Generation of Fluorinated *m*-Benzyne Derivatives in Neon Matrices

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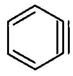
The fluorinated *m*-didehydrobenzenes 5-H-, 5-deuterio-, 5-(trifluoromethyl)-, 5-(trimethylsilyl)-, and 5-iodo-2,4,6-trifluoro-1,3-didehydrobenzene **6b**–**6f** were generated by UV photolysis of the corresponding 1,3-diiodobenzene derivatives **4b**–**4f** in solid neon at 3 K. The photolysis of **1** proceeds stepwise via the phenyl radical intermediates **5b**–**5f**. The radicals **5** and *m*-benzynes **6** were identified by comparison of their experimentally measured IR spectra with those produced by DFT calculations. The formation of mono- and diradicals **5** and **6**, respectively, is reversible, and annealing of the matrix at 7.5 K results in a decrease in all IR absorptions assigned to the radical products and in back-formation of the diiodobenzenes. The influence of the substituents in the 5-position on the geometries and the electronic structures of the diradicals **6** is discussed. The calculations indicate that the singlet-triplet splittings of the substituted *m*-benzynes **6b**–**6f** are larger and the C^1–C^3 distances shorter than those in the parent *m*-benzyne (C_6H_4).

Introduction

The three isomeric didehydrobenzenes (benzynes) are interesting reactive species that have been discussed as intermediates in a number of reaction mechanisms. *o*-Benzyne (**1**) and its derivatives have found many applications in organic synthesis, and its chemical and spectroscopic properties are well understood. *m*-Benzyne (**2**) is much less well understood, and substituent effects on the electronic[1] and spectroscopic[2,3] properties and on the reactivity[4–6] of *m*-benzynes were reported only recently.

So far, the application of matrix isolation spectroscopy for the investigation of derivatives of *m*- and *p*-benzyne has been hampered by a lack of suitable photochemical precursors. Photolysis of matrix-isolated radical precursors always produces radical pairs in matrix cages. If the radical pairs are not separated by inert molecules such as photochemically formed fragments (CO_2 in the photolysis of diacyl peroxides, for example) or the matrix gas, the radical pair will rapidly recombine. To circumvent this problem, *meta*-*para*-cyclophanediones[3] have been used as precursors of *m*-benzyne (**2**) and several of its derivatives. In this case the photochemical fragmentation produces the benzyne and the relatively stable *p*-xylylene instead of radicals. A disadvantage of this precursor is that only very limited substitution patterns of the cyclophane are synthetically available.



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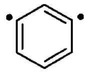

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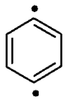

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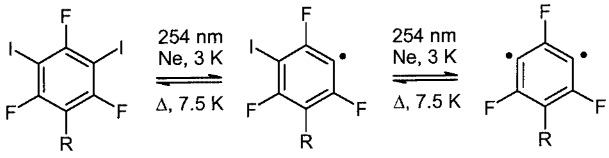
Substituted diiodobenzenes are readily available and should be suitable precursors of substituted *m*- and *p*-benzynes. However, the recombination of iodine atoms with the radical fragments in solid argon is rapid and prevents the formation of detectable amounts of diradicals. In contrast, irradiation in solid neon at very low temperatures (3 K) produced the monoradical and benzyne derivatives in reasonable yields.[2,7] The formation of the benzynes depends not only on the matrix material and temperature, but also on the substituents on the diiodobenzene. Thus, fluorinated diiodobenzenes produce benzynes in moderate to high yields, while the parent 1,3- and 1,4-diiodobenzene yield only traces of the corresponding benzynes. The reason for this striking difference in product formation is not yet clear. Here we describe the photochemical synthesis and spectroscopic characterization of the substituted phenyl radicals **5b**−**f** and the *m*-benzynes **6b**−**f**.



4 **5** **6**

a R = F **d** R = CF_3
b R = H **e** R = $SiMe_3$
c R = D **f** R = I

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Results and Discussion

1,3-Didehydro-2,4,6-trifluorobenzene (6b)

Irradiation (5 min, 254 nm) of 2,4,6-trifluoro-1,3-diiodobenzene (**4b**) in a neon matrix at 3 K results in a reduction of intensity in the IR bands of **4b** and concurrent formation of a new compound **A** which was identified as the 2,4,6-trifluoro-3-iodophenyl radical **5b**, formed by the photochemical cleavage of one of the C−I bonds. This assignment is confirmed by comparison with the spectrum calculated at the B3LYP/6-311G(d,p) level of theory, which nicely reproduces the observed IR spectrum (Table 1). The most intense absorption at 1556.7 cm^{-1} (calculated at 1585.2 cm^{-1}) is due to a C−C stretching vibration of the aromatic ring system.

Table 1. IR spectroscopic data of the 2,4,6-trifluoro-3-iodophenyl radical **5b**

Mode	Sym.	$\tilde{\nu}_{exp.}$ [cm^{-1}][a]	$I_{rel,exp.}$ [b]	$\tilde{\nu}_{calcd.}$ [cm^{-1}][c]	$I_{rel,calcd.}$ [b,c]
9	a′	501.4	0.06	509.6	0.02
10	a′	561.0	0.05	565.1	0.08
11	–	–	–	582.7	0.03
12	–	–	–	583.6	0.02
13	a′	–	–		0.00
14	a"	–	–	621.3	0.01
15	a"	–	–	680.2	0.03
16	a"	831.2 836.1	0.10 0.10	829.2	0.20
17	a′	985.3	0.93	992.8	0.44
18	a′	1039.1	0.56	1047.3	0.23
19	a′	1046.9	0.22	1058.6	0.51
20	a′	1147.0	0.26	1162.3	0.43
21	a′	1272.6	0.10	1314.3	0.13
22	a′	1365.9	0.07	1383.1	0.22
23	a′	1408.7	0.48	1423.5	0.58
24	a′	1425.4	0.67	1443.2	0.42
25	a′	1556.7	1.00	1585.3	1.00
26	a′	1619.7 1624.6	0.30 0.20	1650.3	0.73
27	a′	–	–	3209.0	0.02

[a] Neon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the B3LYP/6-311G(d,p) level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

Prolonged irradiation results in a further decrease in **4b**, the yield of the 2,4,6-trifluoro-3-iodophenyl radical **5b** increases, and a further species **B** appears in the IR spectrum. The formation of both phenyl radical **5b** and the secondary photoproduct **B** is thermally reversible. Several minutes annealing of the matrix at 7.5 K reforms the 2,4,6-trifluoro-1,3-diiodobenzene (**4b**). The IR spectrum of **B** exhibits a broad absorption at 1769 cm^{-1}, similar to the a_1 symmetrical ring stretching vibration at 1823 cm^{-1} observed for 1,3-didehydro-2,4,5,6-tetrafluorobenzene (**6a**). From the stepwise formation, the thermal reversibility, and the analogous reaction of the perfluorinated derivative **6a**, the secondary product is assigned the structure of the diradical 1,3-didehydro-2,4,6-trifluorobenzene (**6b**). This assignment is supported by DFT calculations at the BLYP/6-311G(d,p) level of theory (Figure 1, Table 2).

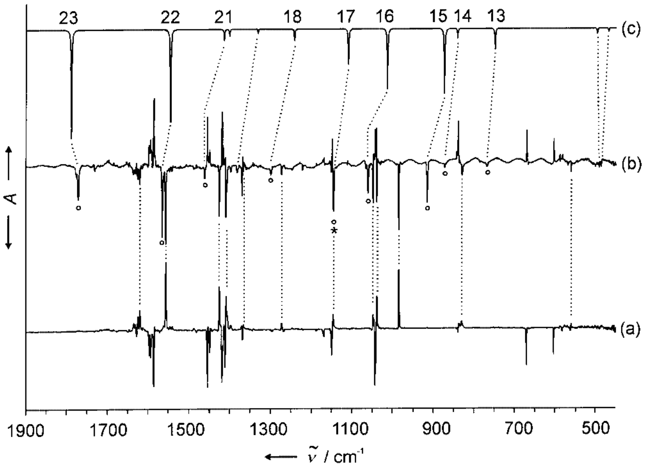


Figure 1. IR spectra illustrating the photochemistry of 2,4,6-trifluoro-1,3-diiodobenzene (**4b**) in solid neon at 3 K; (a) difference spectrum; bands pointing upward increase, bands pointing downward decrease on irradiation (10 min, 254 nm); increasing absorptions are assigned to monoradical **5b**; (b) difference spectrum; bands pointing upward increase, bands pointing downward decrease on annealing the neon matrix (7.5 K, 10 min) after 16 h of irradiation with 254 nm; bands marked with ° are assigned to diradical **6b**; (c) calculated [BLYP/6-311G(d,p), unscaled] spectrum of 1,3-didehydro-2,4,6-trifluorobenzene (**6b**)

Table 2. IR spectroscopic data of 1,3-didehydro-2,4,6-trifluorobenzene *S*-**6b**

Mode	Sym.	$\tilde{\nu}_{exp.}$ [cm^{-1}][a]	$I_{rel,exp.}$ [b]	$\tilde{\nu}_{calcd.}$ [cm^{-1}][c]	$I_{rel,calcd.}$ [b,c]
7	b_1	488.1	0.07	470.1	0.04
8	b_2	492.7	0.07	498.6	0.05
9	a_1	–	–	542.9	0.00
10	b_2	–	–	547.2	0.00
11	a_2	–	–	569.1	0.00
12	b_1	–	–	607.4	0.00
13	a_1	768.5	0.04	750.8	0.20
14	b_1	872.9	0.05	842.0	0.09
15	b_2	916.3	0.53	874.8	0.60
16	a_1	1061.4	0.41	1014.9	0.55
17	b_2	1145.8	0.38	1110.2	0.33
18	b_2	1299.4	0.15	1242.7	0.11
19	a_1	1382.0	0.12	1331.3	0.04
20	b_2	–	–	1401.3	0.07
21	a_1	1461.4	0.19	1414.8	0.10
22	b_2	1565.0	1.00	1545.6	0.85
23	a_1	1770.7	0.48	1788.3	1.00
24	a_1	–	–	3123.7	0.01

[a] Neon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the BLYP/6-311G(d,p) level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

Comparison of the experimentally measured IR spectrum with the calculated one confirms that the band at 1769 cm^{-1} is indeed due to an a_1-symmetrical vibration predicted at 1788.3 cm^{-1}. This absorption is characteristic of *m*-benzynes with a fluorine substituent in the 2-position. The corresponding b_2-symmetrical combination at

1565 cm^{-1} (calculated at 1545.6 cm^{-1}) is the dominant absorption in the IR spectrum of **6b**. A b_2-symmetrical, in-plane ring deformation with strong contribution of the radical centers is found at 492.7 cm^{-1} (calculated at 498.6 cm^{-1}). This band is not much affected by substitution and has been observed in several *m*-benzyne derivatives: at 547 cm^{-1} in 1,3-didehydrobenzene,[8] at 543 cm^{-1} in 1,3-didehydro-5-fluorobenzene,[3] and at 511 cm^{-1} in 1,3-didehydro-2,4,5,6-tetrafluorobenzene.[2] The intensity of this absorption in the fluorinated derivatives is rather low compared to that in the parent *m*-benzyne. The other intense bands of **6b** are due to in-plane ring deformation vibrations and combinations of these with ν(C−F) or ν(C−H) vibrations.

The monodeuterated benzyne **6c** and phenyl radical **5c** were generated analogously, by photolysis of **4c** (Table 3). The most pronounced isotopic shift in **5c** is observed for the δ_{oop}(C−H) vibration [$\tilde{\nu}_D/\tilde{\nu}_H$ = 0.88, $\tilde{\nu}$ = 836.1 cm^{-1} for R−H, $\tilde{\nu}$ = 737.2 cm^{-1} for R−D]. The C−H and C−D stretching vibrations of **5b** and **5c**, respectively, are of low intensity and could not be unequivocally assigned.

Table 3. IR spectroscopic data of the 5-deuterio-2,4,6-trifluoro-3-iodophenyl radical **5c**

Mode	Sym.	$\tilde{\nu}_{exp.}$ [cm^{-1}][a]	$I_{rel,exp.}$ [b]	$\tilde{\nu}_{calcd.}$ [cm^{-1}][c]	$I_{rel,calcd.}$ [b,c]
11	a′	544.9	0.14	548.0	0.08
12	a′	–	–	580.4	0.01
13	a′	–	–	597.0	0.02
14	a"	–	–	620.9	0.02
15	a"	–	–	667.4	0.01
16	a"	737.2	0.12	727.7	0.13
17	a′	–	–	867.5	0.01
18	a′	992.2	0.20	997.0	0.36
19	a′	1039.5	0.66	1050.5	0.70
20	a′	1066.3	0.33	1076.6	0.47
21	a′	1270.7	0.11	1311.9	0.14
22	a′	1366.1	0.17	1379.7	0.24
23	a′	1388.6	0.14	1414.5	0.57
24	a′	1410.4	0.68	1424.9	0.63
25	a′	1544.4	1.00	1574.0	1.00
26	a′	1614.7	0.41	1644.8	0.77
27	a′	–	–	2373.6	0.02

[a] Neon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the B3LYP/6-311G(d,p) level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

The IR spectrum of **6c** agrees well with the calculated spectrum (Figure 2, Table 4), and the experimental isotopic shifts $\tilde{\nu}_D/\tilde{\nu}_H$ are accurately reproduced by these calculations (Table 5).

The largest isotopic shifts are observed for a b_1-symmetrical δ_{oop}(C−H) vibration (mode 14 in **6b**, 13 in **6c**), the corresponding b_2-symmetrical δ_{ip}(C−H) vibration (mode 15), and a combination of the latter with a ring deformation (mode 17 in **6b**, 16 in **6c**). The a_1-symmetrical ring stretching mode 23 is hardly affected by isotopic labelling, while the b_2-symmetrical mode is shifted by 8 cm^{-1} to 1557 cm^{-1}. Again, the ν(C−H) and ν(C−D) vibrations (calculated at 3123.7 and 2313.6 cm^{-1}, respectively) could not be identified in the spectra due to their low intensity.

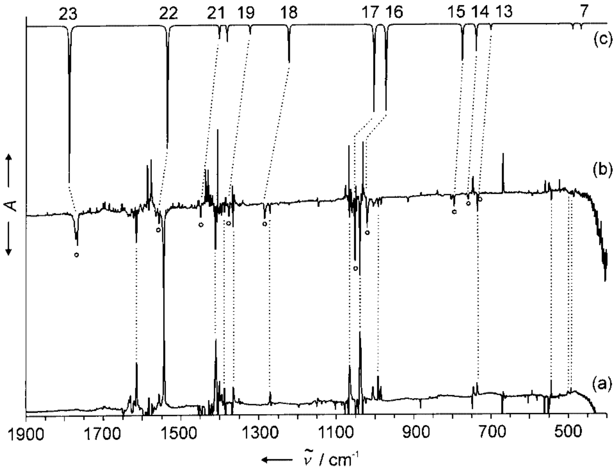


Figure 2. IR spectra illustrating the photochemistry of 5-deuterio-2,4,6-trifluoro-1,3-diiodobenzene (**4c**) in solid neon at 3 K; (a) difference spectrum; bands pointing upward increase, bands pointing downward decrease on irradiation (10 min, 254 nm); increasing absorptions are assigned to monoradical **5c**; (b) difference spectrum; bands pointing upward increase, bands pointing downward decrease on annealing the neon matrix (7.5 K, 10 min) after 16 h of irradiation with 254 nm; bands marked with ° are assigned to diradical **6c**; (c) calculated [BLYP/6-311G(d,p), unscaled] spectrum of 1,3-didehydro-5-deuterio-2,4,6-trifluorobenzene (**6c**)

Table 4. IR spectroscopic data of 1,3-didehydro-5-deuterio-2,4,6-trifluorobenezne *S*-**6c**

Mode	Sym.	$\tilde{\nu}_{exp.}$ [cm^{-1}][a]	$I_{rel,exp.}$ [b]	$\tilde{\nu}_{calcd.}$ [cm^{-1}][c]	$I_{rel,calcd.}$ [b,c]
13	b_1	734.5	0.07	703.6	0.04
14	a_1	761.1	0.10	741.7	0.18
15	b_2	796.7	0.18	776.2	0.24
16	b_2	1021.2	0.43	973.8	0.55
17	a_1	1052.6	0.97	1004.2	0.56
18	b_2	1285.0	0.24	1223.4	0.24
19	a_1	1377.1	0.21	1323.2	0.06
20	b_2	–	–	1382.7	0.11
21	a_1	1449.0	0.20	1402.9	0.09
22	b_2	1556.8	0.23	1536.0	0.78
23	a_1	1766.3 1769.8	0.51 0.49	1787.8	1.00
24	a_1	–	–	2313.6	0.00

[a] Neon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the BLYP/6-311G(d,p) level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

1,3-Didehydro-2,4,6-trifluoro-5-trifluoromethylbenzene (6d)

As a possible explanation for the formation of benzenoid diradicals in solid neon, rotation of the photochemically generated radical fragments inside the matrix cage, which prevents recombination, has been devised by Radziszewski.[9] According to this theory, bulky substituents should hinder the rotation of the mono- and diradicals, thereby lowering the yield of didehydrobenzene derivatives. The introduction of a trifluoromethyl group in the 5-position is

Table 5. Calculated and observed $\tilde{\nu}_D/\tilde{\nu}_H$ values for diradicals **6b** and **6c**

Symm.	Mode R−H	Mode R−D	$(\tilde{\nu}_D/\tilde{\nu}_H)_{calcd.}$	$(\tilde{\nu}_D/\tilde{\nu}_H)_{exp.}$	Assignment
a_1	13	14	0.99	0.99	ν(C−F) + ring def.
b_1	14	13	0.84	0.84	δ_{oop}(C−H)
b_2	15	15	0.89	0.87	δ_{ip}(C−H) + ring def.
a_1	16	17	0.99	0.99	ν(C−F) + ring def.
b_2	17	16	0.88	0.89	δ_{ip}(C−H)
b_2	18	18	0.98	0.99	δ_{ip}(C−H) + ring def.
a_1	19	19	0.99	1.00	ν(C−F) + ring def.
b_2	20	20	0.99	−	δ_{ip}(C−H) + ν(C−C)
a_1	21	21	0.99	0.99	ν(C−F) + ν(C−C)
b_2	22	22	0.99	0.99	δ_{ip}(C−H) + ν(C−C)
a_1	23	23	1.00	1.00	ν(C−F) + ν(C−C)

suitable for study of the steric effects in comparison with those affecting the perfluoro derivative. The radical sites are still surrounded by fluorine atoms (which facilitate the formation of the diradical), while the electronic properties of the molecule are relatively unaffected by the replacement of a fluorine atom by the electron-withdrawing CF_3 group.

Again, short-term photolysis (λ = 254 nm) of 2,4,6-trifluoro-1,3-diiodo-5-(trifluoromethyl)benzene (**4d**), matrix-isolated in neon at 3 K, results in a decrease in the precursor concentration and the formation of a new species. The product is assigned as 2,4,6-trifluoro-3-iodo-5-(trifluoromethyl)phenyl radical **5d** by comparison with the calculated IR spectrum (Table 6). The spectrum is dominated by the ν(C−CF_3) vibration, which is split into two components: at 1273.7 and 1282.8 cm^{-1} [calculated at 1273.6 cm^{-1}, B3LYP/6-311G(d,p)].

Table 6. IR spectroscopic data of the 2,4,6-trifluoro-3-iodo-5-(trifluoromethyl)phenyl radical **5d**

Mode	Sym.	$\tilde{\nu}_{exp.}$ [cm^{-1}]$^{[a]}$	$I_{rel,exp.}$ $^{[b]}$	$\tilde{\nu}_{calcd.}$ [cm^{-1}]$^{[c]}$	$I_{rel,calcd.}$ $^{[b,c]}$
19	−	617.6	0.06	618.6	0.07
20	−	−	−	620.3	0.00
21	−	−	−	659.1	0.01
22	−	699.9	0.04	701.8	0.02
23	−	−	−	746.8	0.01
24	−	−	−	777.0	0.01
25	−	1025.2	0.30	1031.1	0.23
26	−	1070.5	0.03	1079.4	0.04
27	−	1077.3	0.14	1083.0	0.08
28	−	1164.7	0.19	1156.9	0.48
29	−	1168.2	0.22	1175.7	0.16
30	−	1273.7 1282.8	0.69 0.31	1273.6	1.00
31	−	−	−	1314.1	0.00
32	−	−	−	1389.8	0.01
33	−	1416.0	0.32	1427.0	0.27
34	−	−	−	1459.9	0.04
35	−	1543.2 1548.7	0.05 0.07	1570.7	0.31
36	−	1630.6	0.15	1657.7	0.31

[a] Neon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the B3LYP/6-311G(d,p) level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

Continued irradiation generates another species, consistently with the stepwise cleavage of the two C−I bonds of diiodobenzene derivative **4d**. Annealing at 7 K reforms starting material **4d** at the expense of monoradical **5d** and diradical **6d**, which confirms the assignment of the second product as 1,3-didehydro-2,4,6-trifluoro-5-(trifluoromethyl)-benzene. The agreement of the observed and the calculated IR spectra is good, and, as in the case of the *m*-benzyne derivatives described above, the characteristic a_1-symmetrical ring stretching vibration (observed: 1795.1 and 1805.3 cm^{-1}, calculated: 1816.8 cm^{-1}) is identified in the spectrum, as well as the corresponding b_2-symmetrical vibration (observed: 1569.5 cm^{-1}, calculated: 1548.4 cm^{-1}), which is the most intense band of **6d** (Figure 3, Table 7).

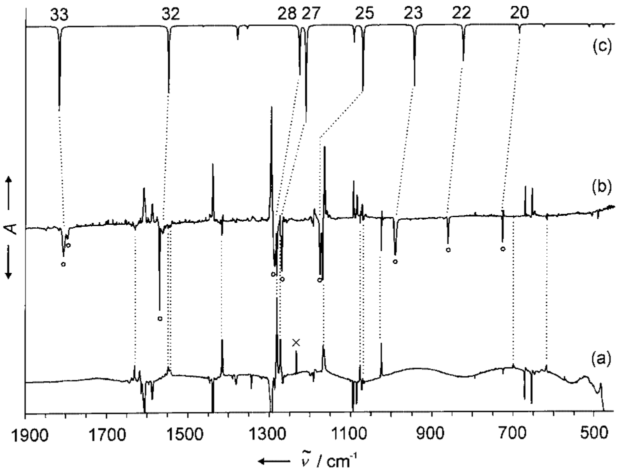


Figure 3. IR spectra illustrating the photochemistry of 2,4,6-trifluoro-1,3-diiodo-5-(trifluoromethyl)benzene (**4d**) in solid neon at 3 K; (a) difference spectrum; bands pointing upward increase, bands pointing downward decrease on irradiation (10 min, 254 nm); increasing absorptions are assigned to monoradical **5d**; (b) difference spectrum; bands pointing upward increase, bands pointing downward decrease on annealing the neon matrix (7.5 K, 10 min) after 16 h of irradiation with 254 nm; bands marked with ° are assigned to diradical **6d**; (c) calculated [BLYP/6-311G(d,p), unscaled] spectrum of 1,3-didehydro-2,4,6-trifluoro-5-trifluoromethylbenzene (**6d**)

The formation of the sterically more demanding diradical **6d** shows that the mere size of the molecule apparently has

Table 7. IR spectroscopic data of 1,3-didehydro-2,4,6-trifluoro-5-trifluoromethylbenzene *S*-**6d**

Mode	Sym.	$\tilde{\nu}_{\text{exp.}}$ [cm^{-1}][a]	$I_{\text{rel,exp.}}$ [b]	$\tilde{\nu}_{\text{calcd.}}$ [cm^{-1}][c]	$I_{\text{rel,calcd.}}$ [b,c]
20	–	727.0	0.32	687.3	0.10
21	–	–	–	704.3	0.00
22	–	861.3	0.33	825.2	0.38
23	–	990.9	0.51	945.8	0.63
24	–	–	–	1034.3	0.01
25	–	1174.9	0.63	1071.7	0.69
26	–	–	–	1094.6	0.18
27	–	1270.2	0.62	1211.3	1.00
28	–	1287.9	0.71	1227.9	0.51
29	–	–	–	1355.5	0.03
30	–	–	–	1379.2	0.15
31	–	–	–	1463.5	0.01
32	–	1569.5	1.00	1548.4	0.69
33	–	1795.1 1805.3	0.17 0.41	1816.8	0.87

[a] Neon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the BLYP/6-311G(d,p) level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

less influence than other substituent effects on the photochemistry of diiodobenzene derivatives in neon matrices.

1,3-Didehydro-2,4,6-trifluoro-5-(trimethylsilyl)benzene (6e)

The successive cleavage of two C−I bonds could also be demonstrated in trimethylsilyl derivative **4e**, although with lower efficiency than with the other derivatives so far reported. The IR spectra of the 2,4,6-trifluoro-3-iodo-5-(trimethylsilyl)phenyl radical **5e** (formed by 5 min of irradiation with 254 nm, Table 8) and 1,3-didehydro-2,4,6-trifluoro-5-(trimethylsilyl)benzene (**6e**) (formed by long-term irradiation with 254 nm, together with additional amounts of monoradical **5e**, Figure 4, Table 9) could be measured and assigned by comparison with calculated spectra. The reverse reaction was observed on annealing, diiodide **4e** once more being formed. The a_1-symmetrical ring stretching vibration described above appears as two broad bands at 1765.3 and 1770.1 cm^{-1} (calculated at 1789.3 cm^{-1}), the corresponding b_2 mode at 1550.8 cm^{-1} (calculated at 1511.9 cm^{-1}).

Photochemistry of 1,3,5-Trifluoro-2,4,6-triiodobenzene (4f)

The formation of mono- and diradicals from diiodobenzene derivatives suggested that it might be possible to generate a triradical from the corresponding triiodobenzene. Since fluorine substitution apparently facilitates the isolation of didehydrobenzenes originating from aromatic diiodides, 1,3,5-trifluoro-2,4,6-triiodobenzene (**4f**) was chosen to test this possibility. Thanks to its high symmetry, the IR spectrum of matrix-isolated **4f** exhibits only a few intense absorptions. Irradiation at 254 nm for 10 min results in the loss of intensity of these bands, and simultaneous formation of the 2,4,6-trifluoro-3,5-diiodophenyl radical **5f**, as confirmed by the calculated IR spectrum (Table 10).

Table 8. IR spectroscopic data of the 2,4,6-trifluoro-3-iodo-5-(trimethylsilyl)phenyl radical **5e**

Mode	Sym.	$\tilde{\nu}_{\text{exp.}}$ [cm^{-1}][a]	$I_{\text{rel,exp.}}$ [b]	$\tilde{\nu}_{\text{calcd.}}$ [cm^{-1}][c]	$I_{\text{rel,calcd.}}$ [b,c]
32	a''	769.5	0.12	789.0	0.11
33	a′	–	–	789.9	0.04
34	a′	849.7	0.12	878.4	0.22
35	a''	856.0	0.16	882.9	0.32
36	a′	862.8	0.11	886.4	0.84
37	a′	1008.7	0.40	1011.9	0.34
38	a′	1046.5	0.16	1051.4	0.04
39	a′	1082.6	1.00	1083.7	1.00
40	a''	1258.1	0.16	1296.9	0.15
41	a′	–	–	1297.3	0.11
42	a′	1260.9	0.08	1300.0	0.14
43	a′	1268.7	0.08	1311.0	0.08
44	a′	–	–	1342.8	0.01
45	a′	1380.1	0.31	1395.6	0.55
46	a′	1403.6	0.09	1426.8	0.14
47	a''	–	–	1453.2	0.00
48	a′	–	–	1458.1	0.00
49	a''	–	–	1462.5	0.00
50	a′	–	–	1468.1	0.03
51	a''	–	–	1469.8	0.02
52	a′	–	–	1480.2	0.03
53	a′	1514.2	0.38	1539.1	0.51
54	a′	1597.6	0.21	1638.9	0.70

[a] Neon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the B3LYP/6-311G(d,p) level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

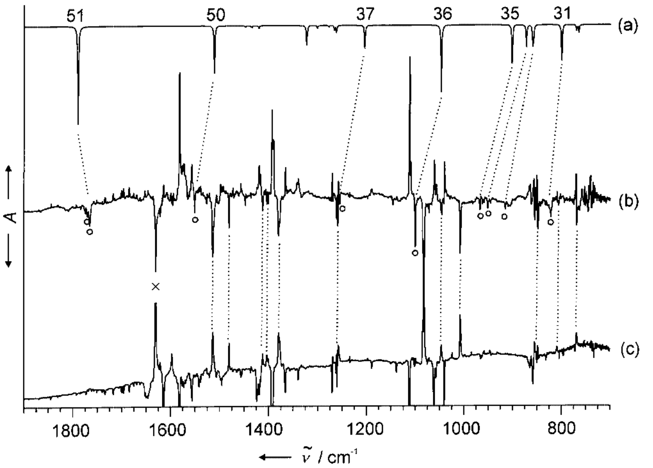


Figure 4. IR spectra illustrating the photochemistry of 2,4,6-trifluoro-1,3-diiodo-5-(trimethylsilyl)benzene (**4e**) in solid neon at 3 K; (a) difference spectrum; bands pointing upward increase, bands pointing downward decrease on irradiation (10 min, 254 nm); increasing absorptions are assigned to monoradical **5e**; (b) difference spectrum; bands pointing upward increase, bands pointing downward decrease on annealing the neon matrix (7.5 K, 10 min) after 16 h of irradiation with 254 nm; bands marked with ° are assigned to diradical **6e**; (c) calculated [BLYP/6-311G(d,p), unscaled] spectrum of 1,3-didehydro-2,4,6-trifluoro-5-(trifluoromethyl)benzene (**6e**)

As anticipated, another compound is formed on continued irradiation, while the intensity of all bands assigned to monoradical **5f** stagnates after approximately 6 h and

Table 9. IR spectroscopic data of 1,3-didehydro-2,4,6-trifluoro-5-(trimethylsilyl)benzene [(*S*)-**6e**]

Mode	Sym.	$\tilde{\nu}_{exp.}$ [cm^{-1}][a]	$I_{rel,exp.}$ [b]	$\tilde{\nu}_{calcd.}$ [cm^{-1}][c]	$I_{rel,calcd.}$ [b,c]
31	–	823.1	0.30	801.5	0.37
32	–	–	–	859.7	0.16
33	–	916.3	0.14	861.3	0.20
34	–	951.9	0.22	874.6	0.23
35	–	968.4	0.26	903.6	0.40
36	–	1100.7	1.00	1048.7	0.69
37	–	1254.8	0.20	1204.2	0.25
38	–	–	–	1262.8	0.07
39	–	–	–	1266.6	0.05
40	–	–	–	1277.9	0.01
41	–	–	–	1301.1	0.03
42	–	–	–	1323.7	0.21
43	–	–	–	1420.7	0.03
44	–	–	–	1422.0	0.00
45	–	–	–	1426.9	0.00
46	–	–	–	1430.6	0.00
47	–	–	–	1434.9	0.02
48	–	–	–	1436.6	0.01
49	–	–	–	1448.3	0.02
50	–	1550.8	0.41	1511.9	0.48
51	–	1765.3 1770.1	0.43 0.24	1789.3	1.00

[a] Neon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the BLYP/6-311G(d,p) level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

Table 10. IR spectroscopic data of the 2,4,6-trifluoro-3,5-diiodophenyl radical **5f**

Mode	Sym.	$\tilde{\nu}_{exp.}$ [cm^{-1}][a]	$I_{rel,exp.}$ [b]	$\tilde{\nu}_{calcd.}$ [cm^{-1}][c]	$I_{rel,calcd.}$ [b,c]
14	b_2	612.0	0.20	608.2	0.18
15	b_1	–	–	613.1	0.02
16	a_2	–	–	637.4	0.00
17	b_2	691.4	0.04	667.6	0.10
18	b_1	712.2	0.03	696.6	0.10
19	a_1	1007.2	0.83	1009.0	0.61
20	b_2	1058.4	0.43	1068.5	0.30
21	a_1			1069.5	0.20
22	b_2	1309.2	0.03	1297.8	0.17
23	a_1	–	–	1386.5	0.00
24	b_2	1400.7	0.88	1413.6	1.00
25	a_1	1403.4	1.00	1418.8	0.81
26	a_1	1526.4	0.65	1552.6	0.82
27	b_2	1588.1	0.16	1641.2	0.45

[a] Neon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the B3LYP/6-311G(d,p) level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

slightly decreases afterwards. The second product shows the broad, split absorption attributable to the characteristic *a$_1$*-symmetrical vibration at 1774 and 1783 cm^{-1}, as well as the *b$_2$*-symmetrical combination at 1550.6 cm^{-1}, and is therefore assigned as 1,3-didehydro-2,4,6-trifluoro-5-iodobenzene (**6f**) (Figure 5, Table 11). All photochemically generated absorptions decrease on annealing at 7.5 K, while the bands of trifluorotriiodobenzene **4f** increase concurrently.

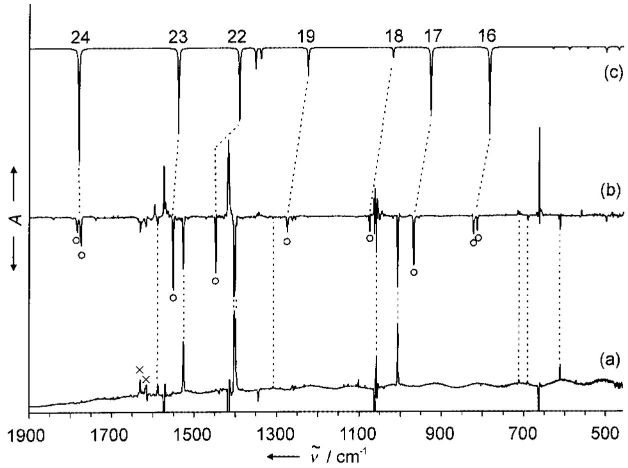


Figure 5. IR spectra illustrating the photochemistry of 1,3,5-trifluoro-2,4,6-triiodobenzene (**4f**) in solid neon at 3 K; (a) difference spectrum; bands pointing upward increase, bands pointing downward decrease on irradiation (10 min, 254 nm); increasing absorptions are assigned to monoradical **5f**; (b) difference spectrum; bands pointing upward increase, bands pointing downward decrease on annealing the neon matrix (7.5 K, 10 min) after 16 h of irradiation with 254 nm; bands marked with ° are assigned to diradical **6f**; (c) calculated [BLYP/6-311G(d,p), unscaled] spectrum of 1,3-didehydro-5-iodo-2,4,6-trifluorobenzene **6f**

Table 11. IR spectroscopic data of 1,3-didehydro-2,4,6-trifluoro-5-iodobenzene [(*S*)-**6f**]

Mode	Sym.	$\tilde{\nu}_{exp.}$ [cm^{-1}][a]	$I_{rel,exp.}$ [b]	$\tilde{\nu}_{calcd.}$ [cm^{-1}][c]	$I_{rel,calcd.}$ [b,c]
16	a_1	814.3 823.8	0.28 0.24	785.5	0.75
17	b_2	968.2	0.72	927.1	0.59
18	a_1	1074.7	0.21	1019.2	0.09
19	b_2	1274.5	0.23	1225.3	0.24
20	b_2	–	–	1339.8	0.09
21	a_1	–	–	1352.4	0.18
22	a_1	1447.4	0.87	1391.9	0.63
23	b_2	1550.6	1.00	1538.4	0.73
24	a_1	1773.5 1782.8	0.50 0.27	1780.1	1.00

[a] Neon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the BLYP/6-311G(d,p) level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

Under no conditions was a third photoproduct potentially attributable to the desired 1,3,5-tridehydro-2,4,6-trifluorobenzene detected.

Comparison of the *m*-Benzyne Derivatives

Two IR absorptions are characteristic of all 2-fluoro derivatives of *m*-benzyne (**2**) so far investigated: an *a$_1$*-symmetrical mode in the 1765 cm^{-1} to 1824 cm^{-1} range and a

b_2-symmetrical ring stretching vibration between 1551 and 1605 cm^{-1} (Figure 6).

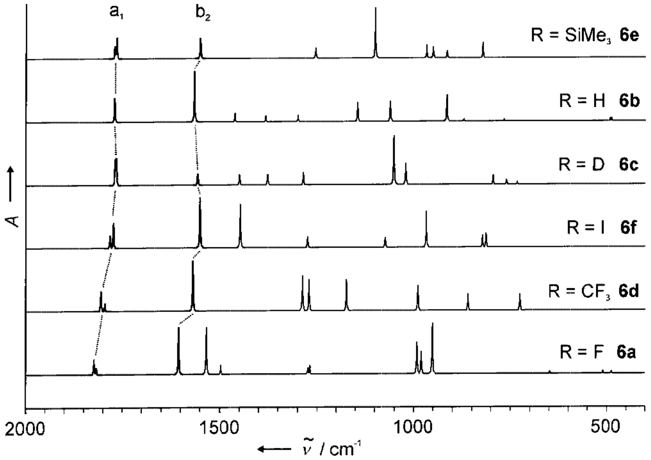


Figure 6. Observed IR absorptions assigned to the *m*-didehydrobenzene derivatives **6a**−**6f**; the characteristic a_1- and b_2-symmetrical vibrations (or the corresponding vibrations for molecules of lower than C_{2v} symmetry) are marked by dotted lines

The substituent at C^5 is hardly involved in these vibrations (very small isotopic shifts in **6b**/**6c**) and so changes in the band positions of these vibrations are mainly the result of electronic effects of the substituent on the ring system. Calculations also predict these vibrations to be present in the parent *m*-benzyne (**2**), but the intensity is much lower than in the fluorinated derivatives. As a result, the a_1-symmetrical mode [calculated at 1681.7 cm^{-1}, BLYP/6-311G(d,p)] cannot be observed in **2**, while the b_2-symmetrical vibration corresponds to a weak absorption at 1486 cm^{-1} [calculated at 1471.1 cm^{-1}, BLYP/6-311G(d,p)].[8]

There is a correlation between the frequency of the a_1-symmetrical mode and the calculated C^1−C^3 distance. For **6a** and **6d**, with the shortest calculated C^1−C^3 distances (1.895 and 1.871 Å, respectively), the band is shifted to higher frequencies than seen in other derivatives with larger C^1−C^3 distances (Table 12). It should be noted, however, that the energy well for change in the C^1−C^3 distance is very flat, and calculations give qualitatively different results depending on the applied method. In an exhaustive study, Winkler et al. tested the performance of various ab initio and DFT methods, finding that the BLYP functional reproduces the vibrational spectra of *m*-benzynes quite accurately.[13] We thus used this level of theory to calculate the C^1−C^3 distances.

The singlet-triplet splitting ΔE_{S-T} values of all fluorinated *m*-benzynes so far investigated are larger than that of the parent *m*-benzyne (**2**). In contrast, the ΔE_{S-T} values of perfluorinated *p*-benzynes are smaller than that of the parent *p*-benzyne (**3**), which is attributable to stabilization of the symmetrical combination φ_S of the singly occupied lone-pair orbitals by the σ*(C−F) orbitals (Figure 7).[7] Through-bond coupling places φ_S energetically above the antisymmetrical combination φ_A,[12,14,15] which gives rise to a lower HOMO−LUMO gap and to a decreased ΔE_{S-T} value (Figure 8).

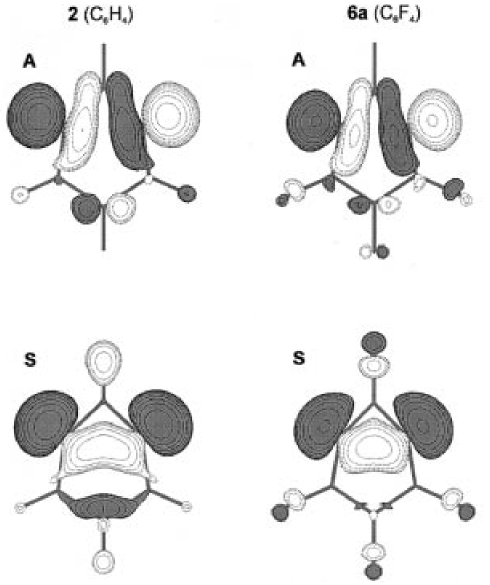
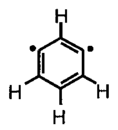
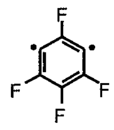
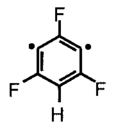
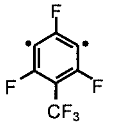
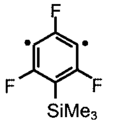
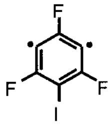


Figure 7. Symmetric (*S*) and antisymmetric (*A*) combination of the singly occupied lone-pair orbitals at the radical centers for parent *m*-benzyne (**2**) (left) and perfluorinated **6a** (right)

As in the *para* derivative, fluorine substitution stabilizes the symmetrical combinations φ_S in *o*- and *m*-benzyne. Because of the increased through-space interaction in these molecules, however, this combination lies below the anti-

Table 12. Selected calculated and experimental data for *m*-benzyne derivatives

	 **2**	 **6a**	 **6b**	 **6d**	 **6e**	 **6f**
ΔE_{S-T}[a]	19.5	26.3	22.4	24.8	20.5	23.7
r(C^1–C^3)[b]	2.004	1.895	1.920	1.871	1.904	1.935
$\tilde{\nu}_{exp.}$[c]	–	1823.8	1770.7	1805.3	1765.3	1773.5

[a] Singlet-triplet splitting [kcal mol^{-1}], calculated at the BLYP/6-311G(d,p) level of theory. [b] Calculated [BLYP/6-311G(d,p)] distance [Å] of the radical centers for singlet diradicals. [c] Observed position of the characteristic C−C/C−F stretching vibration [cm^{-1}].

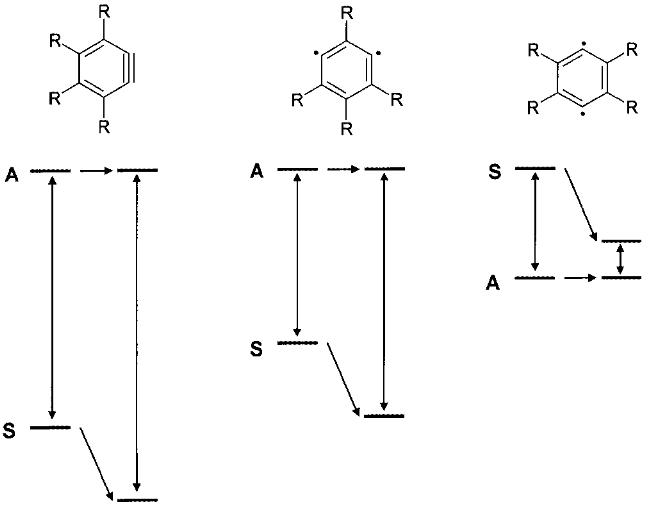


Figure 8. Effect of fluorinesubstitution on the HOMO-LUMO gap of benzynes; stabilization of the antisymmetric (*A*) combination of the singly occupied lone-pair orbitals at the radical centers results in an increased HOMO−LUMO gap for *ortho*- and *meta*-benzynes, while for *para*-benzynes the energy difference is reduced; for *p*-benzynes the order of the *A* and *S* combination is reversed by through-bond interaction[14,15]

symmetrical φ_A, and so the HOMO−LUMO gaps and the ΔE_{S-T} values are increased. This is in agreement with a recent theoretical investigation of substituent effects on benzyne electronic structures reported by Cramer et al., who found that the singlet states are selectively stabilized over the triplets by appropriate substituents.[1]

In summary, we have demonstrated that photolysis of suitably substituted 1,3-diiodobenzenes **4** results in the formation of *m*-benzynes **6** in a stepwise reaction via the phenyl radicals **5**. This allows the substituents in **6** to be varied systematically and the influence of these variations on the spectroscopic properties to be studied.

Experimental Section

Matrix Isolation: Matrix isolation experiments were performed by standard techniques[16] with a Sumitomo Heavy Industries RDK-408D closed-cycle refrigerator. Matrices were produced by co-deposition of a large excess of neon (Messer−Griesheim, 99.9999%) and the trapped species on a cold CsI window (3 K). Infrared spectra were recorded with a Bruker Equinox 55 FTIR spectrometer with a standard resolution of 0.5 cm^{-1} in the range of 400−4000 cm^{-1}. Irradiation was carried out with a Gräntzel low-pressure mercury lamp.

Theoretical Methods: Calculations were performed with the GAUSSIAN98 suite of programs.[17] Geometries and vibrational spectra of diradicals **6b**−**6f** were calculated by use of the RBLYP functional, while the B3LYP functional was applied for phenyl radicals **5b**−**25** for consistency with previous publications. The 6-311G(d,p) basis set was used for all molecules.[18] Tight cutoffs were used for the geometry optimizations. Vibrational frequency calculations were carried out in all cases in order to obtain the IR spectra and to determine the nature of the stationary points. For discussions of the performance of different theoretical methods for didehydrobenzenes, cf. refs.[10−13]

1,3,5-Trifluoro-2,4,6-triiodobenzene (4f): A modification of the literature procedure for the synthesis of tetrafluoro-1,3-diiodobenzene[19] by Neenan et al. was applied for the preparation of **4f**. Periodic acid (3.0 g, 13.2 mmol) was suspended in concentrated H_2SO_4 (20 mL) at 0 °C. Finely ground KI (6.56 g, 40.0 mmol) was added in small portions over 5 min. The dark mixture was stirred and cooled with an ice bath, while 1,3,5-trifluorobenzene (Aldrich, 97%, 1.17 g, 8.86 mmol) was added over 15 min by syringe. The ice bath was removed and the solution was heated to 70 °C for 4 h. After cooling to room temperature, the reaction mixture was poured onto ice (200 g) and extracted with diethyl ether. The organic phase was washed with aqueous sodium thiosulfate and water and dried ($MgSO_4$), and the solvents were evaporated to dryness. The diiodide was sublimed in vacuo to give **4f** as white crystals (89% yield, 4.01 g, 7.86 mmol). The analytical data complies with ref.[20] ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 63.7 (dt), 162.3 (dt) ppm. EI-MS: *m*/*z* (%) = 510 (100) [M$^+$], 383 (15), 256 (30), 129 (40), 79 (30). IR (Ne, 3 K): $\tilde{\nu}$ (%) = 1573 (41), 1440 (2), 1432 (2), 1417 (100), 1345 (5), 1062 (35), 1057 (16), 716 (2), 664 (61) cm^{-1}.

2,4,6-Trifluoro-1,3-diiodobenzene (4b): *n*BuLi (1.6 M solution in hexane, 1.1 mL, 1.7 mmol) was added at −78 °C, under argon, to a solution of 1,3,5-trifluoro-2,4,6-triiodobenzene (**4f**, 850 mg, 1.67 mmol) in dry diethyl ether (10 mL). The mixture was stirred for 30 min, quenched with H_2O (5 mL), and allowed to warm to room temperature. Diethyl ether (80 mL) was added, the organic phase was washed with dilute HCl and water and dried ($MgSO_4$), and the solvents were evaporated to dryness. The crude product was sublimed in vacuo to give **4b** as white needles. The analytical data are identical to those in ref.[20] EI-MS: *m*/*z* (%) = 384 (50) [M$^+$]. IR (Ne, 3 K): $\tilde{\nu}$ (%) = 1597 (15), 1593 (34), 1586 (100), 1454 (81), 1449 (29), 1424 (7), 1419 (80), 1411 (37), 1369 (28), 1169 (10), 1149 (47), 1048 (32), 1043 (91), 1041 (15), 840 (16), 671 (56), 604 (47), 584 (7), 562 (8) cm^{-1}.

5-Deuterio-2,4,6-trifluoro-1,3-diiodobenzene (4c): The synthesis was carried out as described for the non-deuterated derivative **4b**, but the phenyllithium derivative was quenched with D_2O instead of H_2O. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 64.8 (ttd), 100.2 (ttd), 161.8 (dtt), 163.1 (dtt) ppm. EI-MS: *m*/*z* (%) = 385 (100) [M$^+$], 258 (20), 220 (5), 205 (15), 192 (10), 131 (60), 100 (10), 81 (20), 62 (10). IR (Ne, 3 K): $\tilde{\nu}$ (%) = 1595 (6), 1587 (71), 1577 (44), 1455 (8), 1446 (5), 1437 (40), 1434 (9), 1431 (50), 1424 (15), 1419 (7), 1406 (100), 1386 (6), 1368 (32), 1077 (8), 1068 (67), 1050 (14), 1043 (6), 1032 (81), 883 (6), 749 (10), 671 (64), 562 (26), 552 (10), 550 (7) cm^{-1}.

2,4,6-Trifluoro-1,3-diiodo-5-(trifluoromethyl)benzene (4d): Periodic acid (3.0 g, 13.2 mmol) was suspended at 0 °C in concentrated H_2SO_4 (20 mL). Finely ground KI (6.56 g, 40.0 mmol) was added in small portions over 5 min. The dark mixture was stirred and cooled with an ice bath, while 2,4,6-trifluoro-1-(trifluoromethyl)-benzene (Acros, 98%, 1.66 g, 8.3 mmol) was added over 15 min by syringe. The ice bath was removed and the solution was heated to 70 °C for 4 h. After cooling to room temperature, the reaction mixture was poured onto ice (200 g) and extracted with ether. The organic phase was washed with aqueous sodium thiosulfate and water and dried ($MgSO_4$), and the solvents were evaporated to dryness. The diiodide was sublimed twice in vacuo to give **4d** as white crystals (3.0 g, 6.64 mmol, 80% yield) melting at 41 °C. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.0 (dt), 105.3 (t), 120.8 (q), 161.3 (dt); 164.0 (dt) EI-MS: *m*/*z* (%) = 452 (100) [M$^+$], 433 (10), 325 (15), 226 (5), 198 (45), 179 (15), 148 (20), 129 (10), 110 (5), 79 (15), 69 (15). IR (Ne, 3 K): $\tilde{\nu}$ (%) = 1606 (35), 1587 (19), 1438 (64), 1381 (4), 1296 (100), 1286 (12), 1268 (7), 1191 (28), 1166 (20), 1094 (34), 1085 (15), 1073 (7), 725 (3), 671 (20), 654 (23) cm^{-1}.

2,4,6-Trifluoro-1,3-diiodo-5-(trimethylsilyl)benzene (4e): The synthesis was carried out as described for 2,4,6-trifluoro-1,3-diiodobenzene (**4b**), but the phenyllithium derivative was treated with an excess of $ClSi(CH_3)_3$ instead of H_2O. Sublimation in vacuo gave **4e** as a white solid melting at 73 °C. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.36$ (t). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 65.1$ (ddd), 110.4 (dt), 162.3 (td), 166.4 (ddd) ppm. EI-MS: *m/z* (%) = 456 (28), 441 (13), 364 (6), 248 (32), 237 (13), 281 (10), 187 (38), 167 (18), 127 (22), 110 (18), 87 (26), 81 (36), 104 (100), 73 (73). IR (Ne, 3 K): $\tilde{\nu}$ (%) = 2971 (3), 2914 (2), 1582 (100), 1573 (9), 1556 (19), 1424 (5), 1417 (31), 1393 (52), 1366 (13), 1339 (6), 1270 (13), 1260 (23), 1112 (90), 1061 (39), 1058 (8), 1040 (26), 859 (13), 852 (35), 772 (11), 733 (5), 663 (56), 621 (13) cm^{-1}.

Supporting Information Available: Matrix infrared spectra (neon, 3 K) of diiodobenzenes **4b**−**4f** and difference spectra showing the formation of phenyl radicals **5b**−**5f** on short-term irradiation at 254 nm. Calculated geometries (Cartesian coordinates in Å) and vibrational spectra of phenyl radicals **5b**−**5f** and didehydrobenzenes **6b**−**6f** (see also footnote on the first page of this article).

Acknowledgments

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