Electrophilic Substitution of 1,1,2,2,9,9,10,10-Octafluoro[2.2]paracyclophane

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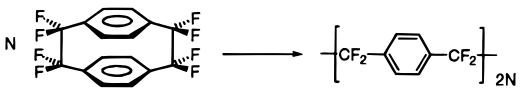
Nitration of octafluoro[2.2]paracyclophane (OFP) provides an entry into the synthesis of a series of 11 monosubstituted OFPs, including the nitro, amino, chloro, bromo, iodo, hydroxy, and trifluoromethyl compounds. The NMR, mass spectrometric, and UV spectral properties of all of these derivatives are presented and discussed, and they are compared with those of its hydrocarbon analogue, [2.2]paracyclophane.

Introduction

Over the last 50 years, cyclophane chemistry has established itself as an integral part of organic chemistry.[1] Fascination arises from their aesthetic appeal and is fueled by the challenging syntheses of such molecules. [2.2]Paracyclophane[2] ([2.2]PCP) is generally heralded as the paradigm of cyclophane chemistry, because it is the smallest stable paracyclophane and therefore exhibits the most obvious examples of unique cyclophane chemistry, such as transannular communication, unusual reactivities, and spectroscopic abnormalities.[1]

Although organic chemists have been treated to a wide variety of excellent [2.2]PCP chemistry over the years, fluorinated cyclophane chemistry has received much less attention, and paracyclophanes bearing more than a couple of fluorine atoms are very scarce in the literature. Filler and co-workers reported *ring*-fluorinated [2.2] and [2.4]paracyclophanes,[3] and there have been several papers and patents concerning the synthesis of the *bridge*-fluorinated 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane[4] **1** (OFP), including two reports from these laboratories.[5] The interest is mainly driven by the industrial application of this compound as a monomer for the Parylene VIP AF4 polymer, which combines low dielectric constant and high chemical and thermal stabilities with low moisture absorption.[6]



1 (OFP) VIP™ AF4 Polymer

A detailed investigation into the chemistry of this bridge-fluorinated paracyclophane has been hampered by the lack of a viable large scale synthesis of the desired compound. However, because of the discovery of two improved synthetic routes to **1**,[5a,7] its use as a precursor to other derivatives has become realistic. We therefore wish to report at this time the syntheses, characterizations, and physical properties of a number of novel monosubstituted derivatives of octafluoro[2.2]paracyclophane (**1**). Until this work, no ring-substituted derivatives of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane had been reported in the literature.[8,9]

Synthetic Results and Discussion

It was presumed that OFP would, in a general chemical sense, behave like a deactivated aromatic system because of the fluoroalkyl substituents,[10] and it was therefore not surprising that the Friedel−Crafts type aromatic bromination, acylation, and alkylation used to functionalize [2.2]PCP[11] resulted only in the quantitative recovery of starting material.

Nitration proved more successful, although relatively harsh conditions had to be employed. Over a period of 24 h, concentrated (69%) nitric acid at 100 °C, whether neat, with concentrated sulfuric acid, or in sulfolane, proved sufficient to a generate mononitro derivative **2** in reasonable yield (56−60%). The severity of the reaction conditions and only moderate yield of the product reflect the low reactivity of this fluorinated arene with respect to electrophilic substitution. The best isolated yield (86%)

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(8) Preparation of various disubstituted octafluoro[2.2]paracyclophanes will be reported in a subsequent publication: Roche, A. J.; Dolbier, W. R., Jr., manuscript in preparation.

(9) Bromination of OFP was reported in two patents. The products were ill-characterized, and in our hands, the reaction was unable to be reproduced. (a) Marvel, C. S. U.S. Patent 4,499,258, 1985. (b) Marvel, C. S. U.S. Patent 4,476,062, 1984.

(10) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: New York, 1973.

(11) (a) Cram, D. J.; Day, A. C. *J. Org. Chem.* **1966**, *31*, 1227. (b) Cram, D. J. *J. Am. Chem. Soc.* **1955**, *77*, 6289. (c) Cram, D. J.; Bauer, R. H.; Allinger, N. L.; Reeves, R. A.; Wetcher, W. J.; Heilbronner, E. *J. Am. Chem. Soc.* **1959**, *81*, 5977.

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of **2** was obtained when nitronium tetrafluoroborate in sulfolane was used as the nitrating medium.[12] The use of sulfuric acid as solvent with NO_2BF_4 gave no product, which was attributed to a solubility problem.

Clearly, the incorporation of one nitro functionality into the product deactivates both rings to further reaction, as no evidence of a dinitro product was observed under any of the above conditions, even when 3 equiv of nitronium tetrafluoroborate was used.

Because all eight fluorines of the starting material are equivalent, OFP appears as a singlet in the ^{19}F NMR spectrum (−118.0 ppm).[4] The introduction of a single substituent into the system destroys the high level of symmetry, and therefore the product now contains eight different fluorine atoms, which appear as four AB quartets, ($^2J_{F-F}$ values typically of about 240 Hz). This provides a very powerful tool to analyze these fluorinated phane derivatives because all of the fluorine signals are clearly resolved. It illustrates the power of ^{19}F NMR as an analytical probe, such that, thus far, each derivative has produced a unique spectrum. This is in sharp contrast to the methylene bridge region in the ^1H NMR spectra of hydrocarbon [2.2]PCPs, which is characteristically redundant because they "generally appear as a complex multiplet". (The ^{19}F and ^1H NMR of the bridge-fluorinated derivatives will be discussed in greater detail later).

Several classical methods[13] were attempted for the reduction of the nitro functionality. All were successful with moderate to good yields (i.e., $SnCl_2$, 64%) with the reducing agent of choice being Fe/HCl because of its superior yield (82%) and ease of product isolation (Figure 1.

It was interesting to observe that the use of H_2/PtO_2 in ethyl acetate gave rise to a high isolated yield (84%) of hydroxylamino derivative **3** after 24 h. Typical hydrogenations of aromatic nitro compounds to aromatic amines do not allow the isolation of the intermediary hydroxylamino compound.[14] Changing the solvent to methanol resulted in partial conversion to **4** (28%), along with 37% of **3**. As expected, **3** gave desired amino-OFP **4** when subjected to Fe/HCl conditions.

The *non*fluorinated [2.2]PCP amine is reportedly prone to oxidative decomposition,[11c] whereas **4** is very stable (over 1 year in air and sunlight). This difference can be attributed to the inductive influence of the bridge fluorines, which should make **4** significantly less prone to oxidation.

Compound **4** was an excellent precursor of a variety of other monosubstituted derivatives of **1**, the simplest being *N*-acyl derivatives. Such amides, potentially effective protecting groups of the amine functionality, were produced in almost quantitative yield. Examining the diazotization and Sandmeyer-type chemistry of **4**, a number of other derivatives including halo-, hydroxyl- and phenyl-OFP derivatives were produced in yields ranging from poor to good. The problem of low solubility of **4** in the aqueous strong acid used for such reactions could be overcome by the use of acetic acid as a cosolvent.

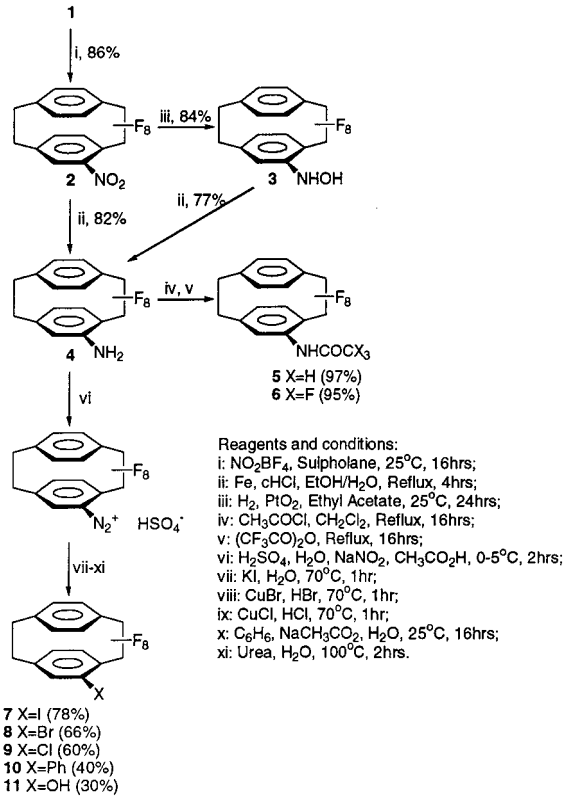
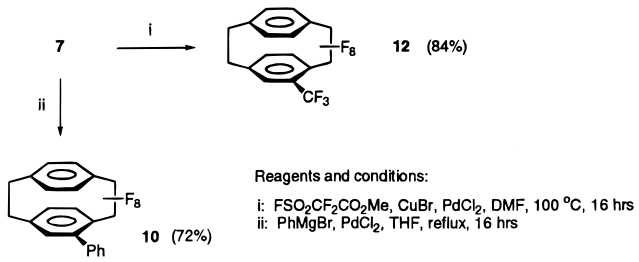


Figure 1. Ring-substituted derivatives of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane.

Whereas the iodo-, phenyl-, and hydroxy-OFP products **7**, **10**, and **11** were isolated as analytically pure compounds by column chromatography, bromo- and chloro-OFP derivatives **8** and **9** were contaminated by 5−10% of parent OFP (**1**) (the product of reduction), which could not be removed by either further column chromatography or recrystallization. Although analytical GC resolution (DB-5 column) was possible, analytically pure samples were not obtained for these two derivatives. (The 90−95% pure compounds were completely suitable for characterization because of the simple spectroscopic properties of impurity **1**).

The iodo and bromo derivatives **7** and **8** are especially important synthetically, because the haloarene functionality is potentially so versatile. Trifluoromethylation was attempted using Chen's methodology,[15] which generates a "$CuCF_3$" intermediate in situ. However, this gave only a poor yield of desired product **12** (<20%),with the major product being the parent cyclophane **1**.



The use of palladium dichloride as a catalyst in this reaction resulted in a much higher yield of desired **12** (84%) and a consequent decrease in the amount of reduc-

(12) For a review: Olah, G. A.; Malhetra, R.; Narang, S. C. *Nitration Methods and Mechanisms;* Organic Nitro Chemistry Series; VCH: New York, 1989.

(13) Larock, R. C. *Comprehensive Organic Transformations*; VCH: New York, 1989; p 411 and references located within.

(14) Rylander, P. N. *Hydrogenation Methods*; Academic Press: New York, 1985; Chapter 8.

(15) Chen, Q.-Y.; Wu, S.-W. *J. Chem. Soc., Chem. Commun.* **1989**, 705.

tion product (3%). There are numerous reports of nucleophilic aromatic substitution using aryl halides, $PdCl_2$, and organometallic reagents,[16] but we are unaware of any other reported application of $PdCl_2$ in *this* trifluoromethylation methodology. This probably is because the published uncatalyzed reactions proceeded in such high yields for the "simpler" substrates used that no further improvements were sought.[15] In a similar fashion, we have used phenylmagnesium bromide and iodo-OFP in the presence of $PdCl_2$ to produce phenyl-OFP (**10**) in 72% yield. When the reaction was performed without $PdCl_2$, only reduction product (**1**) was obtained (98%).

Synthetic Conclusions

Beginning with successful nitration, it has been possible to synthesize a total of 11 diverse, substituted octafluoroparacyclophanes. Because of the highly electron-deficient nature of the OFP system, these novel compounds, as well as other more complex and more highly subsituted examples, should also exhibit novel chemical and physical properties.

Characterization

Crucial to the success of the synthetic work was the ability to reliably characterize the paracyclophane derivatives. NMR and mass spectroscopic analyses are especially powerful probes that reveal unique effects characteristic of the [2.2]paracyclophane system.[1,17] Therefore, the spectroscopic features that were used to characterize the 11 OFP derivatives will be discussed and compared with spectra of their hydrocarbon analogues.

Nuclear Magnetic Resonance. Thorough investigations of the ^{1}H NMR spectra of [2.2]paracyclophanes have been published.[1,17] The major points of interest include the following: (1) the observation that the chemical shifts of the protons on both the substituted and the unsubstituted ring experience a high field shift with electron-donating substituents (and conversely a downfield shift with electron-withdrawing substituents), which has been taken as confirmation of "transannular electronic interactions"; (2) the magnitude and direction of the *ortho* shifts; (3) the magnitude of the pseudo *geminal* shifts, and (4) the calculation of individual substituent chemical shifts (SCS) values, which have allowed prediction of multiply substituted phane derivative NMR chemical shifts.

All of the general rules and strategies that have been derived for the purpose of characterization and interpretation of proton NMR spectra of hydrocarbon paracyclophane compounds appear to be equally valid for these new fluorinated phanes.

Throughout the description of these phane derivatives, the terminology pseudo meta, pseudo para, pseudo ortho, and pseudo geminal, coined by Cram to refer to positions in the unsubstituted ring, will be used throughout this paper in preference to a numbering system, because of inconsistency in the numbering systems for the unsubstituted ring as used by different groups.[18]

^{1}H NMR Spectra. As a result of its symmetric nature, parent OFP **1** shows only a single resonance (at δ 7.30 ppm)[4] for its eight equivalent protons in its ^{1}H NMR spectrum. This is downfield by about 1 ppm from the hydrocarbon analogue,[17] as expected by the decrease of shielding in the fluorinated system. When a single substituent is introduced into one of the rings, the symmetry is destroyed, and all seven remaining protons are become nonequivalent. As expected, they manifest themselves as one singlet (ortho hydrogen) and three AB patterns (meta/para, pseudo ortho/pseudo gem, pseudo meta/pseudo para) with typical splitting of around 8 Hz. All 11 fluorinated [2.2]paracyclophane derivatives exhibit this characteristic ^{1}H NMR format.

In his seminal work on similar hydrocarbon phane systems, Cram noticed that the amino substituent generally gave the most highly resolved, and thus the most readily analyzed, spectrum.[17] Likewise, amino-substituted OFP (**4**) also gave the best resolved spectrum, and it therefore received the most detailed characterization.

Amino-OFP (4). The ^{1}H NMR spectrum of **4** allows clear interpretation. Along with its broad NH_2 signal, it is easy to identify a singlet and six doublets (constituting three AB patterns), all of equal integral. The amino functionality disperses the chemical shifts over a range of almost 2 ppm. (A range of 1.79 ppm was reported for the hydrocarbon amine.)[19,20]

The ortho proton is always the easiest to assign because it is a singlet. In this case (and in most others), the doublet at lowest field was deshielded to that position by the "pseudo gem effect"[1] and was thus assigned as the pseudo geminal proton. The remaining proton resonances can be assigned either by inspection of the shapes of the AB quartets or, more reliably, by a ^{1}H/^{1}H COSY spectrum. This showed that the resonances at 7.986 and 7.180 ppm were components of one AB, as were the peaks at 7.395 and 7.101 ppm and finally 6.943 and 6.539 ppm. The ortho proton was also shown to couple with the AB farthest upfield, and thus these two peaks were designated as the meta and para resonances, with the para signal most upfield. Because the pseudo gem proton had already been identified, its AB counterpart must be the pseudo ortho proton. The remaining AB system must therefore be the pseudo meta and pseudo para pair. The exact assignment of these two resonances was ambiguous, but in keeping with previously verified shifts in the hydrocarbon cyclophane amine system, the upfield proton was tentatively assigned as pseudo meta.

The order of resonances in increasing chemical shift is ortho, para, meta, pseudo meta, pseudo ortho, pseudo para, and pseudo geminal, and this ordering is identical to that of the hydrocarbon amine analogue.[20]

The above assignments then allowed the calculation of SCS values for the amino group for the OFP skeleton, and they are tabulated and compared to the SCS amino values for the analogous hydrocarbon system in Table 1.[20]

The values for both systems are similar and in the same direction but not identical. In a future paper[8] it will be demonstrated that the SCS values for the OFP system are equally additive and are therefore useful for the prediction of spectra of new OFP derivatives. Although

(16) Especially relevant is Rozenberg, V. I.; Sergeeva, E. V.; Kharitonov, V. G.; Vorontsova, N. V.; Vorontsov, E. V.; Mikul'shina, V. V. *Russ. Chem. Bull.* **1994**, *43*, 1018.

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(18) For an example of conflict, compare refs 17c and 20.

(19) Allgeier, H.; Siegel, M. G.; Helgeson, R. C.; Schmidt, E.; Cram, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 3782.

(20) Pelter, A.; Crump, A. N. C.; Kidwell, H. *Tetrahedron: Asymmetry* **1998**, *9*, 713.

Table 1. ^{1}H SCS Values for Amino-OFP

proton orientation	OFP-NH_2	[2.2]PCP-NH_2[a]
ortho	−1.21	−1.11
para	−0.76	−0.36
meta	−0.36	−0.22
pseudo meta	−0.20	−0.11
pseudo ortho	−0.12	−0.11
pseudo para	0.01	0.10
pseudo geminal	0.69	0.68

[a] Values taken from ref 20.

Table 2. Comparison of ortho and gem Shifts of OFP and [2.2]PCP[a]

substituent	OFP gem shift	[2.2]PCP gem shift	OFP ortho shift	[2.2]PCP ortho shift
NO_2	0.24	0.14	0.44	0.73
NH_2	0.69	0.68	−1.21	−1.11
NHOH	0.57		−0.66	
Cl	0.57	0.75	−0.12	
Br	0.57	0.79	0.08	0.02
I	0.57	0.86	0.39	0.44
Ph			−0.06	
CF_3			−0.01	
OH	0.12	0.60	−0.31	−0.89
$NHCOCH_3$			0.76	
$NHCOCF_3$			0.74	

[a] [2.2]PCP values taken from refs 20, 17a, and 17c.

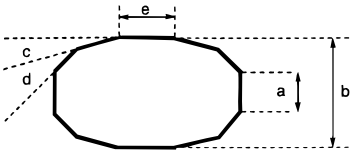


Figure 2. Structural parameters of [2.2]paracyclophane systems.

Table 3. Comparison of Structural Features of OFP and [2.2]PCP

	[2.2]PCP	OFP
a (Å)	1.569	1.577
b (Å)	3.09	3.09
c (deg)	12.6	11.8
d (deg)	11.2	12.6
e (Å)	1.394	1.380

the amino-OFP system is currently the only monosubstituted derivative to have its ^{1}H spectrum fully assigned, the ortho and gem shifts are instantly recognizable for almost all of the other OFP derivatives synthesized here, for the previously described reasons. Values of both of these shifts are listed in Table 2. The overlapping nature of certain proton spectra allowed the identification of only one of these shifts for (a) the chloro- and bromo-OFP derivatives, for which only the geminal shifts are sufficiently separated from a multiplet for unambiguous assignment; (b) the phenyl derivative, in which the phenyl protons mask the cyclophane ring protons; and (c) the trifluoromethyl derivative, which shows no discernible gem effect (thus only ortho shift given).

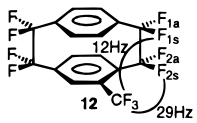
The differences in the magnitude of geminal shift between the fluorinated and hydrocarbon systems are small. This is not unexpected because this effect is believed to be a "through space" phenomena, and crystal structures[21] of OFP and [2.2]PCP (Figure 2, Table 3) show that although there are subtle differences between the ring deformation angles and the C−C bridge lengths (1.577 and 1.569 Å, respectively) of the two molecules, the distance between the two geminal carbons responsible for bearing the appropriate substituent and hydrogen are identical in both structures (3.09 Å). Also the ring hydrogens are known to tilt "inward" in both molecules by a similar amount (0.037 Å for OFP and 0.041 Å for [2.2]PCP, vertical deviations from their appropriate carbon planes). Assuming that both systems suffer similar ring tilt and deformation on introduction of the substituent, the above geometric similarities would lead one to expect very similar pseudo gem shifts for the hydrocarbon and fluorocarbon systems, as is observed. The questions of ring tilt and geometric deformation would be answered by a series of crystal structures of these derivatives, and work in this area is underway.

Ortho shifts are somewhat related to the bond character between the relevant carbons and since Z-protons in vinyl compounds show shifts larger than benzene ortho shifts,[17a] it seems the shorter the bond, the larger the magnitude of shift. Therefore, it might be predicted that larger ortho shifts should be exhibited by OFP derivatives because the middle ring bond distance (e) is shorter in OFP than in [2.2]PCP.[21] However, there seemed to be no discernible correlation between the ortho shifts in these two [2.2]paracyclophane systems.

^{19}F NMR Spectra. The opportunity to observe and distinguish the bridge fluorine atoms using ^{19}F NMR brings a new dimension to the characterization of these fluorinated phanes. Destruction of the symmetric nature of OFP occurs upon introduction of a single substituent onto one of the rings. Thus, all eight fluorine atoms are chemically nonequivalent, leading to four AB patterns in the observed spectra. All 11 new fluorinated phanes not only display this characteristic pattern, but their spectra are uniquely distinct. The introduction of a substituent into the OFP derivatives causes the fluorine chemical shifts to be spread typically over a range of 10−20 ppm. Although one can readily match the partners of each AB system by their $^2J_{F-F}$ coupling constants (typically ∼240 Hz) and their line shapes, it is not so easy to assign exactly which fluorine atom gives rise to which specific resonance. This problem will be more fully assessed in a subsequent publication.[8]

It is pertinent to observe that the direction of the shifts on the bridge fluorine atoms are not as straightforward as for the ^{1}H NMR spectrum of the aromatic ring (i.e., electron-donating functionalities shift upfield, electron-withdrawing groups shift downfield), because all of the derivatives described here have most of their fluorine shifts downfield relative to OFP (δ_F −118.00 ppm). Thus far, all chemical shifts have appeared between δ_F −100 and −120 ppm.

One unusual effect was observable in the ^{19}F NMR of trifluoromethylated OFP derivative **12**. The CF_3 resonance appeared as a doublet of doublets (29.07, 12.14 Hz), and correspondingly, two of the bridge fluorine signals were split into quartets. The two resonances split into quartets were not partners in the same AB and were therefore assigned as the 2-*syn* and 1-*syn* fluorines, respectively.



(21) Hope, H.; Bernstein, J.; Trueblood, K. N. *Acta Crystallogr., Sect. B* **1972**, *28*, 1733.

Clearly this effect must be a "through space" coupling, as the values of $^5J_{F-F}$ and $^6J_{F-F}$ are well above those for typical through bond couplings.[22] This interaction of an NMR active nuclei allows the assignment of four of the bridge fluorines to their resonances. This effect has been demonstrated to allow assignment of all bridge fluorines in disubstituted OFP derivatives and will be reported in a subsequent paper.[8]

Continuing studies directed at further assignments and complete characterization of these derivatives and full ^{1}H, ^{13}C, and ^{19}F correlations will be published separately.[23]

Mass Spectra. Low energy electron ionization mass spectroscopy is a powerful weapon in the characterization of paracyclophanes because it permits the observation of not only the parent ion peak but also the fragments corresponding to the top and bottom halves of the PCP, thereby allowing determination of the number of substituents on each ring.[1,17a] Most of the trends observed in the EI mass spectra of [2.2]PCPs are equally manifest in the mass spectra of these OFP derivatives. Intuitively, one would predict the radical cations of the corresponding tetrafluoro-*p*-xylylene fragments to be less stable than their hydrocarbon counterparts,[10] yet this does not seem to hinder the "classical" fragmentation observed for [2.2]-PCPs from being equally valid and therefore useful for these bridge-fluorinated analogues.

Typically the tetrafluoro-*p*-xylylene fragment dominates the mass spectrum, exceptions being for fragments bearing electron-donating substituents (amino-, phenyl-, and hydroxyl-substituted phanes), in which these substituents lend stability to the radical cation. The *N*-acetyl derivative shows 191 as the 100% peak, which corresponds to the amino-substituted tetrafluoroxylylene, which must be formed via some further fragmentation inside the mass spectrometer. Tetrafluoro-*p*-xylylene fragments bearing a nitro group were not observed[17a] and the trifluoromethyl substituted derivative gave only a minor substituted xylylene fragment.

Other Properties. Melting Points. All of the OFP derivatives reported here have been white, crystalline solids. The melting points of the unsubstituted OFP **1** (mp 262−264 °C) and its corresponding monosubstituted derivatives (see compounds **2**−**7** and **12** in the Experimental Section) are all lower than those of their hydrocarbon analogues ([2.2]PCP mp 285−287 °C), with the average typically being about 20 °C lower.

Ultraviolet Spectra. The UV spectra of OFP and its monosubstituted derivatives closely resemble those of their related hydrocarbon systems, with the OFP derivatives displaying a characteristic red shift and lower intensities relative to the hydrocarbon systems, as one would expect from less electron density in the rings caused by the electron-withdrawing effect of the fluoroalkyl bridges.[10] For example, the λ_{max} values for OFP (**1**) and its hydrocarbon [2.2]PCP analogue are 310 (148) and 302 (160) nm,[11c] respectively.

Characterization Conclusions. It has been demonstrated that the general NMR and mass spectral phenomena that are characteristic of substituted hydrocarbon [2.2]paracyclophanes apply equally to the bridge-fluorinated systems. Certainly, this is not unreasonable because the strain and rigid geometries of the systems are similar. Nevertheless, in view of the interest in the octafluoroparacyclophane system as a source of new materials, it was important to clearly demonstrate and understand the optimal approach to characterization of this series of 11 *mono*substituted octafluoroparacyclophanes to set the table for the expected more demanding characterizations of the various *multi*substituted octafluoroparacyclophanes that will likely be reported in the future.

Experimental Section

General. All NMR spectra were obtained at ambient temperatures in deuterated acetone, with TMS as ^{1}H reference and $CFCl_3$ as ^{19}F reference. All reagents, unless otherwise specified, were used as purchased from Aldrich or Fisher. Column chromatography was performed using chromatographic silica gel 200−425 mesh as purchased from Fisher. Melting points are uncorrected. Mass spectroscopic analyses were obtained at an ionizing potential of 70 eV. UV spectra were taken as dilute samples in acetonitrile.

4-Nitro-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (2). Under a countercurrent of dry nitrogen, nitronium tetrafluoroborate (0.94 g, 7.10 mmol) was added to octafluoroparacyclophane **1** (1.00 g, 2.84 mmol)[5] dissolved in sulfolane (5 mL), and the reaction was stirred at room temperature overnight. The reaction mixture was then added to ice water (100 mL), and the white precipitate was filtered and chromatographed (hexane/chloroform 6/4) to give (R_f = 0.43) 4-nitro-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **2** (0.96 g, 86%): mp 119−119.5 °C; ^{1}H NMR δ 7.736 (s, 1H); 7.683 (s, 2H); 7.628 (d, ^3J = 8.40 Hz, 1H); 7.440 (d, ^3J = 8.40 Hz, 1H); 7.507 (d, ^3J = 8.40 Hz, 1H); 7.544 (d, ^3J = 8.40 Hz, 1H); ^{19}F NMR δ −111.084 (d, ^2J = 247.24 Hz, 1F); −113.787 (d, ^2J = 247.24 Hz, 1F); −115.538 (m, 2F); −116.221 (d, ^2J = 239.90 Hz, 1F); −117.734 (d, ^2J = 239.90 Hz, 1F); −116.221 (d, ^2J = 239.90 Hz, 1F); −117.592 (d, ^2J = 239.90 Hz, 1F); MS *m*/*z* 397 (M^+, 16%), 176 (100); UV λ_{max} = 320 nm (ϵ = 586). Anal. Calcd for $C_{16}H_7F_8NO_2$: C, 48.36; H, 1.76; N, 3.53. Found: C, 48.02; H, 1.58; N, 3.56.

A mixture of octafluoroparacyclophane **1** (1.08 g, 3.07 mmol) and 67% nitric acid (11 mL) was stirred vigorously and heated at 100 °C for 24 h. After the mixture cooled to room temperature, 100 mL of ice water was added, and the precipitates were collected and subjected to column chromatography as above, yielding 4-nitro-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **2** (0.68 g, 56%).

Identical reactions as above employing 98% sulfuric acid (11 mL) or sulfolane (12 mL) as solvents gave isolated yields of 4-nitro-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **2** of 60% and 56%, respectively.

4-Amino-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (4). A suspension of 4-nitro-1,1,2,2,9,9,10,10-octafluoro-[2.2]paracyclophane **2** (4.5 g, 11.3 mmol) in ethanol/water (1/1 v/v, 50 mL) was stirred for 1 h at room temperature. Iron powder (3.8 g, 67.8 mmol) was added, and the reaction mixture was heated to reflux. Concentrated hydrochloric acid (5 mL) was added dropwise to the mixture, and reflux was continued for 4 h. After this time, the reaction was cooled to room temperature and added to ice water (200 mL). The solids thus produced were filtered and redissolved in chloroform. This chloroform solution was filtered and evaporated, and the solid residue was chromatographed (hexane/dichloromethane 1/1) to give (R_f = 0.45) 4-amino- 1,1,2,2,9,9,10,10-octafluoro[2.2]-paracyclophane **4** (3.40 g, 82%): mp 221−223 °C; ^{1}H NMR δ 7.986 (d, ^3J = 8.10 Hz, 1H); 7.395 (d, ^3J = 8.70 Hz, 1H); 7.180 (d, ^3J = 8.10 Hz, 1H); 7.101 (d, ^3J = 8.70 Hz, 1H); 6.943 (d, ^3J = 8.70 Hz, 1H); 6.539 (d, ^3J = 8.70 Hz, 1H); 6.089 (s, 1H); 5.596 (br s, 2H, NH_2); ^{19}F NMR δ −105.052 (d, ^2J = 249.49 Hz, 1F); −111.817 (d, ^2J = 249.49 Hz, 1F); −106.559 (d, ^2J = 237.36 Hz, 1F); −110.568 (d, ^2J = 237.36 Hz, 1F); −114.021

(22) Emsley, J. W.; Phillips, L. Wray, V. *Fluorine Coupling Constants*; Pergamon Press: Oxford, 1977.

(23) Roche, A. J.; Ghiviriga, I.; Dolbier, W. R., Jr., unpublished results.

(d, ^2J = 232.56 Hz, 1F); −117.329 (d, ^2J = 232.56 Hz, 1F); −115.690 (d, ^2J = 237.64 Hz, 1F); −116.157 (d, ^2J = 237.64 Hz, 1F); MS *m*/*z* 367 (M^+, 22%), 191 (100), 176 (14); UV λ_{max} = 356 nm (ϵ = 420). Anal. Calcd for $C_{16}H_9F_8N$: C, 52.32; H, 2.45; N, 3.81. Found: C, 52.38; H, 2.31; N, 3.74.

4-Hydroxylamino-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (3). A solution of 4-nitro-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **2** (0.70 g, 1.76 mmol) and platinum oxide (21 mg, 9.25 × 10^{-5}mol) in ethyl acetate (30 mL) was stirred at room temperature under an atmosphere of hydrogen gas for 24 h. After this time the reaction mixture was diluted with diethyl ether (50 mL) and filtered through a Celite plug. Evaporation of the solvents left a residue that after column chromatography (chloroform) gave (R_f = 0.29) 4-hydroxylamino-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **3** (0.57 g, 84%): mp 160−162 °C; ^{1}H NMR δ 7.865 (d, ^3J = 8.40 Hz, 1H); 7.344 (d, ^3J = 8.10 Hz, 1H); 7.167 (d, ^3J = 8.40 Hz, 1H); 7.078 (s, 2H); 6.803 (d, ^3J = 8.10 Hz, 1H); 6.640 (s, 1H); 8.480 (br s, 1H, NH); 8.148 (br s, 1H, OH); ^{19}F NMR δ −103.370 (d, ^2J = 239.90 Hz, 1F); −111.532 (d, ^2J = 239.90 Hz, 1F); −107.819 (d, ^2J = 239.90 Hz, 1F); −111.400 (d, ^2J = 239.90 Hz, 1F); −113.696 (d, ^2J = 234.818 Hz, 1F); −116.996 (d, ^2J = 234.82 Hz, 1F); −115.421 (d, ^2J = 237.36 Hz, 1F); −116.087 (d, ^2J = 237.36 Hz, 1F); MS *m*/*z* 383 (M^+, 61%), 207(14), 176 (100). Anal. Calcd for $C_{16}H_9F_8NO$: C, 50.13; H, 2.35; N, 3.66. Found: C, 50.50; H, 2.63; N, 3.53.

When an identical reduction was performed using methanol (30 mL) as solvent, after 24 h the reaction mixture was comprised of 4-hydroxylamino-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **3** (37%) and 4-amino-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **4** (28%).

Reduction of 4-Hydroxylamino-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (3). When 4-hydroxylamino-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **3** was subjected to the same iron/hydrochloric acid reduction as described above for 4-nitro-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **2**, it afforded, after chromatography, 4-amino-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **4** (77%).

Typical Diazotization Procedure. A solution of 4-amino-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **4** (0.70 g, 1.91 mmol) in acetic acid (2 mL) was cooled to 0 °C in an ice/brine bath. Ice (0.7 mL) and concentrated sulfuric acid (0.7 mL) were carefully added with stirring, and ensuring the temperature was still below 0 °C, sodium nitrite (0.40 g, 5.80 mmol) was added in one batch. The reaction was stirred at this temperature for 2 h and then used for the following transformations.

4-Iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (7). An aqueous solution (10 mL) of potassium iodide (3.15 g, 18.98 mmol) was warmed to 70 °C, and the diazotization solution previously prepared was added in one batch with stirring. The mixture was kept at 70 °C for 1 h and then left to cool overnight. The precipitated product was filtered and chromatographed (hexane/dichloromethane 9/1) to give (R_f = 0.45) 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **7** (0.71 g, 78%): mp 109−111 °C; ^{1}H NMR δ 7.865 (d, ^3J = 8.40 Hz, 1H); 7.688 (s, 1H); 7.505−7.320 (m, 5H); ^{19}F NMR δ −102.462 (d, ^2J = 244.41 Hz, 1F); −112.356 (d, ^2J = 244.41 Hz, 1F); −111.327 (d, ^2J = 237.38 Hz, 1F); −112.322 (d, ^2J = 237.38 Hz, 1F); −114.639 (d, ^2J = 237.38 Hz, 1F); −116.905 (d, ^2J = 237.38 Hz, 1F); −115.911 (d, ^2J = 237.38 Hz, 1F); −116.251 (d, ^2J = 237.38 Hz, 1F); MS *m*/*z* 478 (M^+, 28%), 302 (19), 176 (100). Anal. Calcd for $C_{16}H_7F_8I$: C, 40.17; H, 1.46. Found: C, 40.51; H, 1.42.

4-Bromo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (8). An aqueous solution (10 mL) of copper(I) bromide (2.80 g, 19.52 mmol) and 47% hydrobromic acid (10 mL) was warmed to 70 °C, and the diazotization solution previously prepared was added in one batch with stirring. The mixture was kept at 70 °C for 1 h and then left to cool overnight. The precipitated product was filtered and chromatographed (hexane/dichloromethane 9/1, R_f = 0.45) to give a mixture of two compounds in a 92:8 ratio (as determined by ^{19}F NMR and GLC analysis) identified as 4-bromo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **8** (1.26 mmol, 66%):^{1}H NMR δ 7.868 (d, ^3J = 8.40 Hz, 1H); 7.378 (s, 1H); 7.305−7.504 (m, 5H); ^{19}F NMR δ −110.230 (d, ^2J = 244.70 Hz, 1F); −111.276 (d, ^2J = 244.70 Hz, 1F); −110.275 (d, ^2J = 237.36 Hz, 1F); −112.518 (d, ^2J = 237.36 Hz, 1F); −116.064 (d, ^2J = 239.90 Hz, 1F); −116.573 (d, ^2J = 239.90 Hz, 1F); −116.705 (m, 2F); MS *m*/*z* 432 (M^+, 3%), 430 (3), 256 (13), 254 (13), 176 (100); HRMS calcd for $C_{16}H_7F_8Br$ 430.9682, found 429.9638; and octafluoroparacyclophane **1** (0.11 mmol, 6%).

4-Chloro-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (9). An aqueous solution (10 mL) of copper(I) chloride (2.03 g, 20.15 mmol) and 47% hydrochloric acid (10 mL) was warmed to 70 °C, and the diazotization solution previously prepared was added in one batch with stirring. The mixture was kept at 70 °C for 1 h and then left to cool overnight. The precipitated product was filtered and chromatographed (hexane/dichloromethane 9/1, R_f = 0.45) to give a mixture of two compounds in a 90:10 ratio (as determined by ^{19}F NMR and GLC analysis) identified as 4-chloro-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **9** (1.15 mmol, 60%):^{1}H NMR δ 7.867 (d, ^3J = 8.40 Hz, 1H); 7.182 (s, 1H); 7.544−7.304 (m, 5H); ^{19}F NMR δ −110.785 (d, ^2J = 244.70 Hz, 1F); −111.869 (d, ^2J = 244.70 Hz, 1F); −111.767 (d, ^2J = 237.36 Hz, 1F); −112.646 (d, ^2J = 237.36 Hz, 1F); −116.210 (d, ^2J = 237.36 Hz, 1F); −116.540 (d, ^2J = 237.36 Hz, 1F); −116.646 (d, ^2J = 239.62 Hz, 1F); −116.940 (d, ^2J = 239.62 Hz, 1F); MS *m*/*z* 386 (M^+, 2%), 388 (1), 210 (21), 212 (5), 176 (100); HRMS calcd for $C_{16}H_7F_8Cl$ 386.0108, found 386.0110; and octafluoroparacyclophane **1** (0.19 mmol, 10%).

4-Phenyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (10). Benzene (10 mL) was added to the chilled diazotization solution, and 1 min later an aqueous (3 mL) solution of sodium acetate (1.00 g, 12.20 mmol) was added. The biphasic mixture was allowed to warm to room temperature overnight with vigorous stirring. Diethyl ether (30 mL) was then added, and the bright orange organic phase was separated, dried, and evaporated. The crude residue was chromatographed (hexane/dichloromethane 9/1) to give (R_f = 0.27) 4-phenyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **10** (0.33 g, 40%): ^{1}H NMR δ 7.241 (s, 1H); 7.606−7.328 (m, 11H); ^{19}F NMR δ −102.098 (d, ^2J = 239.90 Hz, 1F); −110.814 (d, ^2J = 239.90 Hz, 1F); −115.334 (m, 2F); −115.417 (d, ^2J = 237.36 Hz, 1F); −117.901 (d, ^2J = 237.36 Hz, 1F); −116.690 (d, ^2J = 239.62 Hz, 1F); −117.838 (d, ^2J = 239.62 Hz, 1F); MS *m*/*z* 428 (M^+, 11%), 251 (100), 176 (61). HRMS calcd for $C_{22}H_{12}F_8$ 428.0811, found 428.0793.

4-Hydroxy-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (11). An aqueous solution (10 mL) of urea (3 mg, 5.0 × 10^{-5}mol) was heated to reflux, and the diazotization solution previously prepared was added in one batch. Reflux was maintained for 2 h, and then the solution was allowed to cool to room temperature overnight. The resulting precipitate was filtered and chromatographed (chloroform) to give (R_f = 0.42) 4-hydroxy-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **11** (0.21 g, 30%): ^{1}H NMR δ 7.424 (d, ^3J = 8.10 Hz, 1H); 7.246 (d, ^3J = 8.40 Hz, 1H); 7.183 (d, ^3J = 8.40 Hz, 1H); 7.104 (d, ^3J = 8.40 Hz, 1H); 7.054 (d, ^3J = 8.10 Hz, 1H); 6.988 (s, 1H); 6.831 (d, ^3J = 8.10 Hz, 1H); 7.554 (br s, 1H, OH); ^{19}F NMR δ −102.462 (d, ^2J = 244.41 Hz, 1F); −112.356 (d, ^2J = 244.41 Hz, 1F); −111.327 (d, ^2J = 237.38 Hz, 1F); −112.322 (d, ^2J = 237.38 Hz, 1F); −114.639 (d, ^2J = 237.38 Hz, 1F); −116.905 (d, ^2J = 237.38 Hz, 1F); −115.911 (d, ^2J = 237.38 Hz, 1F); −116.251 (d, ^2J = 237.38 Hz, 1F); MS *m*/*z* 368 (M^+, 14%), 192 (100), 176 (20); HRMS calcd for $C_{16}H_8F_8O$ 368.0473, found 368.0382.

4-Acetamido-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (5). A dichloromethane solution (5 mL) of 4-amino-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **4** (150 mg, 0.41 mmol) was warmed to reflux, acetyl chloride (3 mL) in dichloromethane (3 mL) was added dropwise, and the reaction was refluxed overnight. Rotary evaporation afforded a pale brown residue, which after chromatography (chloroform/hexane 8/2) gave (R_f = 0.30) 4-acetamido-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **5** (162 mg, 97%): mp 183−184.5 °C; ^{1}H NMR δ 8.066 (s; 1H); 7.600−7.210 (m, 5H); 7.110 (d, ^3J = 8.10 Hz, 1H); 8.820 (br s, 1H, NH); 2.249 (s, 3H, CH_3); 6.988

(s, 1H); 6.831 (d, ^3J = 8.10 Hz, 1H); 7.554 (br s, 1H, OH); ^{19}F NMR δ −105.978 (d, ^2J = 244.70 Hz, 1F); −112.138 (d, ^2J = 244.70 Hz, 1F); −112.002 (d, ^2J = 237.36 Hz, 1F); −113.581 (d, ^2J = 237.36 Hz, 1F); −116.347 (d, ^2J = 237.36 Hz, 1F); −116.728 (d, ^2J = 237.36 Hz, 1F); −116.363 (d, ^2J = 237.36 Hz, 1F); −116.703 (d, ^2J = 237.36 Hz, 1F); MS *m*/*z* 409 (M^+, 32%), 233 (41), 191 (100), 176 (55). Anal. Calcd for $C_{18}H_{11}F_8NO$: C, 52.80; H, 2.69; N, 3.42. Found: C, 52.70; H, 2.68; N, 3.46.

4-Trifluoroacetamido-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (6). A solution of 4-amino-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **4** (203 mg, 0.55 mmol) in trifluoroacetic anhydride (5 mL) was refluxed overnight. After this time, rotary evaporation yielded a solid residue that after chromatography (chloroform/hexane 8/2) afforded (R_f = 0.61) 4-trifluoroacetamido-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **6** (243 mg, 95%): mp 108−109.5 °C; ^{1}H NMR δ 7.543 (s, 1H); 7.364−7.317 (m, 3H); 7.254−7.156 (m, 3H); 8.510 (br s, 1H, NH); ^{19}F NMR δ −109.776 (d, ^2J = 246.95 Hz, 1F); −112.288 (d, ^2J = 246.95 Hz, 1F); −113.717 (d, ^2J = 239.90 Hz, 1F); −114.724 (d, ^2J = 239.90 Hz, 1F); −116.293 (d, ^2J = 239.90 Hz, 1F); −117.555 (d, ^2J = 239.90 Hz, 1F); −116.726 (d, ^2J = 237.36 Hz, 1F); −117.594 (d, ^2J = 237.36 Hz, 1F); −76.832 (s, 3F); MS *m*/*z* 363 (M^+, 22%), 287 (18), 176 (100). Anal. Calcd for $C_{18}H_8F_{11}NO$: C, 46.65; H, 1.73; N, 3.02. Found: C, 46.39; H, 1.75; N, 2.94.

4-Phenyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (10) (alternative method). A degassed THF solution (2 mL) containing 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2] paracyclophane **7** (320 mg, 0.67 mmol) and palladium dichloride (4 mg, 0.02 mmol) was stirred and brought to reflux under a nitrogen atmosphere. A THF solution of phenylmagnesium bromide (1 M, 2 mL, 2.0 mmol) was added via syringe, and the black solution was refluxed overnight. Evaporation of the solvent was followed by the addition of ice water (50 mL), and the precipitated solids were chromatographed (hexane/dichloromethane 8.5/1.5) to give (R_f = 0.49) octafluoro[2.2]paracyclophane **1** (21 mg, 9%) and (R_f = 0.39) 4-phenyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **10** (206 mg, 72%).

4-Trifluoromethyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (12). A degassed DMF solution (10 mL) containing 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **7** (280 mg, 0.59 mmol), methyl 2-(fluorosulfonyl)difluoroacetate (450 mg, 2.34 mmol), and palladium dichloride (40 mg, 0.23 mmol) was warmed to 80 °C under a blanket of nitrogen. Copper(I) bromide (250 mg, 1.75 mmol) was added in one portion, and the mixture was maintained at that temperature overnight. Then the mixture was cooled to ambient temperature before adding ice water (50 mL). The mixture was stirred for 30 min, and then the precipitates were removed by filtration and subjected to column chromatography (hexane/diethyl ether 9/1), affording (R_f = 0.50) 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **1** (6 mg, 3%) and (R_f = 0.39) 4-trifluoromethyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **12** (208 mg, 84%): mp 76−78 °C. δ 7.693 (s, 1H); 7.623 (s, 2H); 7.554 (d, ^3J = 8.40 Hz, 1H); 7.505 (d, ^3J = 8.40 Hz, 1H); 7.364 (d, ^3J = 8.40 Hz, 1H); 7.323 (d, ^3J = 8.40 Hz, 1H); ^{19}F NMR δ −108.226 (dd, ^2J = 242.16, ^3J = 7.06 Hz, 1F); −113.278 (dq, ^2J = 242.16, ^5J = 29.07 Hz, 1F); −113.811 (dq, ^2J = 235.10, ^6J = 12.14 Hz, 1F); −114.823 (dd, ^2J = 235.10, ^3J = 7.07 Hz, 1F); −114.677 (d, ^2J = 244.70 Hz, 1F); −118.189 (dd, ^2J = 244.70, ^3J = 4.86 Hz, 1F); −115.449 (d, ^2J = 237.36 Hz, 1F); −117.623 (dd, ^2J = 237.36, ^3J = 4.86 Hz, 1F); MS *m*/*z* 420 (M^+, 13%), 244 (7), 176 (100). Anal. Calcd for $C_{17}H_7F_{11}$: C, 48.57; H, 1.67. Found: C, 48.21; H, 1.69.

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