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Phenyl−Perfluorophenyl Stacking Interactions: Topochemical [2+2] Photodimerization and Photopolymerization of Olefinic Compounds

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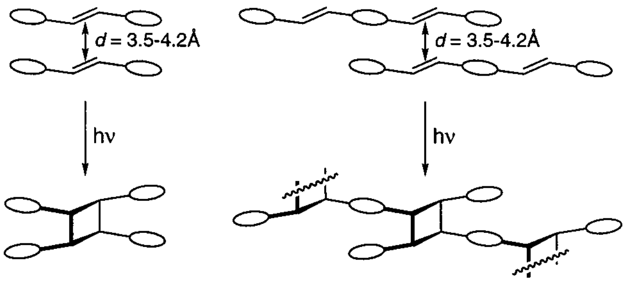
Abstract: The face-to-face stacking interaction between phenyl and perfluorophenyl groups is emerging as a common noncovalent interaction. To explore the generality of this supramolecular synthon, the solid-state packing structure and reactivity of several monoolefins and diolefins substituted with phenyl and perfluorophenyl groups was investigated. Of the seven crystalline or cocrystalline materials investigated, six were found to undergo a photochemically induced [2+2] reaction in the solid state. By determining the stereochemistry of the photoproduct and/or X-ray structural analysis of the olefinic precursors, the stacked interaction between phenyl and perfluorophenyl groups in the photoactive crystals were revealed.

Introduction

The photodimerization of organic molecules in the solid state has been known since the end of the last century.[1] Through the pioneering work of Schmidt and co-workers,[2,3] as well as many other studies,[4−6] the prerequisites for photochemical [2+2] reactions in the solid state are now well established. With few exceptions, olefins arranged in a parallel orientation that have center−center separations of 3.5−4.2 Å undergo the photocycloaddition reaction.[4] Diolefin molecules whose crystals have these same intermolecular olefin parameters typically react to form polymers in the solid state (Scheme 1).[7−9] One of the intriguing aspects of these photocycloaddition and photopolymerization reactions is that the stereochemistry of the products is determined by the relative arrangement of the molecules in the crystal.[10−12] Therefore, topochemical reactions hold great potential for the synthesis of molecules of defined stereochemistry. Unfortunately, it is impossible at the current time to rationally design a molecule that will, with any degree of certainty, crystallize in the necessary arrangement for reaction in the solid state.[13,14] The most common approach to the identification of photoactive olefinic compounds is simply a process of trial and error.

Scheme 1. Olefin Photodimerization and Diolefin Photopolymerization



The identification and detailed understanding of commonly observed interactions in molecular crystals is crucial to the advancement of the field of crystal engineering. Through the study of these interactions (recently termed “supramolecular synthons”),[15] it should be possible to design molecules that have a high probability of packing in the desired crystalline arrangement. For example, chloro-,[16] fluoro-,[17] alkoxyaryl groups,[18] as well as electron donor/acceptor[19] and hydrogen bonding interactions,[20] have been used to align olefinic molecules in the crystal for [2+2] photodimerization.

Noncovalent interactions between aromatic groups have been studied intensively due to their importance in many areas of

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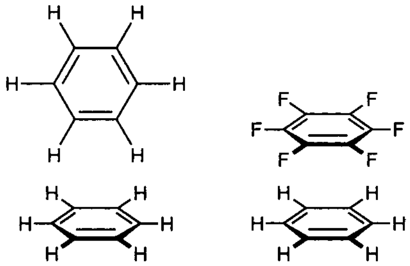

Figure 1. Solid-state packing arrangements of the benzene dimer and the benzene/hexafluorobenzene dimer.

science.[21] These stacking interactions contribute substantially to the stabilization of DNA,[22,23] and are thought to be intimately involved in the tertiary structure and recognition events of proteins.[24,25] The aggregation of porphyrins and aromatic macrocycles in solution has been attributed to aromatic−aromatic interactions,[26,27] as has the liquid-crystalline behavior of some arene-containing molecules.[28] In addition, arene−arene interactions are important in molecular recognition events[29−31] and have been shown to influence selectivity in both the solution phase[32−34] and the solid state.[35,36]

Although a considerable amount of work concerning the stacking of aromatic rings has concentrated on phenyl−phenyl interactions, there is a growing interest in the interactions of phenyl and perfluorophenyl groups.[37−40] Patrick and Prosser first recognized that a 1:1 mixture of benzene (mp 5.5 °C) and hexafluorobenzene (mp 4 °C) forms a complex that melts at 24 °C.[41] Although pure benzene adopts an edge-to-face structure in the solid state,[42] it has been determined that the structure of the lowest temperature phase of the benzene/hexafluorobenzene material consists of face-to-face stacks of alternating molecules (Figure 1).[37,43] This stacking arrangement is thought to result from van der Waals forces and favorable electrostatic attractions between the molecules, not from charge-transfer interactions.[37,44,45] The theoretical electrostatic potential map of benzene[46] reveals concentrations of negative potential above and below the molecular plane, and a ring of positive potential in the plane focused on the hydrogens. Hexafluorobenzene possesses the reverse charge distribution. Stated differently, both benzene and hexafluorobenzene have large molecular quadrupole moments that are similar in magnitude, yet opposite in sign.[37] Further support for the importance of electrostatics in such interactions comes from Cozzi and Siegel's elegant studies of rotational barriers in 1,8-diarylnaphthalenes[47,48] and from recent theoretical studies.[49−53]

We have recently reported the use of the phenyl−perfluorophenyl stacking interactions to align diacetylene molecules for reaction in the crystalline state.[54] These studies revealed that the phenyl−perfluorophenyl arrangement first seen in benzene/hexafluorobenzene may be a fairly general supramolecular motif. The distances between phenyl centroids in these diacetylenes varies from 3.6 to 3.8 Å, and are very close to the separation of the benzene−hexafluorobenzene cocrystal, 3.77 Å.[43] Since these distances are within the range necessary for a solid-state [2+2] photocycloaddition, we investigated the use of the phenyl−perfluorophenyl interaction to orient olefinic molecules in the crystalline state. In this paper we report the application of this interaction for the topochemical photocycloaddition of olefins and photopolymerization of diolefins.

Results and Discussion

Photocycloaddition Reactions. Photodimerizations of *trans*-cinnamic acid and its derivatives are among the most studied topochemical reactions. Two photoactive polymorphs of cinnamic acid are known: the α-form and the *β*-form. The α-form produces α-truxillic acid upon photolysis, while the *β*-form yields *β*-truxinic acid. The *β*-form is metastable and undergoes a phase change to the α-form above room temperature. Due to the electrostatic attraction between coplanar phenyl and perfluorophenyl groups, we anticipated that cinnamic acid (**1**) and pentafluorocinnamic acid[55] (**2**) might cocrystallize to give a *β*-type arrangement. Crystallization of a 1:1 mixture of **1** (mp 133−4 °C, α-form) and **2** (mp 154−6 °C) from ethanol yielded a colorless, microcrystalline material that melted at 169−71 °C. The small crystal size did not permit X-ray structure analysis. ^{1}H NMR spectroscopy revealed a 1:1 ratio of **1**:**2** in the solid. The **1•2** cocrystal was subjected to photolysis at room temperature; after 7 h, only 13% of the material remained unreacted.

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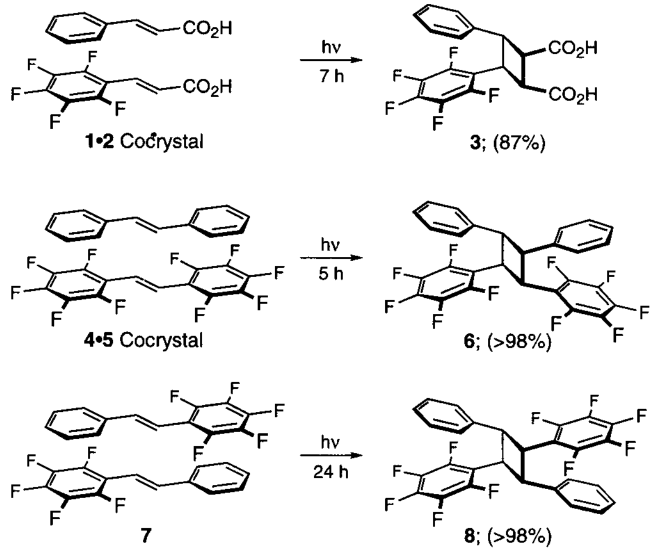
(55) 2,3,4,5,6-Pentafluorocinnamic acid (recrystallized from ethanol) is photostable in the solid state.

Scheme 2. Solid-State Photocycloaddition Reactions of **1•2**, **4•5**, and **7**



^{1}H NMR revealed the formation of only one cyclobutane product (**3**), which has been assigned the stereochemistry depicted in Scheme 2 based on two pieces of information. First, reaction of **3** with P_2O_5 yields the cyclic anhydride, which means the two acid groups of the product must exhibit a cis relationship on adjacent carbons of **3**. Assuming that the trans dispositions of the acid and phenyl groups of **1** and **2** are retained in the product, then the stereochemistry of **3** can be assigned as shown in Scheme 2. Second, the ^{19}F NMR (376.5 MHz) spectrum exhibits a coalescence of the *ortho*-fluorine shifts at −50 °C. From the variable-temperature NMR data, a rotational barrier for the pentafluorophenyl group of 9.3 ± 0.3 kcal/mol (at −50 °C) can be calculated, which is consistent with the *cis* relationship of the phenyl and perfluorophenyl groups in **3**. The stereochemistry of **3**, high photolysis yield, and complete absence of homodimerization products is strong evidence that **1** and **2** pack sequentially in the crystal, in a head-to-head arrangement. To probe the generality of the phenyl−perfluorophenyl interaction in the design of photoactive crystals, the cocrystallization of *trans*-stilbene (**4**) and *trans*-decafluorostilbene (**5**) was investigated. Cocrystallization of a 1:1 mixture of **4** (mp 122−4 °C) and **5** (mp 103 °C) from ethanol yielded colorless needle-shaped crystals that melted at 139 °C. Again, ^{1}H NMR revealed the 1:1 ratio of **4**:**5** in the cocrystal.

Photolysis of the **4•5** cocrystal at ambient temperature for 5 h yielded a new product in quantitative yield. Note that neither **4**[56] nor **5**[57] are photoactive as the pure crystal. The ^{1}H NMR spectrum revealed the complete absence of shifts attributable to **4** or **5**, and is consistent with a sole cyclobutane product (**6**) as depicted in Scheme 2. The assignment of the stereochemistry of **6** is based on the coupling constants of the ^{1}H NMR spectrum (see Experimental Section). In addition, the cis relationship of the H_5- and F_5-phenyls of **6** was confirmed by variable-temperature ^{19}F NMR. At the coalescence temperature of −43 °C (376.5 MHz), the barrier to rotation of the perfluorophenyl group is 9.5 ± 0.3 kcal/mol. This value is consistent with the barrier determined for **3**.

To determine the packing arrangement of **4** and **5** in the cocrystal, the structure was determined by single-crystal X-ray diffraction. As can be seen in Figure 2, **4•5** is stacked in vertical columns in an alternating fashion. Molecules of **4** and **5** are situated on centers of inversion, which results in the equal spacing of adjacent olefins. Significantly, the relative arrangement of **4** and **5** confirms the stereochemistry of **6** as shown in Scheme 2. The angles between reactive olefin carbons in **4** and **5** are 68.4° (C1−C2−C2′), 69.9° (C1−C1′−C2′), 112.2° (C1′−C2′−C2), and 109.6° (C2−C1−C1′), and the olefin−olefin separation is 3.784 (C1−C2) and 3.749 Å (C1′−C2′), consistent with the photochemical reactivity of the crystal.

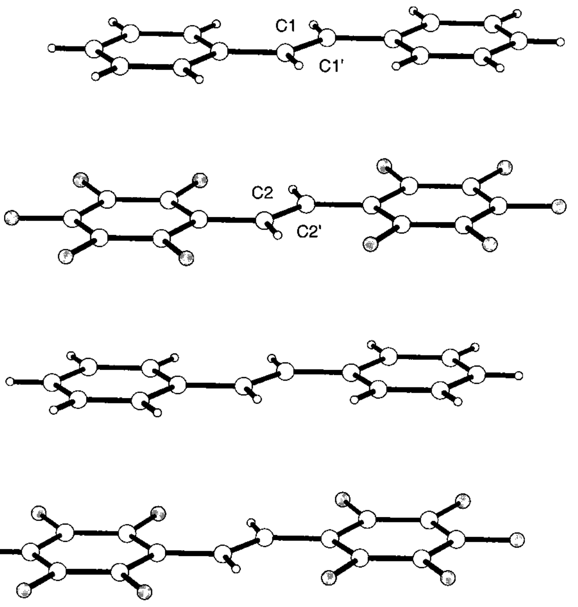


Figure 2. Molecular packing diagram of the *trans*-stilbene (**4**)/*trans*-decafluorostilbene (**5**) cocrystal. The fluorine atoms are shaded.

trans-Pentafluorostilbene (**7**) has been reported to undergo a photochemical dimerization reaction in the solid state.[57] In the absence of X-ray structural data, the stereochemistry of the cyclobutane product (**8**) was not unambiguously determined. The photolysis of **7** (crystallized from diethyl ether/ethanol) was carried out for 24 h under conditions identical to those for **4•5**; a quantitative yield of a single product (**8**) was determined by ^{1}H NMR. The stereochemistry of **8** was assigned in the same manner as for **6**. As with cyclobutanes **3** and **6**, variable-temperature ^{19}F NMR reveals the barrier to rotation of the pentafluorophenyl group of **8** is 9.2 ± 0.3 kcal/mol at the coalescence temperature (−55 °C, 376.5 MHz).

To confirm the stereochemistry of **8**, the structures of **7** and **8** were determined by single-crystal X-ray diffraction. As can be seen in Figure 3, **7** is stacked in vertical columns, and the molecules are packed in a head-to-tail fashion. Although **7** at first glance appears to be packed equally spaced in its stacks, the molecules above and below a given molecule of **7** are related by different inversion centers. The angles between reactive olefin carbons in **7** are 109.4° (C1′−C2′−C1), 70.5° (C2′−C1′−C2), 97.0° (C2′−C1′−C2″), and 82.9° (C1′−C2′−C1″); however, the olefin−olefin separation is nearly identical at 3.707 (C1−C2′) and 3.700 Å (C2′−C1″). These geometrical parameters are consistent with the observed photochemical reactivity of the crystal. To establish that the packing geometry of **7** determines the stereochemistry of the photoproduct, the X-ray structure of **8** was determined. As shown in Figure 4, the stereochemistry of **8** (as predicted by the packing geometry of **7** and NMR spectroscopic information) is confirmed.

A particularly unusual feature of the photodimerization of **4•5** and **7** is that both reactions proceed in virtually quantitative

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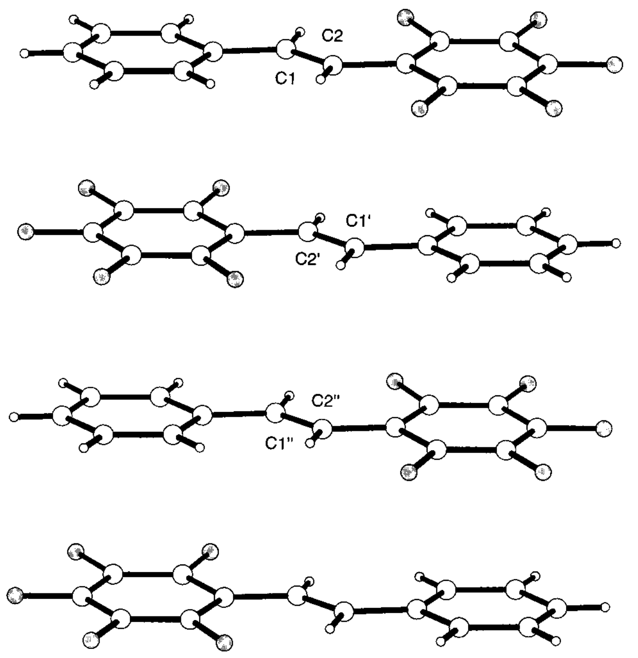


Figure 3. Molecular packing diagram of the *trans*-pentafluorostilbene (**7**). The fluorine atoms are shaded.

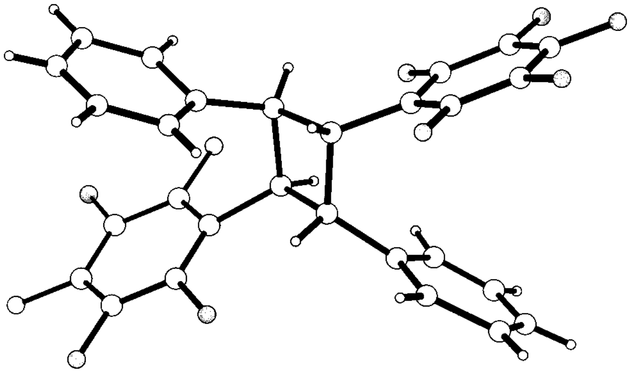
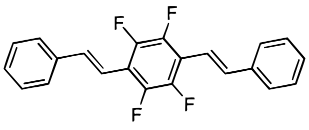


Figure 4. Molecular structure of cyclodimer **8** from the photolysis of *trans*-pentafluorostilbene (**7**). The fluorine atoms are shaded.

yield. Photodimerization reactions typically give less than 100% yields, which has been attributed to olefins that are isolated between cyclobutane molecules in the crystal matrix. Therefore for evenly spaced olefin stacks in the crystal, the theoretical maximum yield is $1 - 1/e^2 = 86.5\%$.[58] From the X-ray structure of **7**, it can be seen that the molecules essentially pack in pairs, explaining the quantitative yield of photodimer **8**. However in the structure of **4•5**, the molecules are not packed in pairs, but are packed in perfectly spaced stacks. At the current time, it is not clear why this photodimerization proceeds in quantitative yield. Possible explanations include the following: perturbation of the olefin spacing following reactions of adjacent olefins; an equilibration between isolated olefins and the cyclodimer; and a heterogeneous photodimerization process where the reaction occurs unevenly from the outside of the crystal inward (along the stacking axis).

Photopolymerization Reactions. In 1967 the first topochemical photopolymerization of a diolefinic molecule was reported. Subsequently, many studies have revealed that the geometrical parameters that dictate reactivity in diolefin systems (parallel alkenes, $d < 4.2$ Å) are the same as those of the monoalkenes (Scheme 1). To determine whether the phenyl−perfluorophenyl interaction could be used to design crystals for photocycloaddition polymerizations, diolefins containing these groups were synthesized and their photoreactivity was investigated.

The packing of **7** in the solid state suggested that extension of this conjugated structure by the appropriate type of styryl group might yield a diolefin capable of photopolymerization. Two such molecules are possible: *trans*,*trans*-1,4-bis(2-phenylethenyl)-2,3,5,6-tetrafluorobenzene (**9**) and *trans*, *trans*-1,4-bis(2-pentafluorophenylethenyl)benzene (**10**). Dienes **9** and **10** were synthesized by a Heck coupling of the corresponding 1,4-diiodobenzenes and styrenes. Compound **9** is a colorless, crystalline solid, while **10** forms very light-green crystals.



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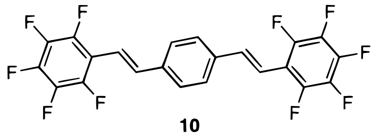

10

Photolysis of **9** for 20 h yielded a white powder that was virtually insoluble in typical organic solvents. Extraction of the solid with boiling toluene gave a soluble fraction (15%); gel-permeation chromatography revealed that this soluble material was composed of oligomers of **9** (predominantly dimer to tetramer). Presumably, the main insoluble fraction (85%) consists of higher molecular weight polymer. ^{1}H NMR spectroscopy demonstrated that the shifts of the cyclobutane protons of the soluble product closely matched those of model compound **8**, suggesting that **9** packs in slanted stacks as depicted in Scheme 1. Single-crystal X-ray structure analysis confirmed this hypothesis (Figure 5). Molecules of **9** are positioned on centers of inversion; therefore all reacting olefins are equally spaced in the crystal. The distance between reactive olefins is 3.823 Å (C1−C2′), and the angles between reactive carbon atoms are 76.4°(C1−C2−C1′) and 103.6° (C2−C1−C2′).

Diolefin **10** was found to be completely photostable, even after photolysis for 24 h. An X-ray structural analysis of **10** (Figure 6) revealed that although the molecules pack in slanted stacks, the olefin separation is 4.86 Å (C1−C2′). This distance is clearly too large for an allowed photochemical reaction. It is unknown why **10** packs in this unanticipated geometry, although it should be mentioned that the stacking is structurally related to the low-energy, parallel-slipped benzene dimer.[59]

Molecular pairs that have complementary arrangements of fluorinated/nonfluorinated aromatic groups typically form cocrystals, where the molecules pack alternately in well-ordered stacked columns. For example, the mated molecular couples benzene/hexafluorobenzene,[43] naphthalene/octafluoronaphthalene,[60] biphenyl/decafluorobiphenyl,[61] *trans*-stilbene/*trans*-decafluoroazobenzene,[62] **4**/**5**, and diphenyldiacetylene/decafluo-

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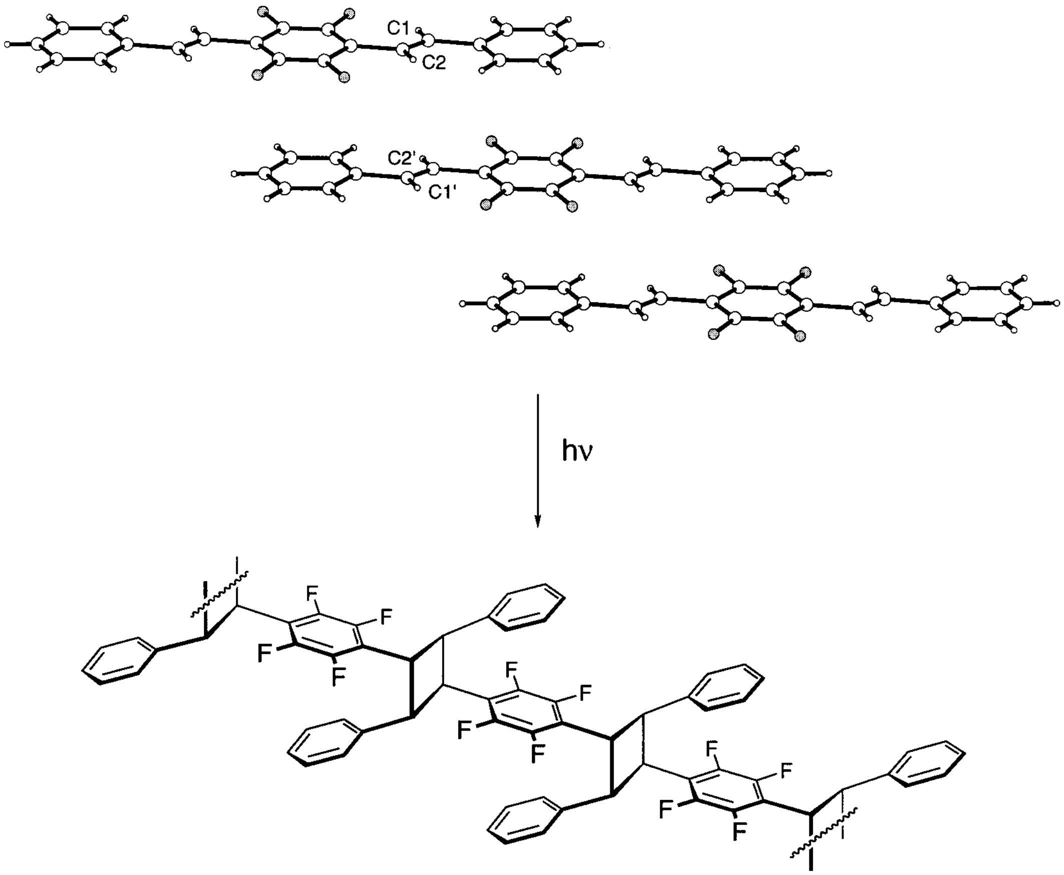

Figure 5. Molecular packing diagram of diolefin **9** (the fluorine atoms are shaded) and the proposed structure of poly(**9**).

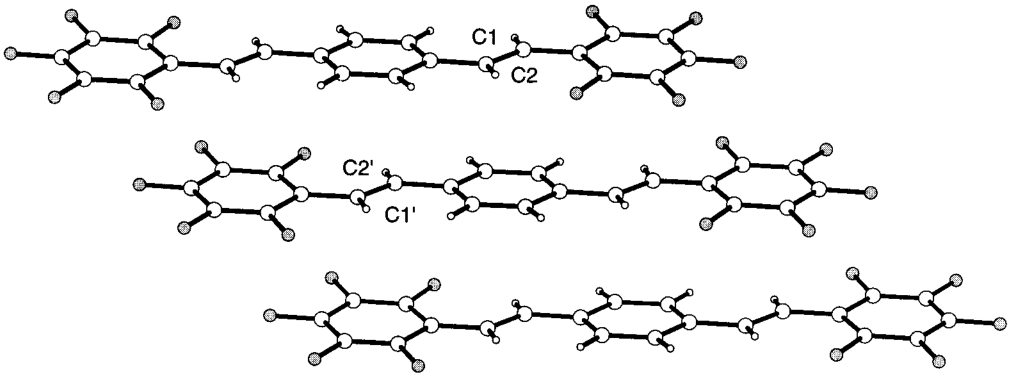

Figure 6. Molecular packing diagram of diolefin **10**. The fluorine atoms are shaded.

rodiphenylacetylene[54] pack in alternating layers of molecules. Since dienes **9** and **10** exhibit complementary electrostatic surfaces, the cocrystallization of these two molecules was explored. Compounds **9** (mp 216 °C) and **10** (mp 208 °C) (1:1 solution in tetrahydrofuran) were cocrystallized by solvent evaporation. ^{1}H NMR revealed that the resultant fine, light green needles (mp 227 °C) contained a 1:1 ratio of **9**:**10**. Photolysis of **9•10** for 20 h gave a polymeric product in quantitative yield. The soluble fraction (67% in boiling toluene) was analyzed by gel permeation chromatography, which confirmed the presence of oligomers. ^{1}H NMR spectroscopy revealed an average degree of polymerization of 22, and that the shifts of the cyclobutane protons closely matched those of model compound **8**. Based on this information alone, we propose that the **9•10** cocrystal consists of columns of alternate molecules, which yields a zigzag type polymer structure[63] upon photolysis (Figure 7). Crystals of the **9•10** cocrystal suitable for X-ray analysis have not yet been obtained.

Cocrystallization of *trans,trans*-1,4-Bis(2-pentafluorophenylethenyl) benzene with Aromatic Solvents. 2,3,4,5,6-Pentafluorobiphenyl,[64] 2,3,4,5,6-pentafluorodiphenylacetylene,[65] 2,3,4,5,6-pentafluorodiphenyldiacetylene,[54] **7**, and the cocrystals listed in the previous section are all known to stack in columns of alternating phenyl−perfluorophenyl groups. One common trait to each of these compounds is the 1:1 ratio of H_5-phenyl: F_5-phenyl groups in these structures. One noticeable feature of photostable diene **10** is the uneven ratio (2:1) of fluorinated arene groups to nonfluorinated arene groups. Therefore, the augmentation of the hydrocarbon arene component of **10** was explored by attempting cocrystallization with a variety of

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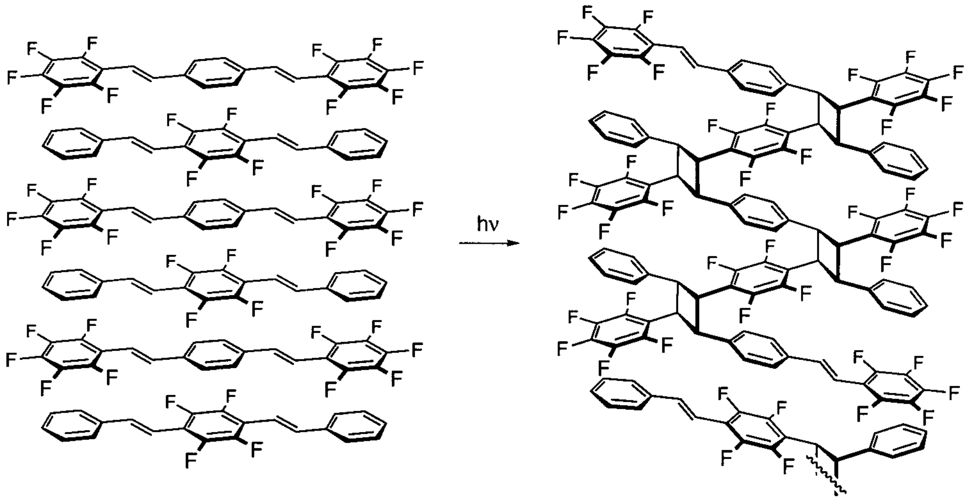

Figure 7. Proposed solid-state packing and polymerization stereochemistry of the **9•10** cocrystal.

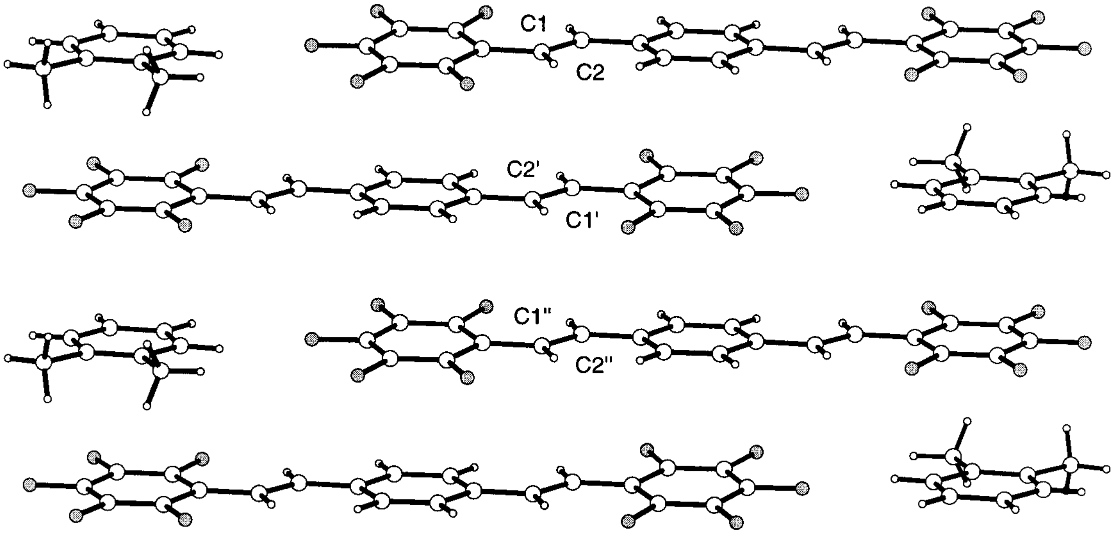

Figure 8. Molecular packing diagram of the cocrystal of **10** with *o*-xylene (**11**). The fluorine atoms are shaded.

unfluorinated aromatic solvents. Recrystallization of **10** from both benzene and toluene yielded photostable crystals with no included solvent. However recrystallization from *o*-xylene (**11**) produced a 1:1 cocrystal, which upon photolysis yielded a soluble cyclobutane product. X-ray structural analysis of the **10•11** cocrystal revealed a staggered, vertical stack of **10** where vacant spaces between the diene "bricks" are filled by *o*-xylene molecules (Figure 8). The angles between reactive olefin carbons in **10•11** are 73.0° (C1′−C2′−C1), 107.0° (C2′−C1′−C2), 80.0° (C2′−C1−C2″), and 99.9° (C1′−C2′−C1″), and the olefin−olefin separation is approximately 3.6 Å (3.638 Å (C1−C2′) and 3.598 Å (C2′−C1″)). An interesting feature of this structure is the edge-to-edge interaction between the para fluorine atom of **10** and the ortho hydrogen of the adjacent xylene (*d* = 2.47 Å). This intermolecular C−F···H−C interaction[66,67] was observed in the structures previously reported in this paper, and is common among structures that contain phenyl and pentafluorophenyl groups. [43,54]

Molecules of **10** are predisposed in the crystal for simple dimerization; however upon photolysis xylene loss decreases the yield and selectivity of the coupling reaction. The resultant product is virtually insoluble in ordinary organic solvents, suggesting that a rearrangement occurs during the reaction with xylene loss, allowing a photopolymerization of **10** to occur.

Conclusions

The current results indicate that the alternating, stacked phenyl−perfluorophenyl arrangement first seen in benzene−hexafluorobenzene is a general supramolecular motif. In monoolefinic and diolefinic systems, these aromatic associations orient the reactive olefinic moieties such that a photochemical cycloaddition reaction is possible (olefins parallel, separated by less than 4.2 Å). Of the seven crystalline olefinic materials investigated in this paper, all but one (diene **10**) undergoes the anticipated photochemical reaction. In this one exceptional case, the diene packs with a slipped-stacked orientation of the aromatic groups, which is known to be a fairly low energy interaction for the benzene dimer. In the other cases, the stereochemistry of the photoproduct and/or X-ray structural analysis of the olefinic precursors reveals the stacked interaction between phenyl and perfluorophenyl groups in the crystals. This face-to-face interaction of phenyl/perfluorophenyl groups appears to direct the geometry of crystallization to yield photoactive crystals. Due to the ease of incorporating phenyl and perfluorophenyl groups into molecules, we believe this novel intermolecular interaction will stimulate new developments in

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areas of science where the ability to control the solid-state geometry of molecules is important.

Experimental Section

General Considerations. All manipulations involving olefin or diolefin synthesis were performed with Schlenk line techniques. Tripropylamine was dried over activated 4 Å molecular sieves, toluene and tetrahydrofuran were passed over solvent purification columns,[68] styrene and 2,3,4,5,6-pentafluorostyrene were passed over a 2 cm plug of silica gel immediately prior to use, and other reagents and solvents were purchased from Aldrich and used as received.

^{1}H and ^{19}F NMR spectra were obtained on a JEOL GX400 spectrometer; ^{13}C NMR spectra were recorded with a General Electric QE−300 spectrometer. Gel permeation chromatography was performed by using an Altex Model 110A pump, an American Polymer Standards Am Gel column (10 μm linear porosity) with chromatography grade CH_2Cl_2 as eluent, and a Kratos Spectroflow 757 UV absorbance detector. Gas chromatography/mass spectroscopy was performed on a Hewlett-Packard 5890A gas chromatograph coupled with a Hewlett-Packard 5970 Series Mass Selective Detector. Low- and high-resolution mass spectra were obtained at the Chemistry and Biology Mass Spectrometry Facility at Caltech or at the Southern California Mass Spectrometry Facility at the University of California, Riverside.

Polymerization reactions were carried out in quartz or Pyrex reaction tubes under argon with use of a quartz-jacketed 450 W Hanovia medium-pressure mercury vapor lamp at ambient temperature.

Procedures: 1•2 Cocrystal. *trans*-Cinnamic acid (**1**, 1.00 g, 6.75 mmol) and *trans*-2,3,4,5,6-pentafluorocinnamic acid (**2**, 1.61 g, 6.75 mmol) were dissolved in 8 mL of hot absolute ethanol. The solution was allowed to cool slowly to room temperature, during which fine white crystals were formed. After crystallizing overnight, the cocrystals were collected by filtration over a medium pore frit, then dried in vacuo to give **1•2** (2.45 g, 94%). ^{1}H NMR confirmed a 1:1 ratio of **1•2**. Mp 169−171 °C.

1α,2α,3*β*,4*β*-3-Pentafluorophenyl-4-phenyl-1,2-cyclobutanedicarboxylic Acid (3) from the Photolysis of 1•2. Crystals of **1•2** (20.0 mg, 0.0517 mmol) were placed in a quartz reaction tube and photolyzed for 7 h at ambient temperature. ^{1}H NMR spectroscopy revealed unreacted **1•2** (13%) and the cyclodimer **3** (87%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.5 (br, s, 1H), 7.22 (m, 3H), 7.05 (m, 2H), 4.77 (m, 1H), 4.36 (m, 2H), 4.05 (m, 1H); ^{13}C NMR {^{1}H} ($CDCl_3$, 100 MHz) δ 36.6, 41.9, 44.3, 44.5, 126.0, 126.5, 128.5, 137.3, 178.6, 179.1, and a series of broad peaks in the aromatic region (Ar C−F); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376.5 MHz) δ −141.6, −156.4, −163.2; variable-temperature ^{19}F NMR data: coalescence temperature 223 K, $\Delta\nu$ = 1530 Hz for the ortho fluorine shifts at 213 K; MS *m/z* (MH^+) calcd for $C_{18}H_{12}F_5O_4$ 387.07, found 387.1.

Dehydration of 3. Crude **3** (17 mg, 0.044 mmol) was dissolved in $CDCl_3$ (1 mL) and ca. 50 mg of P_2O_5 was added. The solution was briefly heated to boiling, then allowed to sit overnight. The solution was decanted from the excess P_2O_5 and analyzed by NMR: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.2 (m, 5H), 4.59 (m, 1H), 4.49 (m, 1H), 4.23 (m, 1H), 4.12 (m, 1H); MS *m/z* (MH^+) calcd for $C_{18}H_{10}F_5O_3$ 369.06, found 369.1.

***trans*-Decafluorostilbene (5).** Compound **5** was synthesized with use of a modified literature preparation.[69] Triphenylphosphine (1.01 g, 3.85 mmol) and 2,3,4,5,6-pentafluorobenzylbromide (0.59 mL, 1.01 g, 3.90 mmol) were measured into a dry 100 mL Schlenk flask under argon. The reactants were dissolved in 25 mL of dry toluene and refluxed for 90 min, resulting in an air-stable white powder upon filtration (1.22 g, 61%). The phosponium salt (1.06 g, 2.02 mmol) was dissolved in 40 mL of dry THF and deprotonated with KO^{t}Bu (0.215 g, 1.92 mmol) over 4.5 h. Next, pentafluorobenzaldehyde (0.380 g, 1.94 mmol) was added to the reaction mixture, which was then stirred at room temperature for 14 h. The reaction mixture was then quenched with several drops of distilled H_2O and diluted with 100 mL of Et_2O. The organic layer was washed three times with 50 mL of 1 M HCl and dried over $MgSO_4$. The organic phase was concentrated under reduced pressure and purified by column chromatography (silica gel/hexanes) yielding **5** as a white, fluffy powder (0.560 g, 81%). Spectral data and physical properties matched those reported in the literature:[69] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 (s, 2H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376.5 MHz) δ −141.7, −153.4, −161.9; MS *m/z* (MH^+) calcd for $C_{14}H_2F_{10}$ 359.9997, found 359.9998; mp 103 °C.

4•5 Cocrystal. *trans*-Stilbene (**4**) and *trans*-decafluorostilbene (**5**) (1:1) were cocrystallized from a saturated, hot absolute ethanol solution. The solution was allowed to cool slowly to room temperature, during which colorless, transparent crystals were formed. After crystallizing overnight, the cocrystals were collected by filtration over a medium pore frit, then dried in vacuo to give **4•5**. ^{1}H NMR confirmed a 1:1 ratio of **4•5**. Mp 139 °C.

1α,2*β*,3*β*,4α-1,2-Bis(pentafluorophenyl)-3,4-diphenylcyclobutane (6) from the Photolysis of 4•5. Crystals of **4•5** were placed in a quartz reaction tube and photolyzed for 5 h at ambient temperature. ^{1}H NMR revealed quantitative conversion to cyclodimer **6**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21 (m, 10 H), 5.09 (d, J = 9.1 Hz, 2 H), 4.551 (d, J = 9.1 Hz, 2 H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376.5 MHz) δ −142.1, −155.5, −162.2; variable-temperature ^{19}F NMR data: coalescence temperature 230 K, $\Delta\nu$ = 1930 Hz for the ortho fluorine shifts at 213 K; MS *m/z* $(M - H)^+$ calcd for $C_{28}H_{13}F_{10}$ 539.0857, found 539.0876.

***trans*-2,3,4,5,6-Pentafluorostilbene (7).** Compound **7** was synthesized with use of a modified literature preparation.[70] Tripropylamine (4.0 mL) and pentafluorostyrene (2.34 g, 12.0 mmol) were separately filtered over silica and then combined with iodobenzene (2.45 g, 12.0 mmol) in a 10 mL Schlenk tube. Palladium acetate (27.8 mg, 0.124 mmol) was added to the solution and the mixture was freeze−pump−thawed twice under argon. The reaction mixture was heated to 100 °C for 20 h. During this time a white precipitate formed and the solution turned red. The reaction mixture was cooled to room temperature and diluted with Et_2O (100 mL) and DI H_2O (50 mL). The aqueous phase was washed with Et_2O (50 mL). The combined organic fractions were washed twice with DI H_2O (25 mL) and once with 1 M HCl (25 mL). The solvent was then removed from the organic phase under reduced pressure yielding a light yellow solid. Chromatography (SiO_2/hexanes) afforded **7** as a white solid (1.70 g, 52.4%). Spectral data and physical properties matched those reported in the literature:[70] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.99 (d, J = 16.8 Hz, 1 H), 7.36 (m, 2 H), 7.50 (d, J = 16.8, 1 H), 7.55 (m, 3 H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376.5 MHz) δ −142.6, −156.4, −162.9; MS *m/z* (M^+) calcd for $C_{14}H_7F_5$ 270.0466, found 270.0468; mp = 138 °C.

1α,2α,3*β*,4*β*-1,3-Bis(pentafluorophenyl)-2,4-diphenylcyclobutane (8) from the Photolysis of 7. Crystals of **7** were placed in a quartz reaction tube and photolyzed for 24 h at ambient temperature. ^{1}H NMR revealed quantitative conversion to cyclodimer **8**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.88 (m, 4 H), 7.2 (m, 10 H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376.5 MHz) δ −141.2, −155.7, −162.4; variable-temperature ^{19}F NMR data: coalescence temperature 218 K, $\Delta\nu$ = 1235 Hz for the ortho fluorine shifts at 213 K; MS *m/z* (M^+) calcd for $C_{28}H_{14}F_{10}$ 540.0936, found 540.0937, 270.0 (from cyclobutane fragmentation); mp = 118 °C.

***trans,trans*-1,4-Bis(2-phenylethenyl)-2,3,5,6-tetrafluorobenzene (9).** Tripropylamine (3.0 mL) and styrene (1.76 g, 16.9 mmol) were separately filtered over silica and then combined with 1,4-diiodotetrafluorobenzene (3.40 g, 8.46 mmol) in a 10 mL Schlenk tube. Palladium acetate (37.9 mg, 0.169 mmol) was added to the solution and the mixture was freeze−pump−thawed twice under argon. The reaction mixture was heated to 100 °C for 20 h. During the course of the reaction the reaction mixture turned brown. The reaction mixture was cooled to room temperature, causing a white solid to precipitate, and diluted with Et_2O (800 mL) and 1 M HCl (100 mL). The organic fraction was washed with 1 M HCl (100 mL) and solvent was then removed in vacuo. Chromatography (SiO_2/hexanes, ethyl acetate) afforded **9** as a white solid, which was recrystallized from a saturated chloroform solution (0.567 g, 18.9%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09 (d, J = 16.8 Hz, 2 H), 7.32 (m, 2 H), 7.39 (m, 4 H), 7.51 (d, J =

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16.8 Hz, 2 H), 7.55 (m, 4 H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376.5 MHz) δ −144.4; MS *m/z* (M^+) calcd for $C_{22}H_{14}F_4$ 354.1032, found 354.1044; mp = 216 °C.

Photopolymerization of 9. Crystals of **9** (43 mg) were placed in a Pyrex reaction tube under argon and photolyzed for 20 h at ambient temperature. The resulting white powder was extracted with 100 mL of refluxing toluene, yielding 6.5 mg of soluble material upon filtration (15% yield). This soluble fraction was analyzed by NMR: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.75 (m, ca. 8 H), 7.15 (m, ca. 20 H), 7.35 (m, ca. 6 H), 7.50 (m, ca. 4 H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376.5 MHz) δ −142.6, −143.1, −144.1. Gel-permeation chromatography showed that oligomers were present.

***trans*, *trans*-1,4-Bis(2-pentafluorophenylethenyl)benzene (10).** Compound **10** was synthesized with use of a modified literature preparation.[70] Tripropylamine (12.0 mL) and pentafluorostyrene (3.97 g, 20.5 mmol) were separately filtered over silica and then combined with toluene (30 mL) and 1,4-diiodobenzene (3.25 g, 9.85 mmol) in a 100 mL Schlenk tube. Palladium acetate (50.2 mg, 0.224 mmol) was added to the solution and the mixture was freeze−pump−thawed twice under argon. The reaction mixture was heated to 100 °C for 20 h. During the course of the reaction a large amount of white precipitate formed. The reaction mixture was cooled to room temperature, causing a white solid to precipitate, and diluted with Et_2O (600 mL) and DI H_2O (300 mL). The organic fraction was washed with 1 M HCl and solvent was then removed in vacuo, giving a reddish-brown solid. The crude product was washed with CH_2Cl_2, giving a pale yellow-green solid which was dissolved in tetrahydrofuran and passed over a short column of silica gel. Removal of solvent in vacuo yielded **10** (2.40 g, 52.7%). Spectral data and physical properties matched those reported in the literature:[71] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.03 (d, *J* = 16.8 Hz, 2 H), 7.44 (d, *J* = 16.8 Hz, 2 H), 7.56 (s, 4 H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376.5 MHz) δ −142.4, −155.9, −162.6; MS *m/z* (M^+) calcd for $C_{22}H_8F_{10}$ 462.0466, found 462.0458; mp = 208 °C.

Attempted Photolysis of 10. Crystals of **10** grown from benzene, tetrahydrofuran, ethanol, CH_2Cl_2/hexanes, and chloroform were determined to be completely photostable by ^{1}H NMR.

9•10 Cocrystal. Dienes **9** and **10** (1:1) were cocrystallized from a saturated, hot mixture of toluene and ethanol (40:60). The solution was allowed to cool slowly to room temperature, during which very fine, light green needles were formed. After crystallizing overnight, the cocrystals were collected by filtration over a medium pore frit, then dried in vacuo to give **9•10**. ^{1}H NMR confirmed a 1:1 ratio of **9•10**. Mp 227 °C.

Photopolymerization of 9•10. Crystals of **9•10** (145 mg) were placed in a quartz reaction tube and photolyzed for 20 h at ambient temperature. The resulting white powder was extracted with 100 mL of refluxing toluene, yielding 97 mg of soluble material upon filtration (67% yield). This soluble fraction was analyzed by ^{1}H NMR. A broad multiplet at 4.75 ppm attributable to protons attached to the cyclobutane ring was present, consistent with the cyclobutane shifts of **8**. Integration of the olefin and cyclobutane resonances yielded an average degree of polymerization of 22. In addition, gel permeation chromatography showed the presence of multiple oligomers.

10•11 Cocrystal. Diene **10** was recrystallized from a hot, saturated solution of *o*-xylene. Thin, light-green plates were formed. ^{1}H NMR confirmed a 1:1 ratio of **10•11**. A melting point could not be measured due to evaporative loss of xylene during the measurement.

Photolysis of 10•11. Crystals of **10•11** were placed in a quartz reaction tube under argon with some *o*-xylene solvent and were photolyzed for 10 h. Over the course of the reaction, the crystals turned from light green to a white powder. This photolysis product is practically insoluble in typical organic solvents; however a^{1}H NMR spectrum of a small soluble fraction showed a multiplet at 4.75 ppm, indicative of the formation of a cyclobutane ring. Further attempts to analyze this product by NMR and mass spectroscopy were unsuccessful.

Single-Crystal X-ray Diffraction Analysis of 4•5. Crystal structure data for **4•5** (single crystal from ethanol): formula $C_{28}H_{14}F_{10}$, *M* = 540.40, crystal dimensions 0.60 × 0.15 × 0.07 mm, triclinic, space group $P\bar{1}$, *a* = 6.0932(7) Å, *b* = 7.5325(9) Å, *c* = 12.5669(15) Å, α = 97.186(2)°, β = 92.450(2)°, γ = 93.592(3)°, *V* = 570.38(12) Å^3, *Z* = 2, ρ_{calcd} = 1.573 g cm^{-3}, $2\theta_{max}$ = 41.02°, *T* = 293 K. SMART CCD Area Detector System (Mo Kα, λ = 0.71073 Å) frames were integrated with the Siemens SAINT program to yield a total of 1977 reflections, of which 1173 were independent (R_{int} = 3.10%) and 851 were above $4\sigma(F)$. Data were corrected for absorption with the SADABS program. Structure solution and refinement: direct methods (SHELXS-86),[72] full-matrix least-squares refinement on F^2,[73] using anisotropic displacement parameters for all non-hydrogen atoms, 172 parameters, R1 = 0.0542, *w*R2 = 0.1330 with $I > 2\sigma(I)$, R1 = 0.0761, *w*R2 = 0.1482 for all data, $\Delta\rho_{max}$ = 0.164 e Å^{-3}, $\Delta\rho_{min}$ = −0.226 e Å^{-3}.

Single-Crystal X-ray Diffraction Analysis of 7. Crystal structure data for **7** (single crystal from diethyl ether/ethanol): formula $C_{14}H_7F_5$, *M* = 270.20, crystal dimensions 0.17 × 0.37 × 0.41 mm, triclinic, space group $P\bar{1}$, *a* = 6.058(2) Å, *b* = 7.329(3) Å, *c* = 12.386(5) Å, α = 85.71(4)°, β = 87.60(3)°, γ = 86.39(3)°, *V* = 546.9(4) Å^3, *Z* = 2, ρ_{calcd} = 1.641 g cm^{-3}, $2\theta_{max}$ = 56°, CAD-4 diffractometer (Mo Kα, λ = 0.7107 Å, graphite monochromator), ω scan, *T* = 160 K, 5431 measured reflections, all 2633 independent reflections used in the refinement, Lorentz and polarization factors were applied, μ = 1.54 cm^{-1}. Structure solution and refinement: direct methods (SHELXS-86),[72] full-matrix least-squares refinement of F^2 (CRYM),[74] 200 parameters, hydrogen atoms were refined isotropically, *R* = 0.036 with $F_o^2 > 3\sigma(F_o^2)$ and 0.044 with $F_o^2 > 0$, *wR* = 0.083, $\Delta\rho_{max}$ = 0.31 e Å^{-3}, $\Delta\rho_{min}$ = −0.29 e Å^{-3}.

Single-Crystal X-ray Diffraction Analysis of 8. Crystal structure data for **8** (single crystal from pentane): formula $C_{28}H_{14}F_{10}$, *M* = 540.39, crystal dimensions 0.60 × 0.50 × 0.30 mm, monoclinic, space group $P2_1$, *a* = 12.888(3) Å, *b* = 15.828(3) Å, *c* = 13.117(3) Å, β = 116.81(3)°, *V* = 2388.1(8) Å^3, *Z* = 4, ρ_{calcd} = 1.503 g cm^{-3}, $2\theta_{max}$ = 41.54°, *T* = 293 K. SMART CCD Area Detector System (Mo Kα, λ = 0.71073 Å), frames were integrated with the Siemens SAINT program to yield a total of 8263 reflections, of which 3887 were independent (R_{int} = 5.62%) and 2879 were above $4\sigma(F)$. Data were corrected for absorption with the SADABS program. Structure solution and refinement: direct methods (SHELXS-86),[72] full-matrix least-squares refinement on F^2,[73] using anisotropic displacement parameters for all non-hydrogen atoms, 696 parameters, R1 = 0.1233, *w*R2 = 0.3289 with $I > 2\sigma(I)$, R1 = 0.1453, *w*R2 = 0.3598 for all data, $\Delta\rho_{max}$ = 0.650 e Å^{-3}, $\Delta\rho_{min}$ = −0.371 e Å^{-3}.

Single-Crystal X-ray Diffraction Analysis of 9. Crystal structure data for **9** (single crystal from chloroform): formula $C_{22}H_{14}F_4$, *M* = 354.33, crystal dimensions 0.50 × 0.05 × 0.03 mm, monoclinic, space group $P2_1/c$, *a* = 7.8076(11) Å, *b* = 5.8086(8) Å, *c* = 18.291(3) Å, α = 90°, β = 97.10(2)°, γ = 90°, *V* = 823.2(2) Å^3, *Z* = 2, ρ_{calcd} = 1.430 g cm^{-3}, $2\theta_{max}$ = 49.54°, *T* = 173(1) K. SMART CCD Area Detector System (Mo Kα, λ = 0.71073 Å), frames were integrated with the Siemens SAINT program to yield a total of 3788 reflections, of which 1408 were independent (R_{int} = 6.51%). Data were corrected for absorption with the SADABS program. Structure solution and refinement: direct methods (SHELXS-86),[72] full-matrix least-squares refinement on F^2,[73] using anisotropic displacement parameters for all atoms, 696 parameters, R1 = 0.0620, *w*R2 = 0.1397 with $I > 2\sigma(I)$, R1 = 0.1289, *w*R2 = 0.1953 for all data, $\Delta\rho_{max}$ = 0.285 e Å^{-3}, $\Delta\rho_{min}$ = −0.271 e Å^{-3}.

Single-Crystal X-ray Diffraction Analysis of 10. Crystal structure data for **10** (single crystal from toluene): formula $C_{22}H_8F_{10}$, *M* = 462.28, crystal dimensions 0.04 × 0.24 × 0.26 mm, monoclinic, space group $P2_1/c$, *a* = 4.8334(9) Å, *b* = 6.1473(8) Å, *c* = 29.262(4) Å, α = 90°, β = 91.191(13)°, γ = 90°, *V* = 869.3(2) Å^3, *Z* = 2, ρ_{calcd} = 1.766 g cm^{-3}, θ_{max} = 27.50°. A Siemens P4 diffractometer was used (Mo Kα, λ = 0.71073 Å, graphite monochromator). The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's

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[74] Duchamp, D. J., American Crystallographic Association Meeting, Bozeman, Montana, 1964; paper B14, pp 29−30.

orientation matrix was carried out according to standard procedures.[75] Intensity data were collected with use of a $2\theta/\omega$ scan technique, $T = 158$ K. The raw data were processed with a local version of CARESS[76] which employs a modified version of the Lehman−Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. Subsequent calculations were carried out by using the SHELXTL program.[77] All 2218 data were corrected for Lorentz and polarization effects and were placed on an approximately absolute scale.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis.[78] The molecule is located about an inversion center. Hydrogen atoms were located from a difference Fourier map and refined (x, y, z and U_{iso}). At convergence, $wR2 = 0.1718$ and GOF = 1.068 for 162 variables refined against all 1988 unique data (as a comparison for refinement on F, $R1 = 0.0591$ for those 1309 data with $F > 4.0\sigma(F)$).

Single-Crystal X-ray Diffraction Analysis of 10•11. Crystal structure data for **10•11** (single crystal from *o*-xylene): formula $C_{30}H_{18}F_{10}$, $M = 568.46$, crystal dimensions 0.30 × 0.46 × 0.55 mm, triclinic, space group $P\bar{1}$, $a = 7.220(4)$ Å, $b = 7.926(3)$ Å, $c = 23.118(13)$ Å, $\alpha = 83.25(4)°$, $\beta = 83.94(5)°$, $\gamma = 67.11(4)°$, $V = 1207.7(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.563$ g cm^{-3}, $2\theta_{max} = 50°$, CAD-4 diffractometer (Mo Kα, $\lambda = 0.7107$ Å, graphite monochromator), ω scan, $T = 160$ K, 9381 measured reflections, 4238 independent reflections used in the refinement, Lorentz and polarization factors were applied, $\mu = 1.44$ cm^{-1}. Structure solution and refinement: direct methods (SHELXS-86),[72] full-matrix least-squares refinement of F^2 (CRYM),[74] 433 parameters, hydrogen atoms were refined isotropically, $R = 0.054$ with $F_o^2 > 3\sigma(F_o^2)$, 0.064 with $F_o^2 > 0$, $wR = 0.119$, $\Delta\rho_{max} = 0.34$ e Å^{-3}, $\Delta\rho_{min} = -0.43$ e Å^{-3}.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **4·5**, **7**, **8**, **9**, **10**, and **10·11** (62 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(75) *XSCANS Software Users Guide, Version 2.1;* Siemens Industrial Automation, Inc.; Madison, WI, 1994.

(76) Broach, R. W., Argonne National Laboratory, Illinois, 1978.

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