JOC*Article*

4,5-Dehydro- and 4,5,15,16-Bis(dehydro)octafluoro[2.2]paracyclophanes: Facile Generation and Extraordinary Diels−Alder Reactivity

Merle A. Battiste,* Jian-Xin Duan, Yi-An Zhai, Ion Ghiviriga, Khalil A. Abboud, and William R. Dolbier, Jr.*

Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, Florida 32611-7200

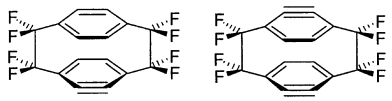
wrd@chem.ufl.edu

Received December 19, 2002

Dehydroiodination of 4-iodo- and 4,15-diiodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane by treatment with KO^{t}Bu in the presence of benzene, naphthalene, anthracene, and [2.2]paracyclophane affords each of the corresponding Diels−Alder mono- and bis-cycloadducts derived from the presumed aryne intermediates in high yield. Monoadducts of *t*-butylbenzene and furan are also obtained in excellent yield. All of the products were characterized by their NMR spectra, with four of them also being confirmed by X-ray crystallography. The extraordinary selectivity/reactivity of the aryne intermediate is discussed.

In the annals of aryne chemistry, following the elucidation of benzyne as a reactive intermediate,[1,2] perhaps the most striking feature of these dehydroaromatic intermediates is their dienophilic reactivity with other aromatic systems as diene partners. Depending on the mode of generation and the nature of the aryne component, however, the yields in these Diels−Alder type reactions can often be modest or poor.[3] For example, 75% is the best yield reported for benzyne addition to anthracene, considered one of the most reactive aromatic substrates in Diels−Alder reactions with arynes.[4,5] In that case, the benzyne was generated from benzenediazonium carboxylate, which is generally considered to be among the best methods for carrying out Diels−Alder chemistry involving benzyne.[6] Benzene is a much poorer Diels−Alder substrate, and it yielded only 9% Diels−Alder adduct in a similar reaction with benzyne,[7,8] although its reactions with tetrafluorobenzyne and tetrachlorobenzyne (among the more reactive arynes) yielded 33 and 62% adduct, respectively.[9,10] In this paper we report the Diels−Alder chemistry of the novel aryne, 4,5-dehydrooctafluoro[2.2]paracyclophane, **1**,[11] and of the nominal bis-aryne, 4,5,15,16-bis-dehydrooctafluoro[2.2]-paracyclophane, **9**.[12]

Examples of 4,5-dehydro[2.2]paracyclophanes in the literature are rare. Diels Alder trapping of the parent



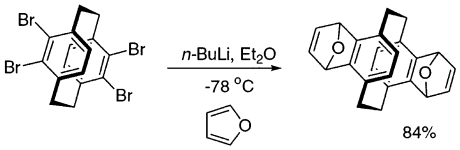
1 **9**

4,5-dehydro[2.2]paracyclophane appears to have been mentioned but once, in 1969 when Longone and Chipman reported its generation by potassium *t*-butoxide-promoted dehydrobromination of 4-bromo[2.2]paracyclophane in *t*-butylbenzene in the presence of excess anthracene, with only a 15% yield of the Diels−Alder adduct being obtained.[13−15] Their yield is similar to that obtained in Cadogan's original report of the use of this method to generate benzyne from bromoaromatics, in which he obtained high yields of *tert*-butyl aryl ethers but obtained only 21% yield of triptycene generated in the presence of anthracene.[16]

Although the Longone and Cram papers are the only mentions of dehydro[2.2]paracyclophanes in the literature, there also exists another report by Cram in 1969 of a bis-dehydro[2.2]paracyclophane, where sequential aryne-furan Diels−Alder reactions of the nominal 4,5,15,16-bis-dehydro[2.2]paracyclophane was carried out via the double dehalogenation of 4,5,15,16-tetrabromo-[2.2]paracyclophane.[17]

(1) Wittig, G. *Naturwissenschaften* **1942**, *30*, 696.
(2) Roberts, J. D.; Simmons, H. E., Jr.; Carlsmith, L. A.; Vaughan, C. W. *J. Am. Chem. Soc.* **1953**, *75*, 3290−3291.
(3) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967.
(4) Miller, R. G.; Stiles, M. *J. Am. Chem. Soc.* **1960**, *82*, 3802.
(5) Friedman, L.; Logullo, F. M. *J. Am. Chem. Soc.* **1963**, *85*, 1549.
(6) Miller, R. G.; Stiles, M. *J. Am. Chem. Soc.* **1963**, *85*, 1798−1800.
(7) Friedman, L.; Lindow, D. F. *J. Am. Chem. Soc.* **1968**, *90*, 2329−2333.
(8) Del Mazza, D.; Reinecke, M. G. *J. Org. Chem.* **1988**, *53*, 5799−5806.
(9) Brewer, J. P. N.; Heaney, H. *Tetrahedron Lett.* **1965**, *6*, 4709−4712.
(10) Heaney, H.; Jablonski, J. M. *Tetrahedron Lett.* **1966**, *7*, 4529−4531.
(11) This work has appeared, in part, as a communication: Battiste, M. A.; Duan, J.-X.; Zhai, Y.-A.; Ghiviriga, I.; Abboud, K. A.; Roitberg, A.; Shelton, G. R.; Dolbier, W. R., Jr. *Tetrahedron Lett.* **2002**, *43*, 7047−7049.
(12) Although the name "4,5,15,16-bis(dehydro)octafluoro[2.2]paracyclophane" is used for convenience, it is recognized that the two aryne moieties are formed and undergo reaction *sequentially* during the course of the reaction.
(13) Longone, D. T.; Chipman, G. R. *Chem. Commun.* **1969**, 1358−1359.
(14) Cram and co-workers[15] had previously generated dehydro[2.2]-paracyclophane in dimethyl sulfoxide, but without a diene trap.
(15) Cram, D. J.; Day, A. C. *J. Org. Chem.* **1966**, *31*, 1227−1232.
(16) Cadogan, J. I. G.; Hall, J. K. A.; Sharp, J. T. *J. Chem. Soc. C* **1967**, 1860−1862.
(17) Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3527−3533.

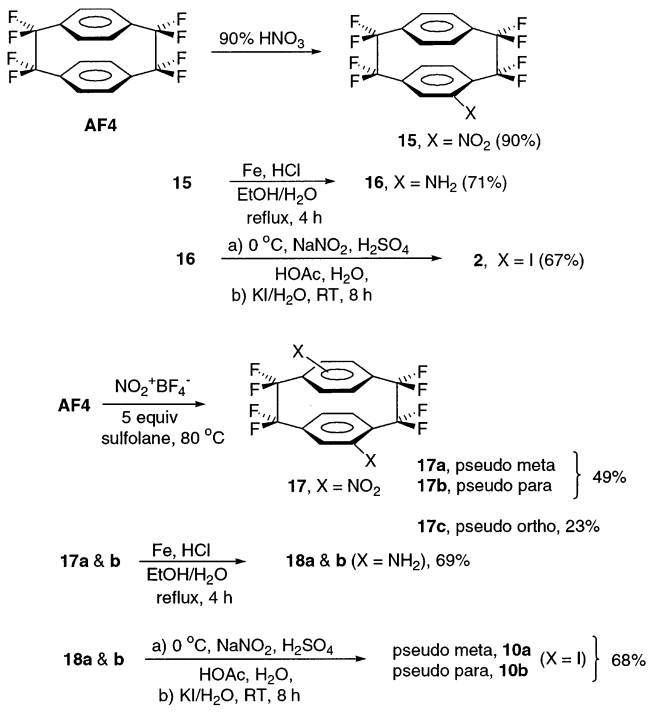
10.1021/jo0268815 CCC: $25.00
Published on Web 03/12/2003



Because of competitive trapping by the nucleophilic *t*-butoxide, the use of Cadogan's *t*-butoxide method for generating arynes has almost never been used to initiate Diels−Alder chemistry. Nevertheless, we now report that using these same conditions for dehydroiodination of 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane, **2**,[18] and for the sequential double dehydroiodination of a mixture of 4,15- and 4,16-diiodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane, **10a** and **10b**, led to efficient Diels−Alder trapping of the intermediate arynes with virtually no observed competitive interception of the intermediates by the *t*-butoxide ion.

Results and Discussion

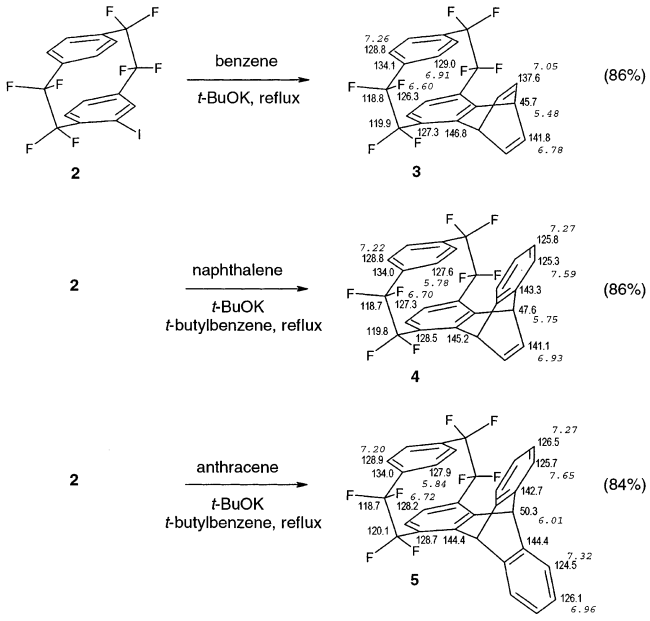
Synthesis of Aryne Precursors. The 4-iodo- and the diiodooctafluoro[2.2]paracyclophane precursors were prepared from 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (**AF4**) by improved procedures based on those previously published.[18,19]



Noteworthy is the double-nitration procedure, in which essentially equal amounts of the *pseudo-ortho* (4,12-dinitro-), *pseudo-meta* (4,15-dinitro-), and *pseudo-para* (4,16-dinitrooctafluoro[2.2]paracyclophane) products (**17a**, **b**, and **c**, respectively) are formed. The *pseudo-meta* and *pseudo-para* isomers are readily separated from the *pseudo-ortho* isomer by column chromatography, and it is this mixture of 4,15- and 4,16-dinitro isomers (**17a** and **17b**, respectively) that is used in subsequent steps to eventually synthesize a mixture of 4,15- and 4,16-diiodooctafluoro-[2.2]paracyclophanes (**10a** and **10b**, respectively). Since both of these isomers lead to the same bis-aryne (**9**), this mixture was used as the "precursor" of 4,5,15,16-bis-dehydrooctafluoro[2.2]paracyclophane.

Reactions of 4,5-Dehydrooctafluoro[2.2]paracyclophane, 1. As reported in a preliminary communication,[11] when monoiodide **2** was treated with potassium *t*-butoxide in refluxing benzene or in refluxing *t*-butylbenzene in the presence of near *stoichiometric* amounts of naphthalene or anthracene, the corresponding Diels−Alder adducts **3**, **4**, and **5**, respectively, were obtained, each in greater than 80% yield. The yields obtained with benzene and naphthalene are the largest yet reported for aryne reactions with these substrates. The structures of the adducts were unambiguously determined by ^{1}H and ^{13}C NMR, where the numerous NOEs on such rigid structures were particularly diagnostic for stereochemical assignment. The ^{1}H and ^{13}C chemical shifts for each adduct are indicated on their structures in italics and in normal font, respectively. The ^{19}F NMR data is given in the Experimental Section. A couple of interesting aspects of the NMR spectra of **3**−**5** are worth mentioning. In each case, the bridgehead carbons appear as a doublet (i.e, for **3**, the signal at 45.7 ppm, $J_{FC} = 10.5$ Hz), due to through-space coupling with one of the bridge fluorine atoms. Second, the aromatic protons that are pointed at the endo bridge of the adduct are significantly shielded for the naphthalene and anthracene adducts (5.78 and 5.84 ppm, respectively, as compared to 6.91 ppm for the benzene adduct) where they encounter the shielding region of a benzene ring. Further elaboration will be found in the NMR Discussion section.

Table 1 contains results of all Diels−Alder reactions of **1**, and the structure of the anthracene adduct was corroborated by X-ray crystal analysis, as will be discussed later.



A somewhat surprising result was the formation of the *endo*-isomer as the major product from reaction with naphthalene. About 8−10% of the minor, *exo*-adduct

(18) Roche, A. J.; Dolbier, W. R., Jr. *J. Org. Chem.* **1999**, *64*, 9137−9143.

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

TABLE 1. Diels–Alder Reactions from Treatment of 4-Iodooctafluoro[2.2]paracyclophane, 2, with Potassium *tert*-Butoxide

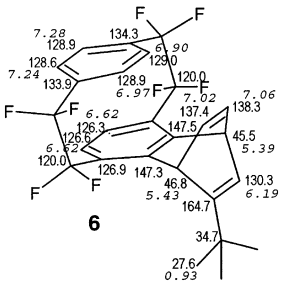
substrate	solvent	temperature (°C)	reaction time (min)	product (yield, %)
benzene	benzene	reflux (80)	20	**3** (86)
naphthalene	di-*n*-butyl ether	reflux (142)	20	**4** (88)
anthracene	*t*-butylbenzene	reflux (169)	15	**5** (84)
t-butylbenzene	*t*-butylbenzene	reflux (169)	40	**6** (78)
furan	*t*-butylbenzene	reflux (142)	20	**7a**,**b** (80)
[2.2]paracyclophane	*t*-butylbenzene	reflux (169)	20	**8** (86)

TABLE 2. Diels–Alder Reactions from Treatment of 4,15-diodooctafluoro[2.2]paracyclophane, 10, with Potassium *t*-Butoxide, in Refluxing Solvent

substrate	solvent	temperature (°C)	reaction time (minutes)	product (yield, %)
benzene	benzene	reflux (80)	150	**11** (83)
naphthalene	dibutyl ether	reflux (142)	30	**12** (86)
anthracene	*tert*-butylbenzene	reflux (169)	30	**13** (80)
[2.2]paracyclophane	*tert*-butylbenzene	reflux (169)	30	**14a**,**b** (84)

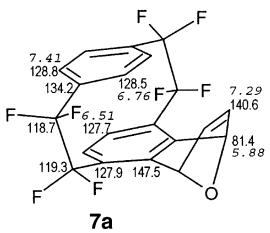
could be observed in the ^{19}F NMR spectrum of the crude product mixture. It was not characterized further. Preliminary computational examination of the relative stabilities of the *endo*- and *exo*-adducts indicates little difference between the two.[11] Thus, there is at present no clear rationale for the observed preference for the *endo*-isomer.

Interestingly, *no* products deriving from nucleophilic capture of the presumed aryne intermediates by the excess *t*-butoxide base were detected in any of these reactions, even when the reaction was carried out in refluxing *tert*-butylbenzene with *no* substrate added. In this case, a surprisingly high (78%) yield of the Diels–Alder adduct (**6**) with *t*-butylbenzene was obtained.

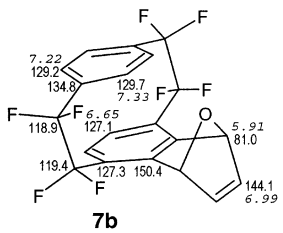


6

Furan has generally been observed to be a good Diels–Alder diene substrate in trapping reactions with arynes. Indeed, when iodide **2** was treated with potassium *t*-butoxide in refluxing *tert*-butylbenzene in the presence of 1.1 equivalents of furan, a mixture of the *endo*- and *exo*-adducts of furan to aryne **1** (ratio = 1.0:0.6) was obtained in 80% yield. The two isomers were clearly distinguished by NMR, but a corroborative X-ray crystal structure of the *endo*-adduct, **7a**, was also obtained.

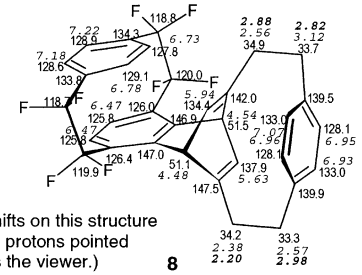


7a



7b

There has been one previous report of the addition of an aryne to [2.2]paracyclophane, that within Heaney's study of tetrafluorobenzyne, wherein he reported a yield of 44% for its addition to [2.2]paracyclophane in 1969.[20] Such reaction also posed no problem for aryne **1**, which, under the usual conditions, underwent Diels–Alder addition to the hydrocarbon [2.2]paracyclophane in 84% yield. Although fully characterized by NMR, an X-ray crystal structure of adduct **8** was also obtained. The regiochemistry of addition observed in the formation of adduct **8** was consistent with that reported earlier for the tetrafluorobenzyne/[2.2]paracyclophane adduct.



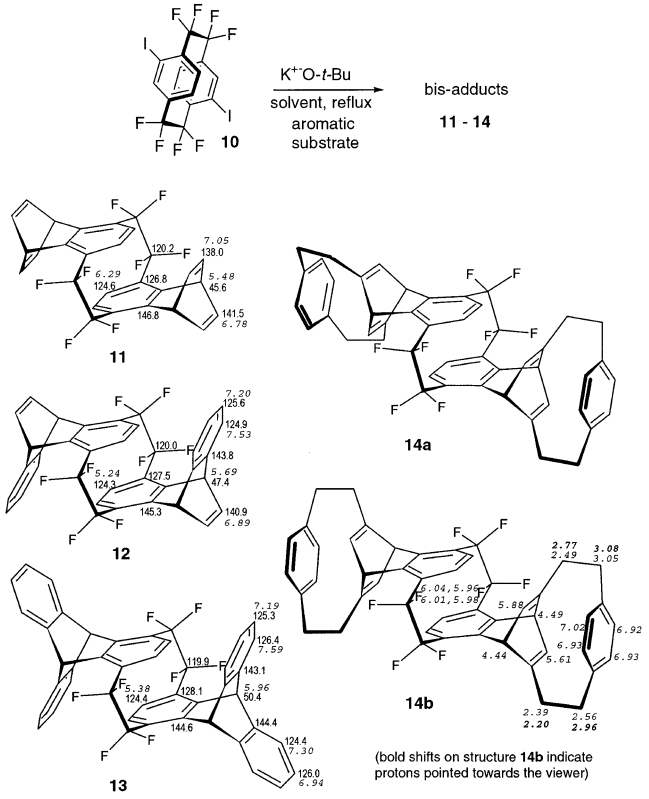
(bold shifts on this structure indicate protons pointed towards the viewer.)

8

Reactions of 4,5,15,16-Bis(dehydro)octafluoro-[2.2]paracyclophane, 9. Surprisingly, the yields of bis-adducts obtained from the sequential bis-dehydroiodination of the isomeric diiodides **10a** and **10b** under analogous conditions were comparable to those for the monoadducts! Adducts **11**–**14** were thus obtained in 83, 86, 80 and 84% yields, respectively. The results are given in Table 2. All adducts were fully characterized by ^{1}H, ^{19}F, and ^{13}C NMR, and an X-ray crystal structure was obtained for bis-naphthalene adduct **12**. Again, the highly shielded aromatic protons of the (former) AF4 benzene ring that face the *endo* benzene rings of adducts **12** and **13** (δ = 5.24 and 5.38 ppm, respectively) are noted with interest.

NMR Discussion.[21] The structural integrity of compounds **3**–**14** and the stereochemistry of compounds **4**,

(20) Brewer, J. P. N.; Heaney, H.; Marples, B. A. *Tetrahedron* **1969**, *25*, 243–245.



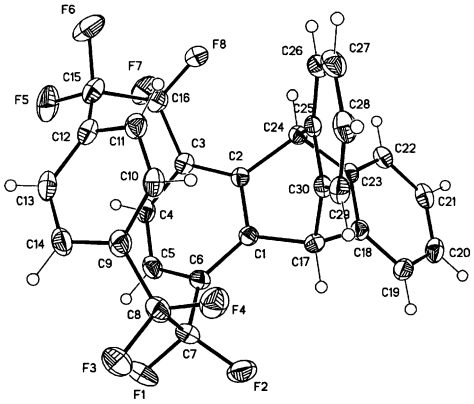


FIGURE 1. ORTEP drawing of anthracene adduct **5**.

6, and **7a**,**b** were demonstrated by NMR.[11] The numerous NOEs on such rigid structures were diagnostic for stereochemical assignment. Of the three pairs of vicinal protons originating from compound **2** (e.g., 6.47 and 6.47, 7.18 and 7.22, and 6.73 and 6.78 ppm for adduct **8**), the one on the formerly benzyne ring (6.47 and 6.47 ppm) can be identified by its couplings to the carbons at ca. 147 ppm, carbons that in turn couple to protons originating from the arene (4.54, 4.48, 5.63, and 5.94 ppm). NOEs with this pair (6.47 and 6.47 ppm) identified the pair (7.18 and 7.22 ppm) syn to it. Long-range couplings between the protons and the carbons in the *para*-phenylene ring of **8** allowed the assignment of the pair anti to the protons originating in the benzyne ring of **1** (6.73 and 6.78 ppm, *meta* to 7.22 and 7.18 ppm, correspondingly). In compound **8**, 6.78 displayed a NOE with 5.94 and 4.48 ppm, which in turn displayed NOEs with 7.07 and 6.96 ppm. Other NOEs afforded positive stereochemical assignment of the aliphatic protons, e.g., 2.88 ppm displayed NOEs with 5.94, 6.78, and 7.07 ppm.

Compounds **14a**,**b** were analyzed as a mixture. The fragments originating from [2.2]paracyclophane displayed very similar proton chemical shifts in both **14a** and **14b**. The protons originating from the fluorinated aryne **1** display two ABs of roughly the same intensity (6.04, 5.96 and 6.01, 5.98 ppm) indicative that **14a** and **14b** are formed in equal amounts. Low solubility precluded obtaining ghmbc spectra. The structural integrity of these compounds was confirmed by NOEs similar to those observed for compound **8**.

For the furan adducts **7a**,**b**, the major isomer was assigned as **7a** on the basis of the NOE between the protons at 6.76 ppm (identified as anti to the protons originating from the aryne ring of **1** as mentioned above) and the protons at 7.29 ppm, originating in the furan.

Isomer **6** would be expected on steric grounds, and the *exo*-structure was unambiguously confirmed on the basis of NOEs that were observed between the cyclophane protons that are pointed toward the former *tert*-butylbenzene (6.97 and 6.90 ppm) and the vinylic protons at 7.02 and 7.06 ppm.[22]

In a similar fashion, in compound **4**, the proton at 5.78 ppm displays NOEs with those at 7.27 and 7.59 ppm and no NOE with the alkene proton at 6.93 ppm, proof for the *endo* stereochemistry.

X-ray Discussion. The crystal structure of the anthracene adduct **5** indicates that, although there are several ways for the AF4 moiety to be distorted upon derivation, the main impact is that the torsion angles around the bridging C7−C8 and C15−C16 moieties (for example, the C6−C7−C8−C9 torsion angle, as seen in Figure 1) open to values of 26.5 and 27.0°, respectively. This is accomplished by twisting the phenyl rings by an angle of 11.6° around an axis perpendicular to them.

According to the X-ray structure of *endo* furan adduct, **7a**, the distortion parameters of its AF4 moiety involve bridging torsion angles of 12.6 and 21.9°, with a twist angle of 7.7°, whereas for [2.2]paracyclophane adduct **8**, the bridging torsion angles are 14.1 and 22.1°, with a twist angle of 8.1°.

The X-ray analysis of bis-naphthalene adduct **12** indicates that there are two molecules of **12** in its asymmetric unit. For molecule A, the bridging torsion angles are 28.0 and 30.1°, with a twist angle of 12.4°, whereas for molecule B the bridging torsion angles are 27.7 and 28.9°, with its twist angle being 23.1°.

In summary, there is a trend observed in these X-ray structures when considering how the AF4 moiety is distorted in order to relieve the strain of adding a large substituent to the benzene rings. Small variations in the dihedral angles between the benzene rings of each of the four crystal structures of from 1.2 to 4.9° are observed. More significantly, and presumably in order to minimize nonbonded interactions, the benzene rings twist around an axis perpendicular to the benzene rings, with more

(21) For a comprehensive review on the NMR of cyclophanes, see: Ernst, L. *Progr. Nucl. Magn. Reson. Spectrosc.* **2000**, *37*, 47−190.

(22) Assignments of the carbon signals at 126.6 and 126.3 ppm on one hand and 147.5 and 147.3 ppm on the other are interchangeable. No cross-peaks were seen in the ghmbc spectrum for the carbons that were not assigned.

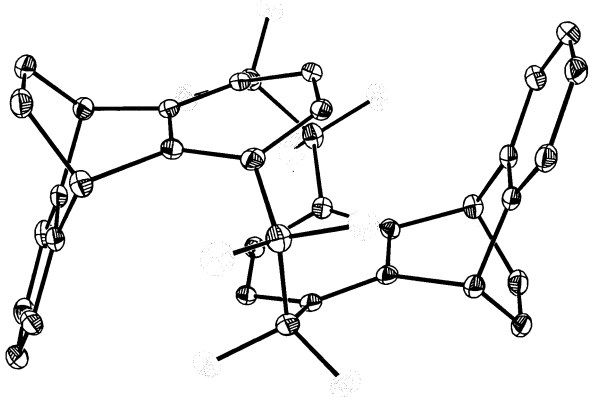


FIGURE 2. ORTEP drawing of bis-naphathalene adduct **12**.

twist being observed for larger substituents. Such twist is coupled with an opening of the bridging torsion angles of the CF_2-CF_2 units.

Conclusion

On the basis of the results that have been presented, it can be concluded that the reactive arynes, **1** and **9**, have been generated and are responsible for the chemistry observed and discussed. The relative ease of their generation (refluxing benzene) can be ascribed to an increase in acidity of the proton vicinal to the halogen, induced by the highly electronegative fluorinated bridges. The fluorinated bridges of **1** and **9** should also make them highly *electrophilic* and therefore more reactive arynes (compared to the nonfluorinated dehydro[2.2]paracyclophane). However, such high electrophilicity should also lead to enhanced reactivity with nucleophiles such as *t*-butoxide ion, which is not observed. At this time, the only potential explanation we have for the chemoselectivity exhibited by arynes **1** and **9** is the possible electrostatic repulsion of the *t*-butoxide nucleophile by the fluorinated bridges of the two arynes. Further experiments will hopefully provide further insight into this hypothesis.

Other characteristic reactions of arynes, including ene reactions, additions of amines, sulfides, and alcohols, as well as employment of other methods for generation of **1** and **9**, are currently under investigation.

Experimental Section

General Methods. ^1H (500 MHz), ^{13}C (125 MHz), and ^{19}F (282 MHz) NMR spectra were recorded using $CDCl_3$ as the solvent, and chemical shifts (δ values) were measured relative to the signals for $CHCl_3$, $CDCl_3$, and $CFCl_3$, respectively**.** ^1H and ^{13}C chemical shift data are directly indicated on the structures of the adducts in the Results and Discussion section above, whereas ^{19}F NMR data are provided in the Experimental Section below. X-ray crystal analyses were performed by the Center for X-ray Crystallography and HRMS and CH micro elemental analyses by the Spectroscopic Services Group at the University of Florida. Column chromatography was performed using chromatographic silica gel, 200−425 mesh, as purchased from Fisher, unless otherwise mentioned.

4-Nitro-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane. Into 200 mL of 90% nitric acid was added 10.0 g (2.8 mmol) of **AF4** in one batch. The mixture was stirred overnight, after which it became a clear solution. This solution was then added to 500 g of ice in an Erlenmeyer flask, and a white precipitate formed. The mixture was filtered to give 10.0 g (90%) of the yellow-white mononitro product, **15**.[18]

Isomeric Dinitro-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophanes. Explicitly following the published procedure,[19] 22.1 g (166 mmol) of nitronium tetrafluoroborate undergoes reaction with 10.2 g (29 mmol) of **AF4** in sulfolane (100 mL) in an overnight reaction at 80 °C to form a white solid product when poured into ice. Column chromatography (hexane/ethyl acetate, 10:1) gave 6.3 g (49%) of an almost 1:1 mixture of the 4,15- and 4,16-dinitrooctafluoro[2.2]paracyclophanes, **17a** and **17b**, respectively, along with 3.0 g (23%) of the 4,12-dinitro isomer.

4-Amino-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane, 16. Following the literature procedure,[18] a suspension of **15** (5.5 g, 13.9 mmol) was reduced by Fe powder in aqueous EtOH to yield 3.6 g (71%) of amine **16**.

Mixture of 4,15- and 4,16-Diamino-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophanes, 18a and 18b.[19] Likewise, 6.3 g (14.3 mmol) of the mixture of **17a,b** was converted to 2.2 g (69%) of a mixture of *pseudo-meta* and *pseudo-para* diamines, **18a** and **18b**, respectively.

4-Iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane, 2.[18] A solution of amine **16** (1.9 g, 5.2 mmol) in acetic acid (4 mL) was cooled to 0 °C in an ice/brine bath. Ice (1.5 g) and 1.5 mL of H_2SO_4 were added with stirring, and ensuring that the temperature was still below 0 °C, Na NO_2 (2.0 g, 29 mmol) was added in one batch. After the reaction was stirred for 2 h at 0 °C, it was poured, with vigorous stirring, into 10 mL of an aqueous solution of KI (5.2 g, 30.8 mmol) at room temperature. After stirring overnight, the mixture was filtered and the solid purified by column chromatography (alumina, hexane/EtOAc, 50:1) to give 1.7 g (67%) of the 4-iodo product, **2**.

Mixture of 4,15- and 4,16-Diiodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophanes, 10a and 10b.[19] A solution of the mixture of 4,15- and 4,16-diaminooctafluoro[2.2]paracyclophanes, **18a** and **18b**, respectively, (2.0 g, 5.2 mmol) in acetic acid (4 mL) was cooled to 0 °C in an ice/brine bath; ice (1.5 mL) and concentrated sulfuric acid (1.5 mL) were added with stirring. With the temperature maintained below 0 °C, sodium nitrite (2.0 g, 29.0 mmol) was added as quickly as possible to the solution. The reaction was stirred at this temperature for 2 h, and then the mixture was added to an aqueous solution (10 mL) of potassium iodide (5.2 g, 30.8 mmol) at room temperature with vigorous stirring. This mixture was kept stirring at room temperature overnight and then filtered with the solid being purified by column chromatography (hexane/ethyl acetate, 50:1) to give 2.2 g (68%) of a mixture of **10a** and **10b**.

Generation of 4,5-Dehydrooctafluoro[2.2]paracyclophane, 1, and its Reaction with [2.2]Paracyclophane. Into a three-necked round-bottomed 50 mL flask were added iodide **2** (0.478 g, 1 mmol) and potassium *t*-butoxide (0.56 g, 5 mmol) along with 10 mL of dry *t*-butylbenzene under a nitrogen flow. Then, [2.2]paracyclophane (0.22 g, 1.1 mmol) was added and the mixture heated to 170 °C and refluxed for 20 min. The oil bath was then removed and the reaction product mixture examined by ^{19}F NMR. The reaction was then worked up by pouring the product mixture onto a short silica gel column, using diethyl ether to wash the product through the column. The product was further purified via silica gel chromatography (hexanes) to give an 86% yield of **8**: mp 140−142 °C; ^{19}F NMR, four equal intensity AB quartets at δ −111.4 (J = 244.2 Hz) and −111.7 (J = 243.9 Hz), −115.0 (J = 243.9 Hz) and −115.7 (J = 244.2 Hz), −116.7 (J = 239.7 Hz) and −117.7 (J = 241.1 Hz), −119.4 (J = 240.8 Hz) and −119.9 (J = 239.7 Hz); HRMS calcd for $C_{32}H_{22}F_8$ 558.1594, found 558.1594.

Reaction of Aryne 1 with Anthracene. The procedure is the same as above, except that 0.18 g (1.1 mmol) of anthracene was used and the reaction was refluxed for 15 min. Two isomers, in a ratio of 93:7 (from ^{19}F NMR) were obtained

in a total yield of 84%. The major isomer was isolated via silica gel chromatography (hexane/EtOAc, 100:1). Major isomer (**5**): mp 296−298 °C; ^{19}F NMR, two equal intensity AB quartets at δ −111.4 (d, J = 243.9 Hz) and −115.1 (d, J = 243.9 Hz), −116.53 (J = 240.8 Hz) and −119.4 (d, J = 240.8 Hz). Anal. Calcd for $C_{30}H_{16}F_8$: C, 68.18, H, 3.05. Found: C, 67.73; H, 2.86. Minor isomer: ^{19}F NMR, two equal intensity AB quartets at δ −111.1 (d, J = 243.9 Hz) and −115.4 (d, J = 243.9 Hz), −116.3 (d, J = 237.7 Hz) and −119.5 (d, J = 240.8 Hz).

Reaction of Aryne 1 with Benzene. The procedure is the same as above, except that the reaction was carried out in refluxing benzene at 80 °C for 20 min. The product was purified by silica gel chromatography (hexane/EtOAc, 100:1) with the yield of **3** being 86%: mp 144−146 °C; ^{19}F NMR, two equal intensity AB quartets, δ −111.9 (d, J = 247.0 Hz) and −115.7 (d, J = 244.0 Hz), −117.79 (d, J = 240.8 Hz) and −119.54 (d, J = 240.8 Hz); MS (EI) 428 (M^+), 368, 252, 192, 176 and 57; HRMS calcd for $C_{22}H_{12}F_8$ 428.0811, found 428.0811. Anal. Calcd for $C_{22}H_{12}F_8$: C, 61.69; H, 2.83. Found: C, 61.52; H, 2.69.

Reaction of Aryne 1 with *t*-Butylbenzene. The procedure was identical to those above, except that the reaction was carried out using refluxing *tert*-butylbenzene (bp 169 °C) as both a solvent and a reactant. The product was purified by silica gel chromatography (hexane/EtOAc, 100:1) with the yield of **6** being 78%: mp 131−133 °C; ^{19}F NMR, four equal intensity AB quartets at δ −111.4 (J = 243.9 Hz) and −112.5 (J = 243.9 Hz), −115.3 (J = 243.9 Hz) and −115.9 (J = 243.9 Hz), −117.2 (J = 240.8 Hz) and −119.8 (J = 240.8 Hz), −118.4 (J = 241.1 Hz) and −119.4 (J = 240.8 Hz). Anal. Calcd for $C_{26}H_{20}F_8$: C, 64.46; H, 4.17. Found: C, 64.22; H, 4.22.

Reaction of Aryne 1 with Naphthalene. The procedure was carried out as above except that di-*n*-butyl ether (bp 142 °C) was used as the solvent and naphthalene as the substrate (0.14 g, 1.1 mmol). Refluxing for 30 min provided a mixture of products (ratio >10:1), which after chromatography in the usual manner gave major product *endo*-adduct **4** in a yield of 88%: mp 204−206 °C; ^{19}F NMR, two equal intensity AB quartets, δ −111.2, −115.5 (J_{AB} = 243.9 Hz), and δ −116.4, −119.5 (J_{AB} = 247.0 Hz); HRMS calcd 478.0967, found 478.0968. Anal. Calcd for $C_{26}H_{14}F_8$: C, 65.28; H, 2.95. Found: C, 65.05; H, 2.89. Minor product (presumably *exo*-adduct): ^{19}F NMR, two equal intensity AB quartets, δ −112.0, −115.3 (J_{AB} = 246.8 Hz) and d −117.8, −119.6 (J_{AB} = 236.9 Hz).

Reaction of Aryne 1 with Furan. This reaction was carried out as above in refluxing *tert*-butylbenzene for 20 min with furan as the substrate. A mixture of the endo and the *exo*-adducts, **7a**,**b**, (ratio = 1:0.6), was obtained in 80% yield. Chromatography in the usual manner provided partial separation of the isomers, such that small amounts of individual, pure isomers could be obtained, along with larger amounts of mutually contaminated fractions. *endo*-Isomer, **7a**: mp 162−163.5 °C; ^{19}F NMR, two equal intensity AB quartets, δ −112.6, −119.2 (J_{AB} = 243.9 Hz), δ −116.1, −117.9 (J_{AB} = 240.8 Hz); HRMS calcd for $C_{20}H_{10}F_8$ 418.0604, found 418.0604. *exo*-Isomer, **7b**: ^{19}F NMR, two equal intensity AB quartets, δ −111.9, −114.3 (J_{AB} = 243.9 Hz), δ −116.2, −118.0 (J_{AB} = 238.0 Hz).

Reaction of Bis-aryne 9 with Benzene. The analogous procedure was carried out using 0.6 g (1 mmol) of the isomeric diiodides, **10a** and **10b**, and 1.12 g (10 mmol) of potassium *t*-butoxide, refluxing in 10 mL of benzene for 2.5 h. The product was purified by silica gel chromatography (hexane/EtOAc, 100:1) with 0.42 g (83%) of the bis-adduct **11** being obtained: mp > 315 °C; ^{19}F NMR, one AB quartet, δ −110.9, −115.5 (J_{AB} = 243.9 Hz); HRMS calcd for $C_{22}H_{16}F_8$ 504.1124, found 504.1120.

Reaction of Bis-aryne 9 with Naphthalene. The reaction was carried out as in the preceding example, except that the solvent was 10 mL of di-*n*-butyl ether, refluxing at 142 °C, and 0.28 g (2.2 mmol) of naphthalene was added as the substrate. The product was purified by silica gel chromatography (hexane/EtOAc, 100:1) with 0.52 g (86%) of a white, solid bis-adduct **12** being obtained: mp 253 °C (dec.); ^{19}F NMR, one AB quartet, δ −108.9, −115.0 (J_{AB} = 243.9 Hz); HRMS calcd 604.1437, found 604.1437. Anal. Calcd for $C_{36}H_{20}F_8$: C, 71.52; H, 3.33. Found: C, 71.10; H, 3.28.

Reaction of Bis-aryne 9 with Anthracene. The procedure was the same as in the preceding examples, except that the reaction was carried out for 30 min at 169 °C in 10 mL of refluxing *tert*-butyl benzene, using 0.39 g (2.2 mmol) of anthracene as a substrate. The product was purified by silica gel chromatography (hexane/EtOAc, 100:1) with 0.56 g (80%) of the bis-adduct, **13**, being obtained: mp > 310 °C; ^{19}F NMR, one AB quartet, δ −109.1, −114.7 (J_{AB} = 243.9 Hz); HRMS calcd for $C_{44}H_{24}F_8$ 704.1744, found 704.1748.

Reaction of Bis-aryne 9 with [2.2]Paracyclophane. The procedure was carried out in refluxing *tert*-butylbenzene, as in the previous example, and 0.46 g (2.2 mmol) of [2,2]-paracyclophane was used as a substrate. The crude product was purified by silica gel chromatography (hexane/EtOAc, 100:1) with 0.64 g (84%) of a 50:50 mixture of the diastereoisomeric, white bis-adducts **14a** and **14b** being obtained: mp 315 °C (dec.); ^{19}F NMR (*isomer 1*) two equal intensity AB quartets, δ −109.6, −115.0 (J_{AB} = 243.9 Hz), δ −110.9, −115.6 (J_{AB} = 240.8 Hz); (*isomer 2*) two equal intensity AB quartets, δ −109.7, −115.2 (J_{AB} = 231.8 Hz), δ −110.6, −115.4 (J_{AB} = 231.5 Hz); HRMS calcd for $C_{48}H_{36}F_8$ 764.2689, found 764.2689.

Acknowledgment. Support of this research in part by the National Science Foundation (WRD) is gratefully acknowledged. The authors also wish to thank Specialty Coating Systems, Inc., for a generous donation of AF4. K.A.A. and I.G. wish to acknowledge the National Science Foundation and the University of Florida for funding of the purchase of the X-ray and NMR equipment, respectively.

Supporting Information Available: Tables of X-ray data for adducts **5**, **7a**, **8**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0268815