

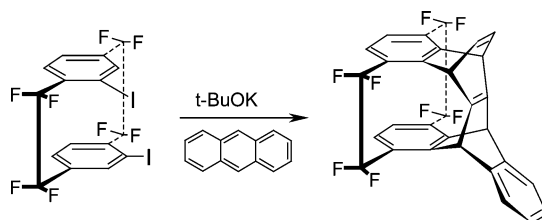
A Highly Pyramidalized Cage Alkene Formed via the Double Diels–Alder Cycloaddition of *syn*-4,5,13,14-Bis(dehydro)octafluoroparacyclophane to Anthracene

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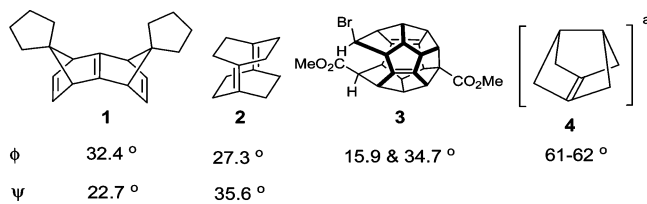
A double Diels–Alder reaction of the formal *syn*-bis(dehydro)octafluoroparacyclophane with anthracene leads to formation of a novel cage compound that contains a highly pyramidal double bond. The measures of pyramidalization of this double bond constitute what appear to be the highest combined values of ψ and ϕ (34.3° and 33.5°, respectively) yet reported to have been determined by X-ray crystallography. This cage compound, although stable indefinitely as a crystalline compound in air, exhibits the high reactivity with both triplet and singlet O₂ in solution that is characteristic of such highly pyramidal π systems.

Introduction

During the course of our investigation of the scope of the Diels–Alder chemistry of bis(dehydro)octafluoro[2.2]-paracyclophanes,¹ the potential of preparing cage compounds via the double Diels–Alder cycloadditions of the *syn*-bis(dehydro)octafluoro[2.2]paracyclophane to appropriate dienes was considered. As will be reported in the present paper, it has indeed been possible to prepare such a surprisingly stable cage compound containing a highly pyramidalized double bond with such strategy.

Pyramidal Alkenes. Pyramidalized alkenes are molecules that contain a double bond in which the two π -carbons and their four substituents are not coplanar.² Such nonplanarity can derive simply from a combination of strain and unsymmetric steric effects, as in the case of Paquette’s *syn*-sesquinorbornatriene (**1**),³ or it can derive from the geometric constraints of polycyclic olefins such as Wiberg’s tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (**2**),⁴ Prinzbach’s substituted *seco*-diene (**3**),⁵ or Camps’ tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene (**4**),^{6,7} as shown in Scheme 1. All

SCHEME 1. Some Representative Highly Pyramidalized Alkenes



^a Formed and reacted in situ, structure parameters calculated.

four of these compounds contain double bonds that are significantly, and (for compounds **1**, **2**, and **4**) because of their symmetry, identically pyramidalized *syn* at the affected alkene carbon atoms. The structures of **1–3** were determined by X-ray crystal analysis, but because of its great reactivity, that of **4** has only been determined computationally. There are two commonly used measures of the degree of pyramidalization of such carbon atoms.^{2,8} The first, designated ϕ , is called the *pyramidalization*

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(2) Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095–1109.

(3) Paquette, L. A.; Shen, C.-C. *J. Am. Chem. Soc.* **1990**, *112*, 1159–1164.

(4) Wiberg, K. B.; Adams, R. D.; Okarma, P. J.; Matturro, M. G.; Segmuller, B. *J. Am. Chem. Soc.* **1984**, *106*, 2200–2206.

(5) Irngartinger, H.; Reifentahl, U.; Prinzbach, H.; Pinkos, R.; Weber, K. *Tetrahedron Lett.* **1990**, *31*, 5459–5462.

(6) Camps, P.; Font-Bardia, M.; Mendez, N.; Perez, F.; Pujol, X.; Solans, X.; Vazquez, S.; Vilalta, M. *Tetrahedron* **1998**, *54*, 4679–4696.

(7) Camps, P.; Luque, F. J.; Orozco, M.; Perez, F.; Vazquez, S. *Tetrahedron Lett.* **1996**, *37*, 8605–8608.

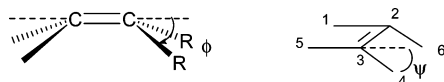
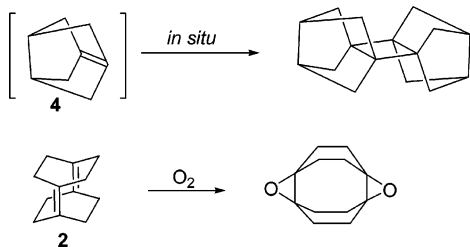


FIGURE 1. Definition of alkene pyramidalization parameters.

SCHEME 2. Characteristic Reactions of Pyramidalized Alkenes



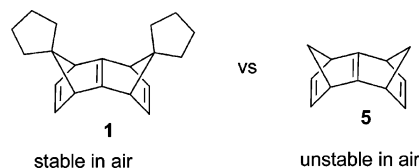
angle, and it is defined as the angle between the plane defined by one of the doubly bonded carbons and its two substituents (R) and the extension of the double bond. It can be readily calculated by use of the following formula: $\cos \phi = -\cos(R-C-C)/[\cos(1/2(R-C-R))]$. The other, designated ψ , is called the *butterfly bending angle* or *folding angle*, and it can be calculated from the dihedral angle, D , defined by the bonding sequence 1–2–3–4 in Figure 1 by the formula $\psi = 180 - |D|$. One generally must consider *both* of these criteria when evaluating the relative degree and the kinetic impact of pyramidalization of alkene systems, but Williams and Margetic⁸ have, we think, quite reasonably chosen ψ to be the single, most useful criterion for comparing double bond pyramidalizations.

The dodecahedralene **3** is claimed by the authors, on the basis of the 34.7° value for ϕ at the “closed” end of the double bonds, to have the “largest crystallographically determined pyramidalization of olefinic carbon” yet reported.^{5,9} However, data were not provided that would allow calculation of ψ values.

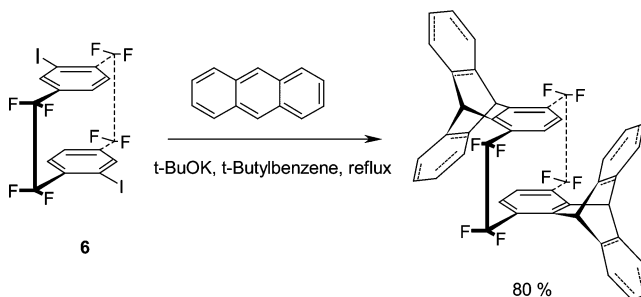
The reactivity of such distorted alkenes, as might be expected, is generally enhanced, with this reactivity being reflected by instability in air, rapid dimerization reactions, or in situ Diels–Alder reactions with various 1,3-dienes. For example, the formation of such distorted alkenes as **4** is deduced on the basis of the formation of its dimer, as shown in Scheme 2.⁷ The structural parameters of such highly reactive alkenes can only be estimated computationally, as was the case for **4**. Even those pyramidalized alkenes, such as **1**, **2**, and **3**, that have sufficient kinetic stability to allow X-ray characterization still exhibit unusual characteristic chemistry, such as their reaction with air in solution to form epoxides, as is exemplified by the reaction of **2** with O_2 .¹⁰

The kinetic stability of pyramidalized alkenes can be increased by the presence of steric shielding on the reactive plane of the double bond, as is exemplified by the contrasting stabilities of alkenes **1** and **5** in air (Scheme 3).³

SCHEME 3. Impact of Sterics on Kinetic Stability



SCHEME 4. Diels–Alder Chemistry of *anti*-Bis(dehydro)octafluoroparacyclophane



Thus, it has been possible for us to prepare a cage compound containing a highly pyramidalized double bond that is sufficiently kinetically stable to undergo full characterization by NMR and X-ray crystal analysis.

Diels–Alder Reactions of Bis(dehydro)octafluoro-[2.2]paracyclophanes. We recently have reported that double dehydroiodination of pseudo-para, 4,15-diiodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (**6**) under classic Cram conditions^{11,12} using potassium *tert*-butoxide as base in a nonpolar solvent led to surprisingly high yields of bis-Diels–Alder adducts with benzene, naphthalene, and anthracene (exemplified for anthracene in Scheme 4).¹ During the preparation of the pseudo-para diiodide (**6**) (generally used as a mixture of the pseudo-para and the pseudo-meta isomers, which will give the same bis-aryne), an equivalent (one-third) amount of the pseudo-ortho isomer (**7**) was also obtained as a matter of course.¹³ With this diiodide in hand, it seemed reasonable to see whether it could be used as a precursor of the “formal” *syn*-bis-aryne, which would have the potential to undergo a sequential, double Diels–Alder addition to anthracene to form the caged compound **8** (Scheme 5).

Indeed, we were gratified to find that the hypothesized reaction occurred, at least to a degree, as planned.

Results and Discussion

Formation of Cage Compound. When pseudo-ortho AF4-diiodide (**7**) was allowed to react with potassium *tert*-butoxide in refluxing dibutyl ether ($142^\circ C$) in the presence of 2 equiv of anthracene, the desired cage compound (**8**) was formed in 16% yield along with 34% of the monoanthracene adduct (**9**) (with the second iodide having been reduced) and a very small amount (4%) of a highly congested dianthracene adduct (**10**), as indicated in eq 1. All of the products were isolated by column chromatography, and the proton and carbon NMR as-

(8) Williams, R. V.; Margetic, D. *J. Org. Chem.* **2004**, *69*, 7134–7142.

(9) The ϕ values reported by the authors were slightly different (15.5° and 35.5° , respectively). However, when calculated with the bond angles provided in the paper, the values given in Scheme 1 were obtained.

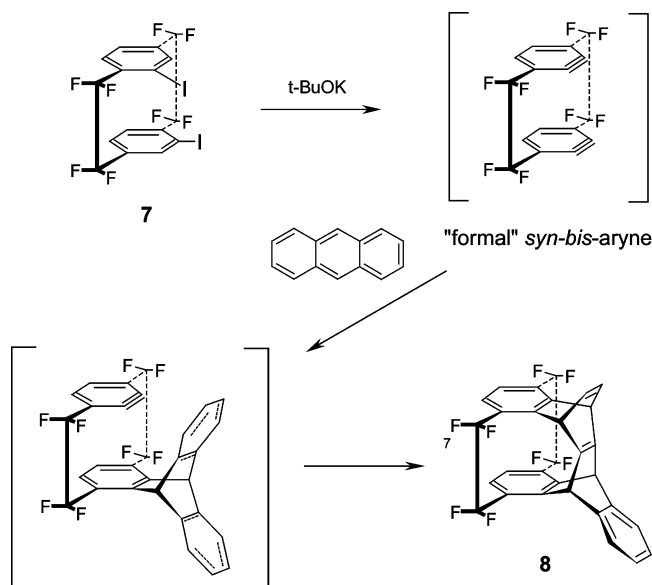
(10) Wiberg, K. B.; Matturro, M. G.; Okarma, P. J.; Jason, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 2194–2200.

(11) Cram, D. J.; Day, A. C. *J. Org. Chem.* **1966**, *31*, 1227–1232.

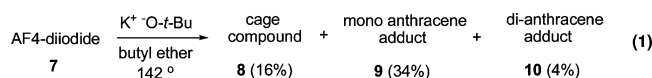
(12) Cadogan, J. I. G.; Hall, J. K. A.; Sharp, J. T. *J. Chem. Soc. C* **1967**, 1860–1862.

(13) Roche, A. J.; Dolbier, W. R., Jr. *J. Org. Chem.* **2000**, *65*, 5282–5290.

SCHEME 5



signments for **8** and **10** are given in Figure 2. Those for the **9** have already been reported.¹



It was found that, under the usual conditions of reaction ($\text{K}^+\text{-O-}t\text{-Bu}$ in refluxing butyl ether at 142 °C), the yield of cage compound (**8**) was highly irreproducible, but if the reaction was carried out with microwave heating, yields of **8** became reproducible in the 16–17% range. When carried out under microwave irradiation,¹⁴ an additional product (**11**) derived from trapping by *tert*-butoxide was observed in 10% yield.

The low yields of the cage compound can be attributed to various detrimental steric influences in the reaction: the steric impact of the remaining iodine on the anthracene addition to the initially formed aryne, the steric

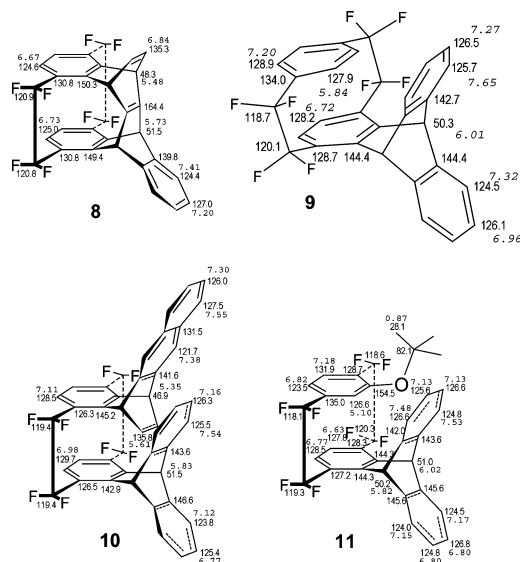
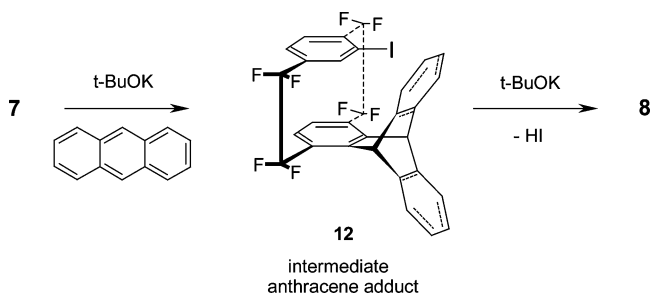


FIGURE 2. Proton and Carbon NMR Assignments for **8**, **9**, **10**, and **11**.

SCHEME 6



shielding imparted by the anthracene in the intermediate adduct (**12**), and the steric impact of the *tert*-butoxide base upon its ability to eliminate the second HI from **12** (Scheme 6).

Structure of Cage Compound. The structure of cage compound **8** was unambiguously determined by X-ray crystal analysis. An ORTEP drawing of **8** is given below (Figure 3), and a table of bond length and bond angle parameters is provided in the Supporting Information (Table S1). The pyramidalized double bond (C20–C29) has an almost normal bond length of 1.341(3) Å, just slightly longer than the normal double bond at C17–C18 in **8** (1.320(4) Å).

The degree of pyramidalization of the pyramidalized double bond can be defined by using the standard criteria discussed in the Introduction. With bond angles $\angle\text{C19-C20-C21} = 121.40^\circ$, $\angle\text{C19-C20-C29} = 113.75^\circ$, and $\angle\text{C21-C20-C29} = 114.42^\circ$, $\phi = 34.5^\circ$ and 32.4° , respectively. On the other side, $\angle\text{C28-C29-C30} = 121.86^\circ$, $\angle\text{C28-C29-C20} = 113.77^\circ$, and $\angle\text{C30-C29-C20} = 114.08^\circ$, yield $\phi = 34.0^\circ$ and 32.9° , respectively. The average ϕ thus equals 33.5° .

The dihedral angles, D , for C19–C20–C29–C28 and for C30–C29–C20–C21 are -145.7° , and $+145.8$, which yields values for ψ of 34.3° and 34.2° , respectively.

These values for ϕ and ψ indicate that the C20–C29 double bond of **8** is certainly among the most pyramidal

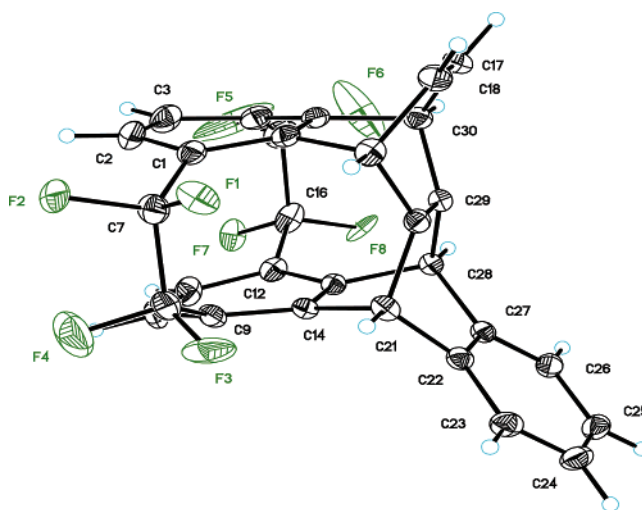
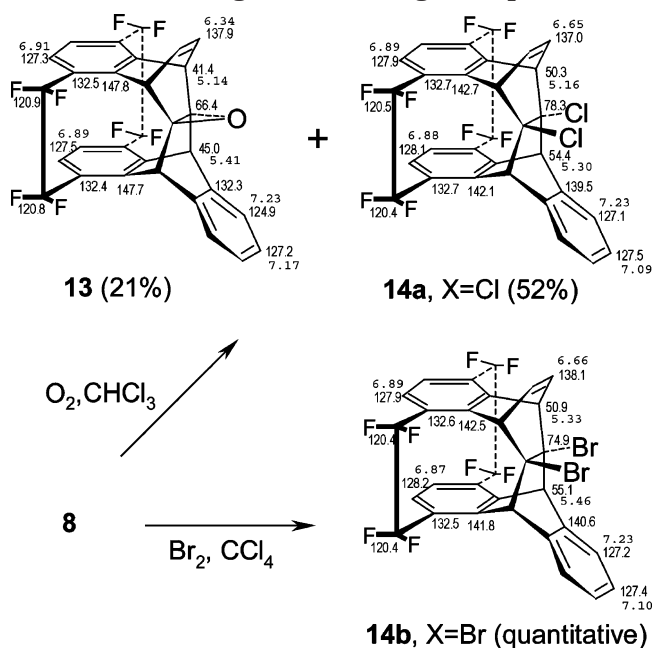


FIGURE 3. ORTEP drawing of cage compound **8**.

ever observed in a kinetically stable, X-ray characterized

(14) Lidstrom, P.; Tierney, J.; Wathey, B.; Westman, J. *Tetrahedron* 2001, 57, 9225–9283.

SCHEME 7. Halogenation of Cage Compound



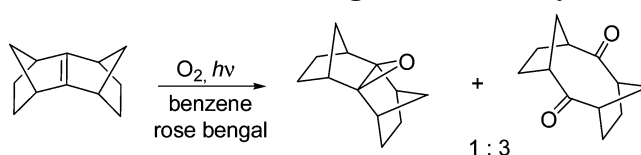
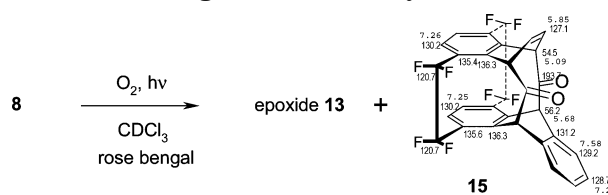
compound. Another indication of the degree of distortion of these carbons is their ^{13}C chemical shift, δ 164.4 ppm, which can be compared to the typical value of 127.3 ppm for the double bond carbon of 2,3-dimethyl-2-butene. The analogous ^{13}C δ values for other highly pyramidalized alkene compounds **1** and **3** are 172.0 and 172.2 ppm, respectively.^{3,15}

A peculiarity of the ^{19}F spectra of the cage compounds **8**, **13**, and **14a,b** is their large vicinal couplings (10–15 Hz), presumably a through space coupling between the exo fluorines, which for **8** are an average of 2.23 Å apart, compared to 2.41 Å for the endo fluorines, according to the X-ray structure.

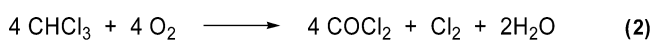
Reactivity of Cage Compound. When an NMR sample of cage compound **8** in CDCl_3 was allowed to stand at room temperature for 3 days, it was found that half of the sample had been converted to a single decomposition product, which was initially characterized by NMR (shift of the π carbon signal at 164.4 to a peak at 66.4 ppm for the epoxide) and later by X-ray crystal analysis as the epoxide (**13**). Formation of the epoxide by reaction with triplet O_2 is, of course, consistent with the nature of the reactivity of such highly reactive “ π ” systems, as discussed in the Introduction.

When an attempt was made to specifically synthesize the epoxide from **7** by bubbling O_2 into a chloroform solution of **8**, to our surprise epoxide **13** was only formed as the minor product (21%), with a new product being formed in 52% yield (Scheme 7). This new product was obviously of similar structure, since it differed essentially only in the chemical shift of the former π carbons, which was at 78.3 ppm in the new compound.

X-ray characterization confirmed what the mass spectrum had indicated, that this compound was the dichloride (**14a**). The dichloride was apparently formed from the reaction of **8** with Cl_2 that had been generated from

SCHEME 8. Precedent Singlet O_2 ChemistrySCHEME 9. Singlet O_2 Chemistry of **8**

the somewhat obscure, but nevertheless characteristic Cl_2 -forming reaction of CHCl_3 with O_2 .¹⁶



In principle, reactions of pyramidal alkenes with *singlet* oxygen should lead to dioxetanes, which because of the strain of such systems would be expected to undergo homolytic cleavage to produce diketones. Indeed, as can be seen from the reaction in Scheme 8, this has been demonstrated to be the case, although it appears that the epoxide-forming reaction of triplet oxygen competes with the singlet chemistry.¹⁷

When cage compound **8** was similarly exposed to singlet oxygen, epoxide **13** and diketone **15** were obtained in a 2:1 ratio (Scheme 9).

Last, when bromine was added to a solution of cage compound **8** in CCl_4 , the red color disappeared immediately, and the dibromide adduct (**14b**) was obtained quantitatively (Scheme 7). The ^{13}C chemical shift of the former π bond carbons now appeared at 74.9 ppm (compared to 78.3 ppm for the dichloride).

Conclusion

A double Diels–Alder reaction of the formal *syn*-bis-(dehydro)octafluoro[2.2]paracyclophane with anthracene leads to formation of the novel cage compound **8**, which contains a highly pyramidal double bond. This double bond has ψ and ϕ values (34.3° and 33.5°, respectively) that are, in combination, among the highest yet observed crystallographically. This cage compound, although stable indefinitely as a crystalline compound in air, exhibits the distinctive reactivity with both triplet and singlet O_2 in solution that is characteristic of such pyramidalized π systems.

Experimental Section

4,12-Diiodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (7). A solution of 4,12-diamino-octafluoro[2.2]-paracyclophane¹³ (5.0 g, 13 mmol) in acetic acid (10 mL) was cooled to 0 °C in an ice/brine bath; ice (5 mL) and concentrated sulfuric acid (5 mL) were added with stirring. With the temperature maintained below 0 °C, sodium nitrite (5.0 g, 72.0 mmol) was added as quickly as possible to the solution in one

(16) Schulte, J. W.; Suttle, J. F.; Wilhelm, R. *J. Am. Chem. Soc.* **1953**, *75*, 2222–2227.

(17) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553–7559.

(15) Melder, J.-P.; Pinkos, R.; Fritz, H.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 95–99.

batch. The reaction was stirred at this temperature for 2 h, and then the mixture was poured into an aqueous solution (10 mL) of potassium iodide (13 g, 77 mmol) at room temperature with vigorous stirring. This mixture was kept stirring at room temperature overnight and then filtered. The solid was purified by column chromatography (hexane/ethyl acetate, 50:1) to give 4.98 g (63%) of the pseudo-ortho diiodide (**7**).¹³

Generation of 4,5,12,13-Bis(dehydro)octafluoro[2.2]-paracyclophane and Its Reaction with Anthracene. Into a three-necked round flask were charged pseudo-ortho diiodide **7** (0.12 g, 0.2 mmol), anthracene (78 mg, 2.2 mmol), and potassium *tert*-butoxide (0.23 g, 2.0 mmol), followed by 10 mL of butyl ether. The mixture was then refluxed for 30 min, after which the ¹⁹F NMR spectrum showed no starting material. The mixture was allowed to cool, and it was then filtered through a short pad of silica gel and washed with 3 × 10 mL of dichloromethane. Solvent was evaporated under vacuum and the products were further purified through silica gel column. The first product to elute (**9**, 34%) was identical with that obtained from the reaction of AF4-yne with anthracene¹ whereas the second product to elute was the cage compound **8** (isolated 18 mg, 17%). The final product to elute was the pseudo-*o*-bisanthracene adduct **10** (4%).

Microwave reaction procedure: A 50-mL one-neck round flask was charged with pseudo-*o*-diiodide **7** (0.12 g, 0.2 mmol), anthracene (78 mg, 2.2 mmol), and potassium *tert*-butoxide (0.23 g, 2.0 mmol) followed by 10 mL of butyl ether. The mixture was degassed with a vacuum pump three times. A nitrogen balloon was attached to the reaction vessel, which was put into the microwave reactor with care. The parameters were set as follows: heating model, standard; solvent, dimethyl sulfoxide; no pressure; power, 180 W; temperature, 150 °C; run time, 20 min; hold time, 20 min; stirrer, on; cooling, on. Products **8**, **9**, and **10** were obtained in amounts similar to those described above, whereas a fourth product (**11**, 10%) was obtained in the microwave-heated reaction.

Crystals of cage compound **8** were submitted for X-ray crystal analysis. These crystals were obtained by recrystallization in a small vial from ether/hexane (1:1). The top of the vial was covered with filter paper to allow slow evaporation of the solvent to obtain good crystals.

8: ¹H NMR, δ 7.41 (m, 2H), 7.20 (m, 2H), 6.84 (m, 2H), 6.73 (s, 2H), 6.67 (s, 2H), 5.73 (s, 2H), 5.48 (m, 2H); ¹³C NMR δ 164.4, 150.3, 149.4, 139.8, 135.3, 130.8, 130.8, 127.0, 125.0, 124.6, 124.4, 120.9, 120.8, 51.5, 48.3; ¹⁹F NMR δ -104.2 (d, *J* = 243.9 Hz, 2F), -104.6 (d, *J* = 243.9 Hz, 2F), -107.6 (dd, *J* = 242.2, 12.1 Hz, 2F), -108.0 (dd, *J* = 242.2, 12.1 Hz, 2F); IR (cm⁻¹) 3076, 3034, 2966, 2868, 1954, 1916, 1810, 1706, 1658, 1601, 1474, 1454, 1378, 1268, 1150, 1117; MS (EI) *m/z* 1052 (2M⁺), 526 (47) [M⁺], 352 (10), 300 (100), 276 (11), 250 (95); HRMS calcd for C₃₀H₁₄F₈ 526.0968, found 526.0967 (EI); UV (CH₂Cl₂) λ_{max} 328, 309, 246 nm.

10: ¹H NMR δ 7.55–7.54 (two unresolved multiplets, 4H), 7.38 (s, 2H), 7.30 (m, 2H), 7.16 (m, 2H), 7.12 (m, 2H), 7.11 (s, 2H), 6.98 (s, 2H), 6.77 (m, 2H), 5.83 (d, *J* = 2.6 Hz, 2H), 5.61 (m, 2H), 5.35 (m, 2H); ¹⁹F NMR δ -111.2 (d, *J* = 250.1 Hz, 2F), -116.35 (d, *J* = 250.1 Hz, 2F), -113.7 (d, *J* = 250.1 Hz, 2F), -117.05 (d, *J* = 250.1 Hz, 2F); ¹³C NMR, δ 146.6, 145.2, 143.6, 142.9, 141.6, 135.8, 131.5, 129.7, 128.5, 127.5, 126.5, 126.3, 126.3, 126.3, 125.5, 125.4, 123.8, 121.7, 119.4, 119.4, 51.5, 46.9; MS (EI) *m/z* 705 (30), 704 (74) [M⁺], 352 (49), 180 (23), 178 (52), 149 (30), 77 (100), HRMS calcd for C₄₄H₂₄F₈ 704.1750, found 704.1765 (EI)

11: ¹H NMR δ 7.53 (m, 1H), 7.48 (m, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.17 (m, 1H), 7.15 (m, 1H), 7.13 (m, 2H), 6.82 (d, *J* = 7.9 Hz, 1H), 6.80 (m, 2H), 6.77 (d, *J* = 9.4 Hz, 1H), 6.63 (d, *J* = 9.4 Hz, 1H), 6.02 (d, *J* = 2.0 Hz, 1H), 5.82 (s, 1H), 5.10 (s, 1H), 0.87 (s, 9H); ¹⁹F NMR δ -106.95 (d, *J* = 240.8 Hz, 1F), -116.2 (d, *J* = 240.8 Hz, 1F), -109.25 (d, *J* = 241.1 Hz, 1F), -112.0 (d, *J* = 241.1 Hz, 1F), -115.2 (d, *J* = 214.9 Hz, 1F), -116.1 (d, *J* = 214.9 Hz, 1F), -117.95 (d, *J* = 240.8 Hz, 1F), -119.0 (d, *J* = 240.8 Hz, 1F); ¹³C NMR δ 154.5, 145.6, 145.0,

144.3, 144.3, 143.6, 142.0, 135.0, 131.9, 128.7, 128.5, 128.3, 127.8, 127.2, 126.8, 126.8, 126.6, 126.0, 125.6, 124.8, 124.8, 124.5, 124.0, 123.5, 120.3, 119.3, 118.6, 118.1, 82.1, 51.0, 50.2, 28.1; MS (EI) *m/z* 600 (M⁺) (0.67), 585 (3), 544 (100), 353 (21), 352 (84); HRMS calcd for C₃₄H₂₄F₈O 600.1699, found 600.1713 (EI).

Reaction of Cage Compound **8** with Triplet Oxygen.

Compound **8** (6 mg, 0.01 mmol) in a loosely stoppered 5 mm NMR tube with 0.5 mL of CDCl₃ was stored at room temperature for 3 days, after which its NMR spectra indicated that half of the cage compound had been converted to epoxide **13**. No other product was detected: mp 161 °C (begins to turn brown), 216–217 °C melts; ¹H NMR δ 7.23 (m, 2H), 7.17 (m, 2H), 6.91 (s, 2H), 6.89 (s, 2H), 6.34 (m, 2H), 5.41 (s, 2H), 5.14 (m, 2H); ¹⁹F NMR δ -105.85 (d, *J* = 240.8 Hz, 2F), -106.3 (d, *J* = 243.9 Hz, 2F), -109.9 (dd, *J* = 240.8, 13.0 Hz, 2F), -110.4 (dd, *J* = 243.9, 13.0 Hz, 2F); ¹³C NMR δ 147.8, 147.7, 137.9, 132.5, 132.4, 132.3, 127.5, 127.3, 127.2, 124.9, 120.9, 120.8, 66.4, 45.0, 41.4; MS (EI) *m/z* 542 (M⁺) (22), 514 (100), 288 (47), 226 (20); HRMS calcd for C₃₂H₁₄F₈O 542.0917, found 542.0916 (EI); UV (CH₂Cl₂) λ_{max} 330, 290, 280.

Crystals of epoxide **13**, obtained by crystallization from dichloromethane/hexane (1:3), were submitted for X-ray crystal analysis. The recrystallization was carried out in the same manner as for **8**.

Reaction of Cage Compound **8** with Bromine.

Cage compound **8** (3.4 mg, 0.006 mmol) and 5 mL of CCl₄ were placed in a 10-mL round flask in an ice bath. Bromine (1 mg, 0.33 μL, 0.0063 mmol) was added 1 μL at a time through a syringe and the red-brown color disappeared immediately after the addition. The mixture was stirred at this temperature for another 5 min, and then solvent was evaporated under vacuum. Pure bromine adduct **14b** (~100%) was obtained without further purification: mp 154 °C (begins to turn brown), 251–253 °C melts; ¹H NMR δ 7.23 (m, 2H), 7.10 (m, 2H), 6.89 (s, 2H), 6.87 (s, 2H), 6.66 (m, 2H), 5.46 (s, 2H), 5.33 (m, 2H); ¹³C NMR δ 142.5, 141.8, 140.6, 138.1, 132.6, 132.5, 128.2, 127.9, 127.4, 127.2, 120.4, 74.9, 55.1, 50.9; ¹⁹F NMR δ -107.4 (d, *J* = 240.8 Hz, 2F), -107.5 (d, *J* = 243.9 Hz, 2F), -112.2 (dd, *J* = 240.8, 11.5 Hz, 2F), -112.5 (dd, *J* = 243.9, 11.5 Hz, 2F); MS (EI) *m/z* 687 (19), 685 (36), 683 (16), 526 (21), 352 (10), 276 (23), 226 (19), 149 (100); HRMS calcd for C₃₀H₁₄Br₂F₈ 683.9334, found 683.9341 (EI); UV (CH₂Cl₂) λ_{max} 330, 291, 282.

Reaction of Cage Compound **8** with Triplet Oxygen.

Photooxygenation was performed with a 250 W Sylvania mercury lamp. The output of the lamp was filtered with 0.05 M K₂Cr₂O₇ solution to remove light of higher energy than 460 nm. The photolysis was carried out in NMR tubes with outside water flow to keep the temperature around 25 °C. Oxygen was bubbled into a 0.5 mL CDCl₃ solution of cage compound (5.6 mg, 0.01 mmol) in a 5-mm NMR tube at room temperature overnight. Yields were determined by internal standard α,α,α-trifluoromethyltoluene by ¹⁹F NMR. The mixture was separated by preparative TLC plates after the starting material had been completely consumed. Epoxide **13** and chlorine adduct (**14a**) were obtained in 21% and 52% yield, respectively.

14a: mp 166 °C (begins to turn brown), 237–238 °C melts; ¹H NMR δ 7.23 (m, 2H), 7.09 (m, 2H), 6.89 (s, 2H), 6.88 (s, 2H), 6.65 (m, 2H), 5.30 (s, 2H), 5.16 (m, 2H); ¹³C NMR δ 142.7, 142.1, 139.5, 137.0, 132.7, 128.1, 127.9, 127.5, 120.5, 120.4, 78.3, 54.4, 50.3; ¹⁹F NMR δ -107.4 (d, *J* = 243.9 Hz, 2F), -107.5 (d, *J* = 241.1 Hz, 2F), -112.2 (dd, *J* = 243.9, 13.6 Hz, 2F), -112.5 (dd, *J* = 241.1, 13.6 Hz, 2F); MS (EI) *m/z* 598 (25), 597 (11), 596 (M⁺) (37), 370 (100), 276 (33), 226 (28), 149 (44); HRMS calcd for C₃₀H₁₄Cl₂F₈ 596.0345, found 596.0353 (EI).

Crystals of dichloride, **14a**, obtained by recrystallization from dichloromethane/hexane (1:2), were submitted for X-ray crystal analysis. The recrystallization was carried out in the same manner as for **8**.

Photooxygenation of Cage Compound **8.** A 0.5-mL CDCl₃ solution of cage compound (3 mg, 0.006 mmol) containing rose bengal (5 mg) was immersed into a flow-cooling water

bath to maintain the vessel at room temperature. Oxygen was bubbled into the solution through a long metal needle while the solution was irradiated by a 250 W Sylvania mercury lamp through a 0.05 M $K_2Cr_2O_7$ solution filter. Reaction was complete after 5 h with epoxide **13** and diketone **15** being obtained in a ratio of 2:1, as determined by 1H and ^{19}F NMR spectra of the mixture. The two products were separated by preparative silica gel TLC plates.

Diketone 15: 1H NMR δ 7.58 (m, 2H), 7.29 (m, 2H), 7.26 (s, 2H), 7.25 (s, 2H), 5.85 (m, 2H), 5.68 (s, 2H), 5.09 (m, 2H); ^{19}F NMR δ -106.2 (d, $J = 250.1$ Hz, 2F), -106.2 (d, $J = 250.1$ Hz, 2F), -109.7 (dd, $J = 240.8, 19.4$ Hz, 2F), -110.3 (d, $J = 240.8, 19.4$ Hz, 2F); ^{13}C NMR, δ 193.7, 136.3, 136.3, 135.6, 135.4, 131.2, 130.2, 130.2, 129.2, 128.7, 127.1, 120.7, 120.7, 56.2, 54.5; MS (EI) m/z 558 (M^+) (3), 276 (100), 226 (63); HRMS calcd for $C_{30}H_{14}O_2F_8$ 558.0866, found 558.0892 (EI).

X-ray Experimental. Data for the three compounds, **8**, **13**, and **14a**, were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Cell parameters were refined by using up to 8192 reflections. A hemisphere of data (1381 frames) was collected with the ω -scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was <1%). Absorption corrections by integration were applied based on measured indexed crystal faces.

The three structures were solved by the Direct Methods in SHELXTL6,¹⁸ and refined by using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. For compound **8**, all eight F atoms are disordered and each was refined in two parts with their site occupation factors dependently refined. The disorder was not large enough to allow the resolution of their parent C atoms. A total of 419 parameters were refined in the final cycle of refinement, using 4088 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 5.99% and 13.03%, respectively. For compound **13**, a total of 352 parameters were refined in the final cycle of refinement, using 4138 reflections with $I > 2\sigma(I)$

to yield R_1 and wR_2 of 4.30% and 11.49%, respectively. And for compound **14a**, the structure was initially solved in space group $P\bar{1}$, which gave a molecule in a general position and another located on a center of inversion (1/2 in the asymmetric unit). Not having a molecular inversion symmetry would mean that the second molecule should be completely disordered. The structure was then solved and refined in space group $P1$, which gave three molecules in the asymmetric unit (unit cell in $P1$) neither of which is disordered; two molecules (A and B) are related by a pseudo-inversion center. No disorder was observed in the third molecule, which confirms that the correct space group is indeed $P1$ and not $P\bar{1}$. The Flack x parameter refined to a value of -0.01(5) confirming that the correct stereochemistry is presented in this report. A large peak of $1.29 e\cdot\text{Å}^{-3}$ was observed near C17c and C18c perhaps due to a small disorder in molecule C. A total of 1081 parameters were refined in the final cycle of refinement, using 11283 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 6.02% and 15.75%, respectively. Refinement was done with F^2 .¹⁹

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Supporting Information Available: NMR data, including GHMQC, GHMBC, and NOERSY spectra for compounds **10**, **11**, **14b**, and **15**; table of structural data for **8**; ORTEP drawing of epoxide **13**; and three CIF files containing X-ray structural data for compounds **8**, **13**, and **14a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) The crystal structure data for compounds **8**, **13**, and **14a** have been deposited at the Cambridge Database: CCDC nos. 277451, 277452, and 277453, respectively. Data are available on request from the Director of the Cambridge Crystallographic Data Center, University Chemical laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

(18) SHELXTL6; Bruker-AXS, Madison, Wisconsin, 2000.