifluoromethyl)phenyl-1,3-butadiene **1** (Scheme 1). In attempt to synthesize **1**, (*E*)-(*o*,*p*-bisCF_3)-$C_6H_4CH{=}CHCHO$, which was prepared by C_2-extension of *o*,*p*-bisCF_3-C_6H_4CHO with $(C_6H_5)_3P{=}CHCHO$, was coupled in a Horner−Wadsworth−Emmons olefination with *o*,*p*-bisCF_3-$C_6H_4CH_2P(O)(OC_2H_5)_2$ using sodium hydride as a base. The product precipitated as a white solid during the regular ether extraction was insoluble in most common organic solvents, except for THF. The colorless crystals of **1** were obtained from THF in an overall yield of 60%.

Scheme 1



A view of the X-ray crystal structure of **1** determined at 100 K (Figure 1a) indicates that there are two molecules in the unit cell, each of which is located on an inversion center. The crystal structure shows that the diene unit is coplanar with the torsional angles ranging from 179 to 180°, and the two phenyl rings are slightly twisted from the conjugated 1,3-butadiene unit with a torsional angle (∼167.11°, C2−C1−C3−C4). The offset-stacked orientation formed by intermolecular $\pi\cdots\pi$ stacking interactions between the phenyl rings of neighboring molecules has been found in the crystal packing (Figure 1b). Compound **1** crystallizes to a layered structure in which olefins of neighboring layers are separated by 3.55 Å. As a result, the double bonds of the diene units conform to Schmidt's topochemical principle for [2 + 2] photodimerization.[9] Further analysis of the crystal structure (**1**) suggests that the distances of H···F hydrogen bonds ($C_{10}-F_4\cdots H_8$ = 2.53 Å and $C_{10}-F_4\cdots H_2$ = 2.63 Å) are slightly smaller than the sum of the van der Waals radii for H and F (H = 1.20 Å, F = 1.47 Å).[10] Thus, hydrogen bonding is considered to be a weak force that joins the nearby columns of the crystal lattice. Also, trifluoromethyl groups in the same layers of the neighboring columns tend to come closer to each other at a distance of 2.90 Å ($F_1\cdots F_6$) due to the weak F···F nonbonded contacts. Because of the weak strength of the short-distance contacts, we believe that noncovalent $\pi\cdots\pi$ stacking interaction is mainly responsible for the observed self-assembling of **1**.

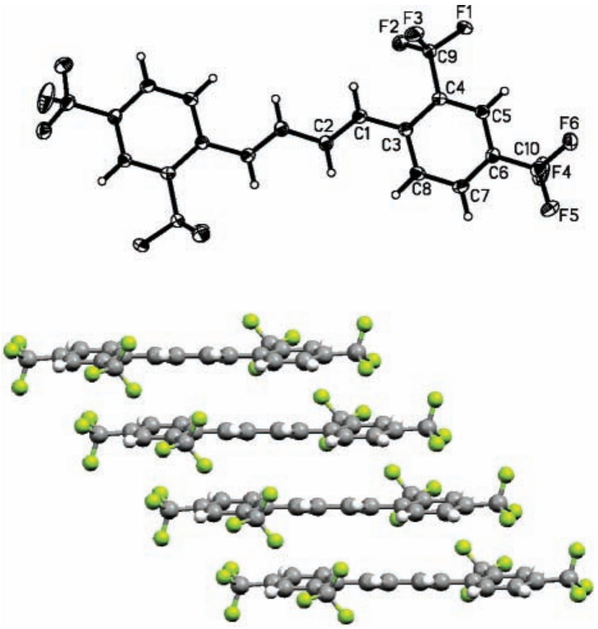


Figure 1. (a) Thermal ellipsoid diagram of **1**. (b) The molecules (**1**) stack in an offset arrangement. The distance between the layers in the same column of the crystal lattice is 3.55 Å.

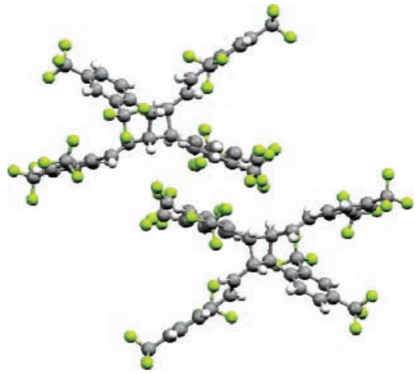


Figure 2. Packing diagram of **D1** shows that the closest distance between two offset-stacked molecules is 4.27 Å.

UV irradiation of the powdered crystalline sample **1** using a 200 W Hg medium-pressure lamp with a Pyrex filter at room temperature for 15 h furnished a single product (**D1**) in 80% yield (Scheme 1). The product yield remained the same after 15 h, and the remaining 20% was found to be the unreacted starting material. The product was purified from the remaining starting material by using column chromatography. The cyclobutane ring of **D1** was characterized by two proton signals at 4.55 and 4.19 ppm (Figure 3). Also, as evidenced by a doublet (d) and a doublet of doublets (dd) at 6.74 and 5.96 ppm, respectively, the existence of carbon−carbon double bonds was suggested in **D1**. The

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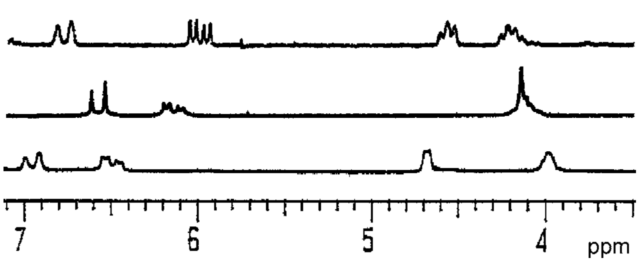


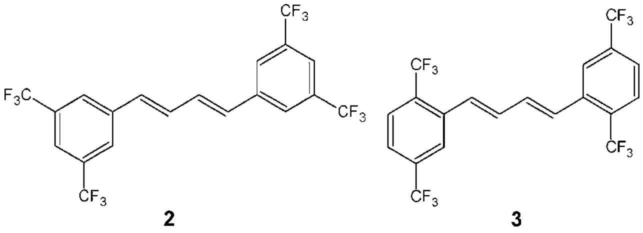
Figure 3. Partial ^{1}H NMR spectra of **D1** (top), **D2** (middle), and **D3** (bottom) obtained from photodimerization of **1**, **2**, and **3**, respectively.

spectroscopic data indicated that two DPB molecules underwent a single [2 + 2] addition reaction to form **D1**.

To unequivocally elucidate the stereochemistry, the crystal structure of **D1** was solved (Figure 2). Examination of the crystal structure indicates that the C2−C1 double bond of **1** (Figure 1a) reacted with the C1′−C2′ double bond of the neighboring molecule to form a four-membered ring. The regioselectivity of this addition is due to the closest distance (3.55 Å) between the C2−C1 and C1′−C2′ bonds, while the distance (4.82 Å) between two neighboring C2−C1 double bonds is exceeded for the topochemical reaction. It appears that the $\pi\cdots\pi$ stacking interaction between phenyl rings directed the geometry of crystallization to yield photoactive crystals of **1** in the solid state.

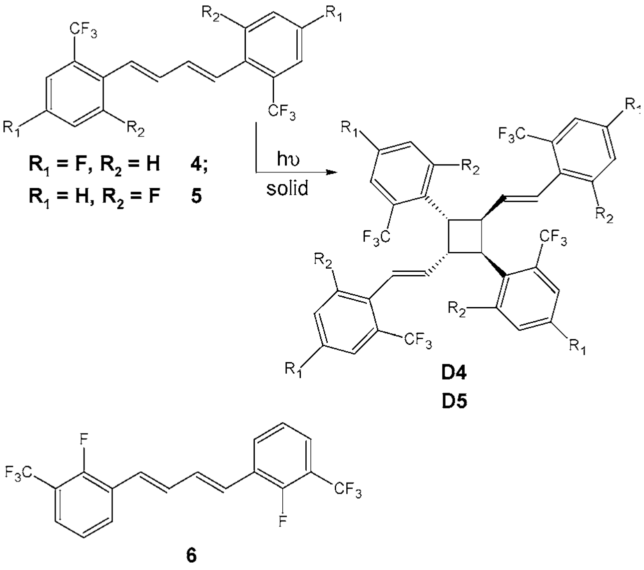
To further probe the generality of trifluoromethyl groups in exerting direct control of the crystal packing of tetra-CF_3-substituted DPB molecules for topochemical reactions in the solid state, we prepared (*E*,*E*)-1,4-di(*m*,*m*′-bistrifluoromethyl)phenyl-1,3-butadiene **2** and (*E*,*E*)-1,4-di(*o*,*m*′-bistrifluoromethyl)phenyl-1,3-butadiene **3** by the procedure described above. Crystals of the two compounds were also obtained from THF. UV irradiation of the powdered crystalline samples **2** and **3** for 15 h at 25 °C afforded a single photoproduct in 50∼60% yield, respectively. Each photoproduct isolated by way of silica gel column (hexanes as the eluant) was suggested by MS to be a dimer from a single [2 + 2] reaction (See Supporting Information). Also, as evidenced by proton signals at 3.80−4.80 ppm (Figure 3) and two carbon signals in the range of $\delta = 47.0-44.0$ ppm, the cyclobutane ring in each photoproduct was confirmed. Moreover, in the ^{1}H NMR spectrum of each photoproduct, the appearance of a pair of d and dd in the range of $\delta =$ 7.10−5.80 ppm showed a strong resemblance to the proton absorptions characterized for the olefinic hydrogens of **D1**. All the structural data strongly supported that **2** and **3** underwent a single [2 + 2] cycloaddition, analogous to **1**. The results further prove that trifluoromethyl groups have the capability of juxtaposing DPB molecules in a parallel fashion for an intermolecular [2 + 2] cycloaddition by a means of $\pi\cdots\pi$ offset-stacked interactions.

Scheme 2



To understand the compatibility of trifluoromethyl groups with fluorine atoms as substituents in the self-assembling, three substituted DPBs (**4**−**6**) (Scheme 3) were prepared, and crystals (**4**−**6**) were afforded by way of recrystallization of the three compounds in THF. The X-ray crystal structure of **4** determined at 100 K (Figure 4a) indicates that the molecule is related by an inversion center, so only half the structure is crystallographically unique. Moreover, the offset-stacked arrangement between the phenyl rings of neighboring molecules (3.55 Å) has been found in the crystal packing (Figure 4b). It is of interest to note that only the offset-stacked alignment was found in the crystal structures of the trifluoromethyl-substituted DPBs.[6] We believe that the formation of the face-to-face orientation of identical trifluoromethyl-substituted phenyl rings is unfavorable due to the steric crowding between the substituents. Further analysis of the crystal structure (**4**) shows H•••F hydrogen bonds ($C_7-F_4\cdots H_6$ 2.63 Å, $C_4-F_1\cdots H_5$ 2.66 Å, $C_4-F_1\cdots H_3$ 2.61 Å) and F•••F nonbonded contacts ($F_2\cdots F_2$ 2.77 Å, $F_4\cdots F_3$ 2.88 Å).

Scheme 3



UV irradiation of the powdered crystalline sample **4** for 15 h at 25 °C afforded a single photoproduct in 50∼60% yield. The photoproduct isolated by way of silica gel column chromatography was characterized by using spectroscopic methods, and the [2 + 2] photoadduct was further recrystallized from ethyl acetate. To specifically account for the stereochemistry of **D4**, crystallographic data was obtained (Figure 5). Examination of the crystal structure indicates that

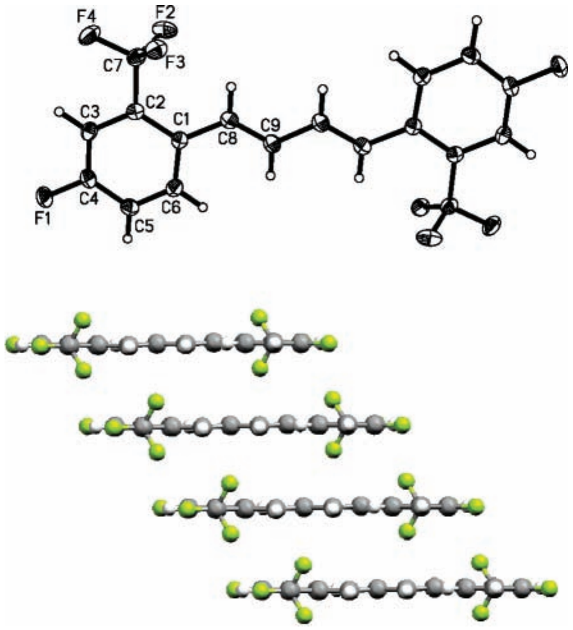


Figure 4. (a) Thermal ellipsoid diagram of **4**. (b) The molecules (**4**) stack in an offset arrangement. The distance between the layers of the molecules is 3.55 Å.

the C8–C9 double bond of **4** (Figure 4a) reacted with the C9′–C8′ double bond of the neighboring molecule to form a four-membered ring. The regioselectivity of this addition is dependent on the closest distance (3.55 Å), while the distance is 4.78 Å between two neighboring C8–C9 double bonds. In addition, under the same irradiation conditions, UV photoirradiation of DPB–**5** afforded a single photoproduct in 55% yield. By comparing the proton signals of **D5** in the ranges of δ 3.80–4.50 and 5.80–6.80 ppm with those of **D4**, we determined the cyclobutane ring in the photoproduct **D5** (Supporting Information). All other spectroscopic data strongly supported that **5** indeed underwent a single [2 + 2] photodimerization in the same fashion as **1**–**4**. However, DPB–**6** was found to be photostable under the same irradiation conditions in the solid state. We reason that the fluorine atom at the ortho position with respect to the trifluoromethyl group weakens the effects of the directing groups.[11]

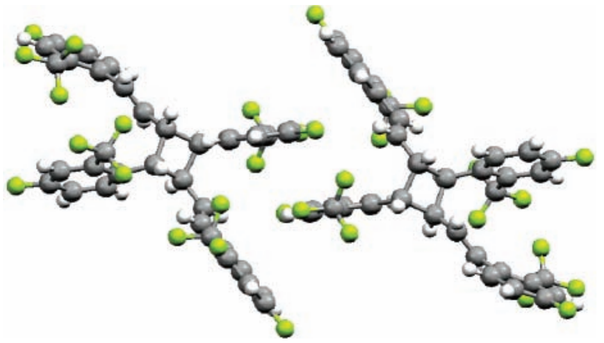


Figure 5. Packing diagram of **D4** shows that the closest distance between two offset-stacked molecules is 4.36 Å.

In summary, we have demonstrated that addition of the second trifluoromethyl group to each phenyl ring of (*E*,*E*)-1,4-di(trifluoromethyl)phenyl-1,3-butadiene has no disruption effect on the formation of the parallel, stacking arrangement of substituted DPBs. Moreover, the trifluoromethyl group is compatible with the fluorine atom, while the fluorine substituent is in a position meta or para to the trifluoromethyl group. We are now investigating the application of trifluoromethyl groups as the new directing groups to some longer polyene systems in the solid state as well as in frozen media.[12]

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Supporting Information Available: Crystallographic reports (CIF) and spectroscopic data of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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