Matrix Isolation and Spectroscopic Characterization of Perfluorinated *ortho*- and *meta*-Benzyne

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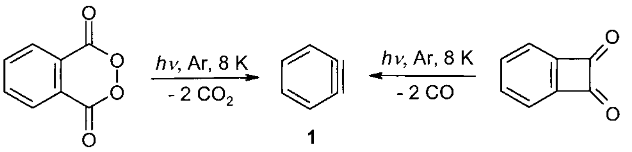
Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 60th birthday

Abstract: The matrix isolation and spectroscopic characterization of two C_6F_4 isomers, the perfluorinated *o*-benzyne **4** and the *m*-benzyne **5**, is reported. UV photolysis of tetrafluorophthalic anhydride **6** in solid argon at 10 K results in the formation of CO, CO_2, and 1,2-didehydro-3,4,5,6-tetrafluorobenzene (**4**) in a clean reaction. On subsequent 350 nm irradiation **4** is carbonylated to give the cyclopropenone **7**. 1,3-Didehydro-2,4,5,6-tetrafluorobenzene (**5**) was synthesized by UV irradiation of 1,3-diiodo-2,4,5,6-tetrafluorobenzene (**8**) via 2,3,4,6-tetrafluoro-5-iodophenylradical **9**. Photolysis of **8** in solid neon at 3 K produces good yields of both radical **9** and benzyne **5**, while in argon at 10 K no reaction is observed. Thus, the photochemistry in neon at extremely low temperature markedly differs from the photochemistry in argon. The formation of **5** from **8** via **9** is reversible, and annealing the neon matrix at 8 K leads back to the starting material **8**. The benzynes **4** and **5** and the radical **9** were characterized by comparison of their matrix IR spectra with density functional theory (DFT) calculations.

Keywords: benzyne · didehydrobenzene · IR spectroscopy · matrix isolation · radicals

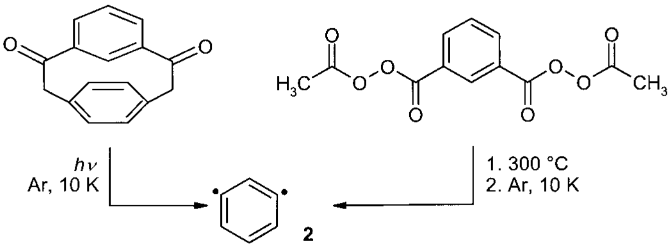
Introduction

The didehydrobenzenes (benzynes) **1**–**3** (Schemes 1, 2, and 3, respectively) are reactive C_6H_4 molecules that have been studied by trapping in solution as well as by a variety of spectroscopic and theoretical methods. The renewed interest in the benzynes during the last few years results from the discovery of biologically highly active molecules with derivatives of **3** and related diradicals as key intermediates,[1] but also from the challenge to theoretical chemistry by these unusual molecules. The intense interest in *o*-didehydrobenzene (**1**; Scheme 1) is illustrated by the wealth of information which has been gained with a broad spectrum of experimental and theoretical methods. These include gas-phase UV/Vis spectroscopy,[2] mass spectrometry,[3] matrix isolation IR spectroscopy,[5] microwave,[6] photoelectron,[7] and negative-ion photoelectron spectroscopy (NIPES),[8, 9] collision-induced dissociation threshold,[10] and NMR spectroscopy[11]. Recent theoretical calculations were performed by using CCSD(T)[12, 13] and CASPT2.[14] The singlet–triplet splitting was determined to be 37.5 kcal mol^{-1} by NIPES.[8]



Scheme 1. Matrix isolation of *o*-benzyne (**1**).

The fact that the knowledge about *m*-didehydrobenzene (**2**; Scheme 2) is scarcer than that of **1** can be attributed partially to its higher reactivity and partially to the lack of synthetically feasible precursors. As a consequence, reports of a direct spectroscopic observation of **2** are relatively new[4] with the exception of an early gas-phase UV/Vis and mass spectro-



Scheme 2. Matrix isolation of *m*-benzyne (**2**).

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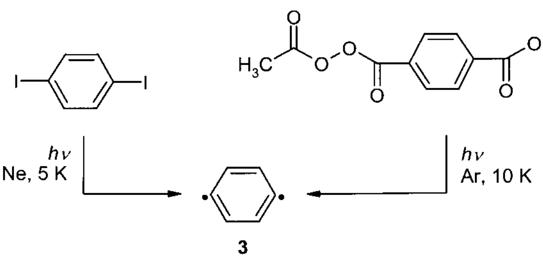
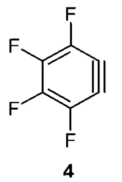
metric study.[3] The singlet–triplet splitting of 21.0 kcal mol^{-1}[8] is lower than that of **1**, leading to a more pronounced diradicaloid character. The parent benzyne **2** (Scheme 2) and a few derivatives were investigated by direct spectroscopic methods. 5-Fluoro- and 5-methyl-*m*-didehydrobenzene were prepared by UV photolysis of the corresponding [2.2]meta-paracyclophanediones in argon matrices;[15] however, the synthesis of the precursors is tedious and limited to sterically favorable cases. 2,4-Didehydrophenols were synthesized from diazoquinone carboxylic acids by a reaction path which is unique to OH-substituted *m*-didehydrobenzenes.[16] An interesting mass spectrometric method for the investigation of the chemistry of *m*-benzynes in the gas phase has recently been developed.[17]

The generation and matrix isolation of *p*-didehydrobenzene **3** from two different precursors (Scheme 3) was reported recently.[18] Given the low C–I bond dissociation energy, diiodobenzenes should be ideal precursors of the benzynes. However, photolysis of *para*-diiodobenzene, matrix-isolated in argon at 10 K produces no detectable trace of **3**, and in neon at 5 K only very low yields of **3** are obtained. Evidently, the thermal in-cage recombination of the photochemically generated radical pairs (iodine atoms and phenyl radicals) leads to the low overall yields in these reactions.



Scheme 3. Matrix isolation of *p*-benzyne (**3**).

1,2-Didehydro-3,4,5,6-tetrafluorobenzene (**4**) is the only C_6F_4 isomer that has been studied experimentally. These studies are restricted to solution-trapping chemistry with a wide range of reagents (Scheme 4).[19–24] In general, these reactions of **4** resemble those of the unsubstituted *o*-benzyne **1**,[25] but as a consequence of the electron-withdrawing fluorine substituents the yields of 1,4-addition products with dienes are increased drastically.[26]



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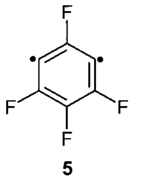

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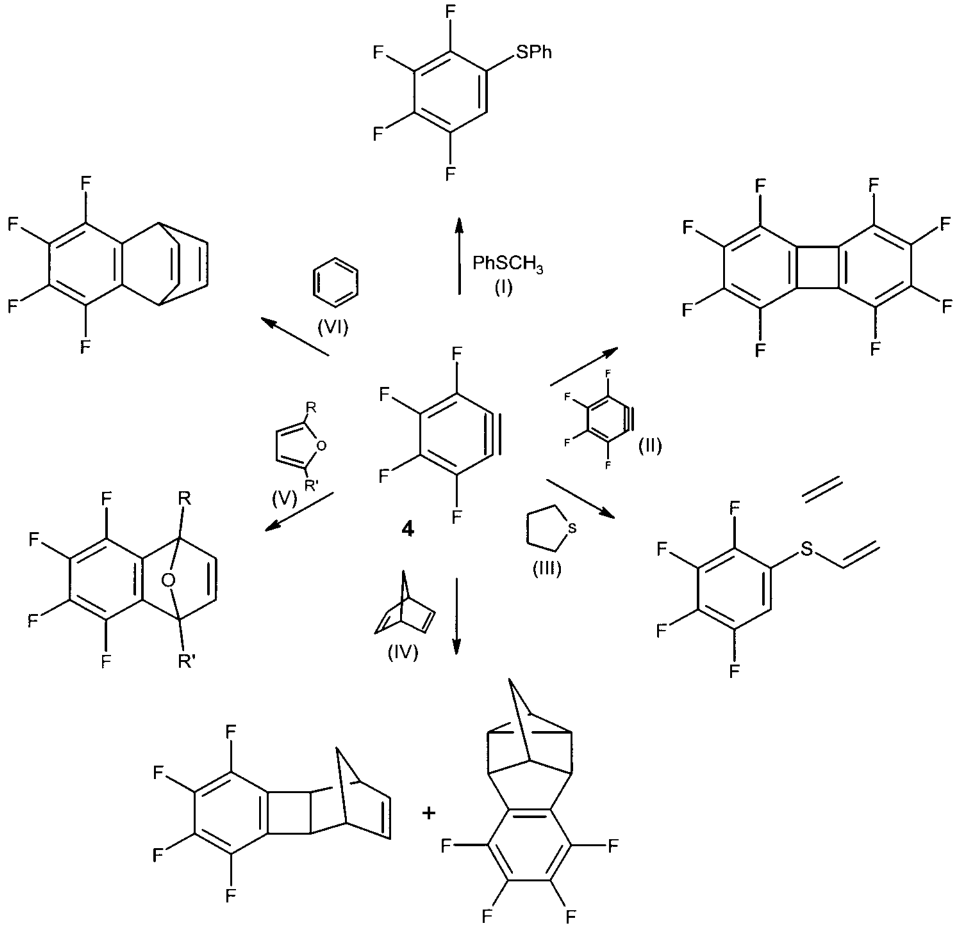
The only theoretical study on perfluorinated benzynes is based on semiempirical INDO calculations and was published in 1970.[27] The singlet–triplet splittings ΔE_{S-T} were calculated to be 83.0 and 55.0 kcal mol^{-1} for **4** and **5**, respectively. However, the same study predicts a ΔE_{S-T} value of 12.5 kcal mol^{-1} for *o*-benzyne (**1**) and −26.5 kcal mol^{-1} for *m*-benzyne (**2**), which does not agree with the experimentally determined data.

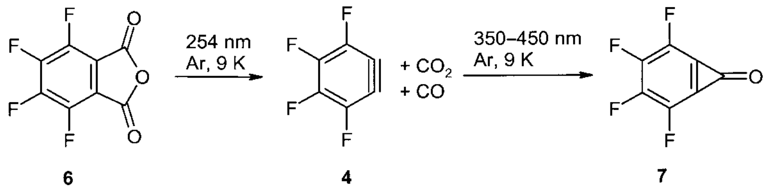


Scheme 4. Chemistry of the perfluorinated *o*-benzyne **4** from trapping reactions.

Here we describe the matrix isolation and spectroscopic characterization of the two perfluorinated benzynes **4** and **5**.

Results and Discussion

1,2-Didehydro-3,4,5,6-Tetrafluorobenzene (4): The UV photolysis of matrix-isolated phthalic anhydride has been shown to produce *o*-benzyne, CO, and CO_2 in a clean reaction.[5d] Analogously, tetrafluorophthalic anhydride **6** should be a suitable precursor for the synthesis of 1,2-didehydro-3,4,5,6-tetrafluorobenzene (**4**; Scheme 5). UV irradiation (254 nm) of



Scheme 5. Synthesis of benzyne **4** by photolysis of anhydride **6**, and reaction of **4** with CO to give the cyclopropenone **7**.

tetrafluorophthalic acid anhydride **6**, matrix-isolated in solid argon at 9 K, results in the decrease of the IR bands of **6** and formation of CO (2144.3 cm^{-1}) and CO_2 (658.6 and 2342.2 cm^{-1}). Simultaneously a new compound with the strongest IR absorptions at 1488.6, 1076.2, and 972.7 cm^{-1} is formed (Table 1, Figure 1). These new absorptions are in excellent agreement with the IR spectrum of the fluorinated *o*-benzyne **4**, calculated at the BLYP/6-311++G(d,p) level of theory.

Table 1. Observed and calculated IR bands of **4**.

Mode	Symm.	$\tilde{\nu}_{exp.}$ [cm^{-1}][a]	$I_{rel., exp.}$[b]	$\tilde{\nu}_{calcd}$ [cm^{-1}][c]	$I_{rel., calcd}$
10	b_2	465.6	0.04	449.3	0.04
11	b_2	586.6	0.07	545.4	0.03
12	b_1	–	–	590.9	0.00
13	a_2	–	–	632.9	0.00
14	b_2	–	–	634.0	0.00
15	a_1	–	–	672.2	0.02
16	b_2	972.7	0.55	927.9	0.48
		981.4	0.14		
17	a_1	1073.5	0.18	1023.1	0.22
		1076.2	0.32		
18	b_2	-	-	1143.4	0.04
19	a_1	1289.0	0.01	1239.7	0.01
20	a_1	1459.1	0.30	1382.2	0.29
21	b_2	1483.4	0.41	1420.3	1.00
		1488.6	1.00		
22	a_1	1495.9	0.16	1420.5	0.04

[a] Argon, 9 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the BLYP/6–311++G(d,p) level of theory. Band positions are unscaled. The assignment is based on band positions and intensities.

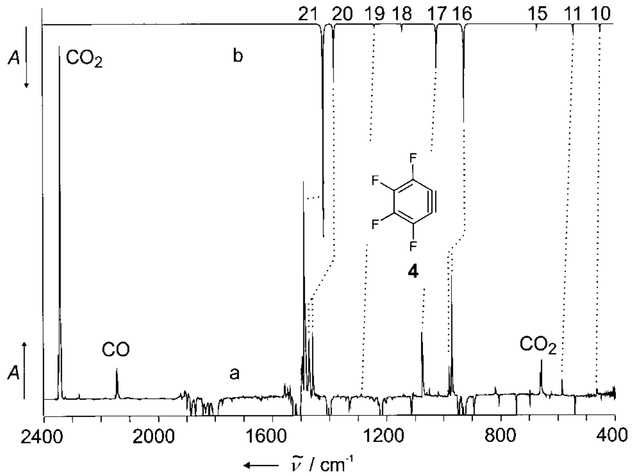


Figure 1. Photochemistry of tetrafluorophthalic anhydride **6** in solid argon. a) Difference spectrum. Bands pointing upwards appear on irradiation of **6** with 254 nm. b) Calculated (BLYP/6–311++G(d,p), unscaled) spectrum of 1,2-didehydro-3,4,5,6-tetrafluorobenzene (**4**).

The most intense absorption in the IR spectrum of **4** is a combined in-plane ring deformation/C–F stretching mode at 1488.6 cm^{-1}, which is split into several components. A similar splitting of matrix IR absorptions was reported by Radziszewski et al. for the parent benzyne **1**, generated by photolysis of phthalic anhydride.[5d] This effect was attributed to the interactions of **1** with CO and CO_2, isolated in the same matrix cage (pressure induced van der Waals complex).

The C≡C stretching vibration could not be identified in the IR spectrum of **4**. Denstiy functional theory (DFT) calculations (BLYP/6-311++G(d,p)) predict this vibration to be of very low intensity (0.6 km mol^{-1}, compared to 621 km mol^{-1} calculated for the most intense band) at 1935.6 cm^{-1}. For the parent benzyne **1** the C≡C stretching vibration was assigned to a very weak absorption at 1846 cm^{-1}.[5d]

The electronic structure of benzyne **1** resembles more that of a strained alkyne or a cumulene[11] than that of an open-shell diradical, and is thus well described by single-determinant methods. Therefore the calculated geometry of **4** is rather insensitive to the theoretical method employed (BLYP, B3LYP, or CASSCF, Figure 2). The hybrid functional B3LYP

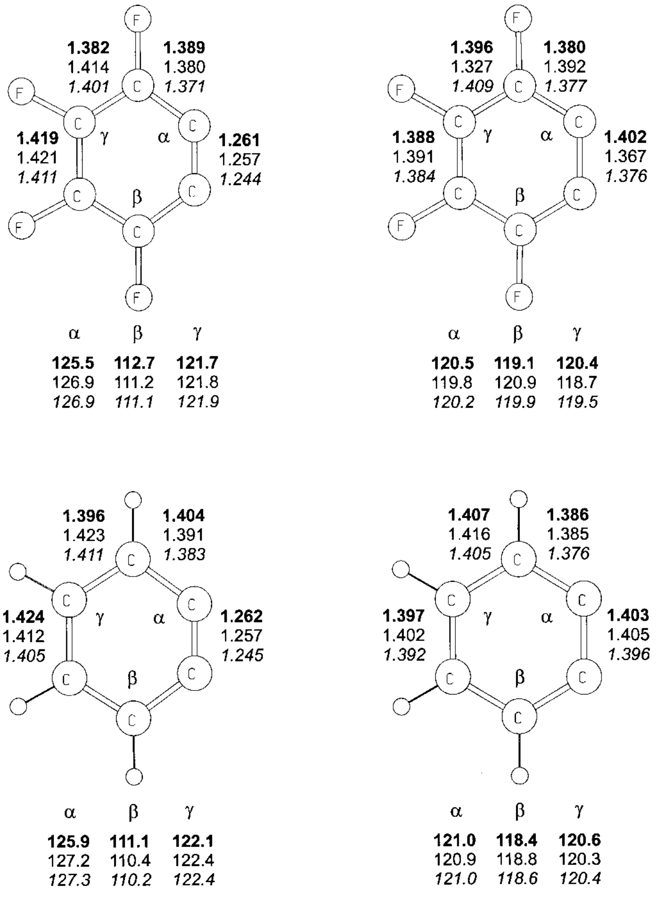


Figure 2. Calculated geometries of singlet (left) and triplet (right) *o*-didehydrobenzenes **1** and **4**. C–C Bond lengths in Å, bond angles in degrees (bold: CASSCF(8,8)/cc-pVDZ; regular: BLYP/6–311++G(d,p); italic: B3LYP/6–311++G(d,p)).

predicts a slightly shorter $C_1{\equiv}C_2$ bond length than the other methods. The singlet–triplet splitting of **4** is at all levels of theory calculated to be several kcal mol^{-1} larger than that of **1** (see Table 5). Both BLYP and B3LYP predict nonplanar C_2 symmetric structures for triplet **4**, whereas CASSCF predicts a planar molecule with C_{2v} symmetry.

Subsequent irradiation of the photoproducts with 350–450 nm light results in a decrease of the bands assigned to **4** (but not those of remaining **6**) and formation of new bands. These bands excellently match the calculated spectrum of tetrafluorobenzocyclopropenone **7**, which is formed by addition of carbon monoxide to **4** (Table 2, Figure 3). This carbonylation of **4** requires a photochemical activation and does not occur thermally on annealing the matrix at 30 K. A similar reaction was observed with 3,3,6,6-tetramethylcyclohexyne, which is photocarbonylated in CO-doped argon matrices to give the corresponding cyclopropenone.[28] For the parent *o*-benzyne (**1**) a photochemical equilibrium between cyclopentadienylideneketene and **1** + CO was observed.[29] The irradiation of matrix-isolated phthalic anhydride produces benzocyclopropenone as a byproduct, the direct formation from **1** + CO was not reported in this case.[5d] The different reactivity of **1** and **4** towards CO might result from the higher electrophilicity of **4**, caused by the electron withdrawing fluorine substituents.

Table 2. Observed and calculated IR bands of **7**.

Mode	Symm.	$\tilde{\nu}_{exp.}$ [cm^{-1}][a]	$I_{rel., exp.}$[b]	$\tilde{\nu}_{calcd}$ [cm^{-1}][c]	$I_{rel., calcd}$
12	a_1	548.1	0.06	532.1	0.01
13	b_1	580.6	0.01	560.9	0.01
14	a_2	–	–	573.6	0.00
15	b_2	623.2	0.08	597.0	0.04
16	b_1	–	–	620.0	0.00
17	b_2	691.0	0.04	657.6	0.02
18	a_2	–	–	672.6	0.00
19	b_2	818.1	0.22	774.4	0.10
20	a_1	884.6	0.05	850.0	0.02
21	b_2	1050.2	0.19	996.6	0.16
22	a_1	1108.4	0.23	1048.8	0.11
23	b_2	–	–	1212.5	0.03
24	a_1	1288.7	0.08	1236.4	0.04
25	a_1	–	–	1358.6	0.02
26	a_1	1470.7	0.79	1395.8	0.38
27	b_2	1494.4	1.00	1419.2	0.67
28	b_2	1605.6	0.05	1541.4	0.01
29	a_1	1610.5	0.05	1553.1	0.03
		1859.8	0.16		
30	a_1	1894.1	0.22	1869.0	1.00
		1904.4	0.35		
		1920.3	0.25		

[a] Argon, 9 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the BLYP/6–311++G(d,p) level of theory. Band positions are unscaled. The assignment is based on band positions and intensities.

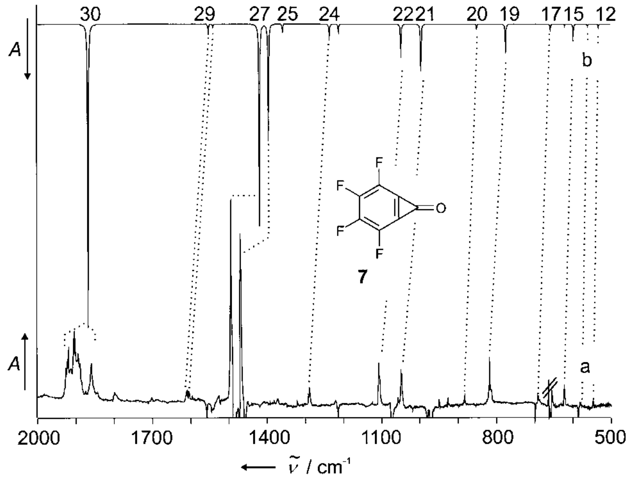
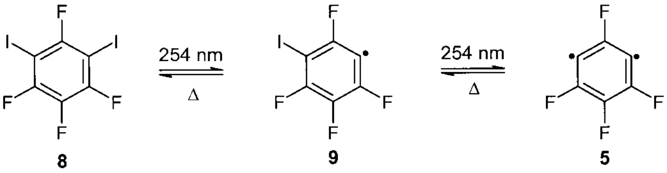


Figure 3. Irradiation (350–450 nm) of 1,2-didehydro-3,4,5,6-tetrafluorobenzene (**4**) generated by photolysis of tetrafluorophthalic anhydride **6**. a) Difference spectrum. Bands pointing upwards appear on irradiation. b) Calculated (BLYP/6–311++G(d,p), unscaled) spectrum of tetrafluorobenzocyclopropenone (**7**).

1,3-Didehydro-2,4,5,6-tetrafluorobenzene (**5**): Our first attempts to generate 1,3-didehydro-2,4,5,6-tetrafluorobenzene (**5**) were made by flash vacuum pyrolysis (FVP) of 1,3-diiodo-2,4,5,6-tetrafluorobenzene (**8**) and subsequent trapping of the products in solid argon at 10 K (Scheme 6). However, the only detectable products were SiF_4 (reaction with the quartz pyrolysis tube) and traces of CF_2 and CF_3, indicating complete breakdown of the aromatic ring system. This is in accord with an unsuccessful attempt to generate pentafluorophenyl radical by FVP of pentafluoroiodobenzene.[30] In contrast, FVP of the parent 1,3-diiodobenzene produces hex-3-ene-1,5-diyne as the major product.[18]



Scheme 6. Synthesis of the perfluorinated *m*-benzyne **5** by stepwise loss of iodine atoms of diiodobenzene **8**.

UV irradiation of **8** in solid argon does not result in any change in the IR spectrum, indicating the highly efficient in-cage recombination of the radical pairs under these conditions. In solid neon at 3 K, however, 254 nm irradiation rapidly generates a new compound A with the strongest IR absorptions at 1030.4, 1073.4, and 1484.4 cm^{-1} (Figure 4, Table 3).

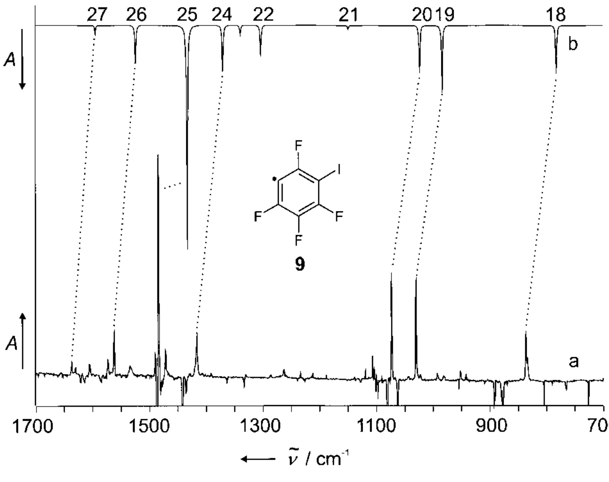


Figure 4. Photochemistry of 1,3-diiodotetrafluorobenzene (**8**) in a neon matrix at 3 K. a) Difference spectrum. Bands pointing upwards appear on irradiation (10 min) with 254 nm light. b) Calculated (BLYP/CEP-31G(d), unscaled) spectrum of 3-iodotetrafluorophenyl radical **9**.

Table 3. Observed and calculated IR bands of **9**.

Mode	Symm.	$\tilde{\nu}_{exp.}$ [cm^{-1}][a]	$I_{rel., exp.}$[b]	$\tilde{\nu}_{calcd}$ [cm^{-1}][c]	$I_{rel., calcd}$
18	a′	837.0	0.21	782.8	0.22
19	a′	1030.4	0.40	983.6	0.30
20	a′	1073.4	0.48	1023.5	0.23
21	a′	–	–	1149.1	0.02
22	a′	–	–	1303.5	0.13
23	a′	–	–	1339.7	0.04
24	a′	1416.6	0.18	1370.3	0.21
25	a′	1484.4	1.00	1433.3	1.00
26	a′	1562.3	0.19	1524.8	0.16
27	a′	1636.8	0.06	1595.4	0.04

[a] Neon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the BLYP/CEP-31G(d) level of theory. Band positions are unscaled. The assignment is based on band positions and intensities.

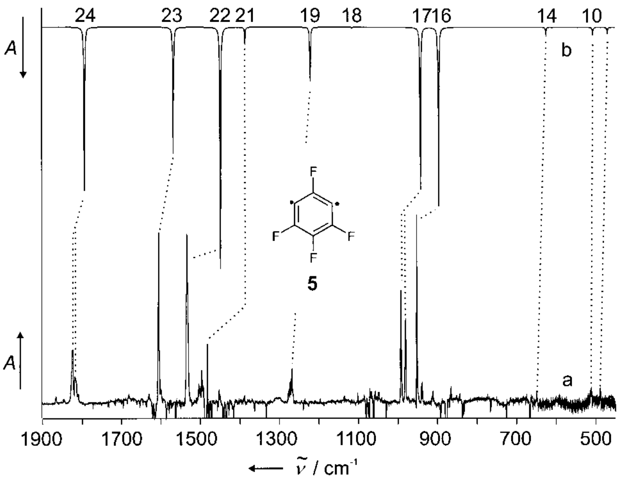


Figure 5. Prolonged irradiation of 1,3-diiodotetrafluorobenzene (**8**) in solid neon at 3 K. a) Difference spectrum (5.5 h – 4 h irradiation). Bands pointing upwards appear on irradiation with 254 nm light. b) Calculated (BLYP/6-311++G(d,p), unscaled) spectrum of 1,3-didehydro-2,4,5,6-tetrafluorobenzene **5**.

Prolonged irradiation results in formation of a second photoproduct B with intense bands at 952.3, 981.3, 992.7, 1534.2, 1605.4 and 1823.8 cm^{-1} (Figure 5, Table 4). The spectra of the two products can be clearly differentiated by plotting the band intensity versus irradiation time (Figure 6). The concentration of A rapidly increases at short irradiation times (<1 h), reaches a maximum, and slightly decreases on prolonged irradiation (several hours). The concentration of B rises much slower at short irradiation times, and only traces of B are present after 10 min. At longer irradiation times, when the concentration of A already decreases, the concentration of B still increases, until finally a photostationary equilibrium of **8**, A, and B is reached. This indicates a reaction sequence **8** → A → B with A being the precursor of B.

Table 4. Observed and calculated IR bands of **5**.

Mode	Symm.	$\tilde{\nu}_{exp.}$ [cm^{-1}][a]	$I_{rel., exp.}$[b]	$\tilde{\nu}_{calcd}$ [cm^{-1}][c]	$I_{rel., calcd}$
9	b_1	488.2	0.05	469.4	0.02
10	b_2	511.6	0.07	506.9	0.03
11	a_1	–	–	512.9	0.00
12	a_2	–	–	542.1	0.00
13	a_1	–	–	608.5	0.00
14	b_2	649.1	0.05	624.3	0.03
15	b_1	–	–	643.8	0.00
16	a_1	952.3	1.00	897.0	0.74
17	b_2	981.3	0.44	942.8	0.67
		992.7	0.62		
18	a_1	–	–	1116.2	0.00
19	b_2	1268.5	0.19	1221.2	0.22
		1273.3	0.12		
20	a_1	–	–	1385.9	0.00
21	b_2	1497.0	0.19	1387.4	0.06
22	a_1	1534.2	0.92	1449.3	1.00
23	b_2	1605.4	0.93	1568.3	0.52
24	a_1	1817.7	0.15	1794.4	0.68
		1823.8	0.30		

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

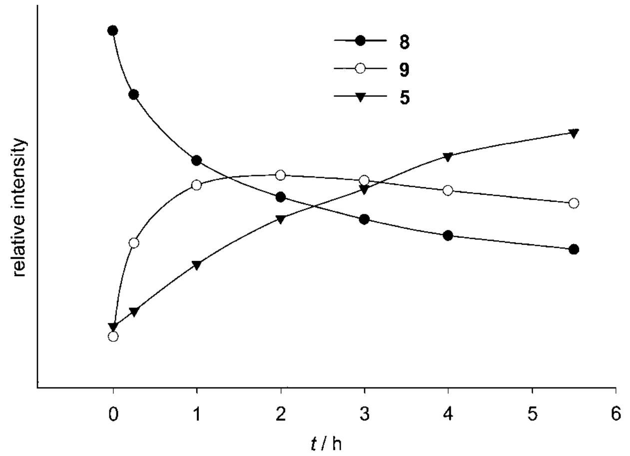


Figure 6. Relative intensity of IR absorptions versus irradiation time for the species formed on photolysis of 1,3-diiodotetrafluorobenzene (**8**) in solid neon.

On warming the matrix from 3 to 7.5 K both products A and B disappear (the latter faster than the former) and 1,3-diiodotetrafluorobenzene **8** is formed back again. These observations are in accord with the consecutive photochemical cleavage of the two C–I bonds in **8**: breaking of the first C–I bond leads to the 3-iodo-2,4,5,6-tetrafluorophenyl radical (**9**: compound A) and an iodine atom, and breaking of the second C–I bond finally produces benzyne **5** and a second iodine atom (see Scheme 6). The iodine atoms remain in the proximity of **9** and **5**, respectively. Annealing of the matrix leads to a higher mobility of trapped species and thus to the thermal radical recombination.

The yield of **9** and of **5** is much dependent on the matrix (in argon the yield of both radicals is essentially zero) and on the matrix temperature. While in solid neon at 7 K radical **9** is formed exclusively, the yields of **9** and **5** (estimated from the IR intensities) are almost equal after prolonged irradiation at 3 K. The formation of **9** and **5** requires radical pairs separated by the matrix, otherwise the thermal recombination is rapid even at low temperatures. Evidently, the smaller neon atoms are more suitable for the separation of radical pairs than argon atoms; however, details of these matrix effects are still not understood.

The assignment of the photoproducts A and B to **9** and **5**, respectively, is confirmed by comparison of the experimental with the DFT-calculated IR spectra. The IR spectrum of **9**, calculated at the (BLYP/CEP-31G(d)) level of theory, nicely reproduces the matrix (neon, 3 K) IR spectrum of A (Figure 4). The dominant absorption is an in-plane ring deformation mode at 1484.4 cm^{-1} (calculated at 1433.3 cm^{-1}). Although in argon at 10 K the concentration of **9** is too low to be observable by IR spectroscopy, an EPR signal indicates the formation of low concentrations of a radical, most likely **9**, in an argon matrix.

The assignment of the secondary photoproduct B to benzyne **5** is also supported by DFT calculations of the IR spectrum. The diradical character of *m*-benzynes is higher than that of *o*-benzynes, and the best agreement of the experimental IR spectrum of **2** with calculations was obtained by using the computationally expensive CCSD(T) method.[12] On the other hand, it was shown that DFT methods perform surprisingly well for the calculation of open-shell singlet molecules.[31–33] Whether pure DFT (BLYP)[34] or hybrid HF/DFT (B3LYP)[35] is more adequate for these systems is still controversial. For *m*-benzynes **2** and **5** B3LYP seems to overestimate the interaction of the radical centers resulting in a bicyclic rather than diradicaloid structure with a very short C(1)–C(3) distance and a very small bond angle at the carbon atom C(2) connecting the radical centers (Figure 7). This problem can be overcome by using an UB3LYP wavefunction.[32, 36] To reproduce the IR spectra of *m*-benzyne UB3LYP and BLYP perform similarly well, and for the sake of compatibility to earlier publications in this field we only discuss IR spectra calculated at the BLYP level of theory.

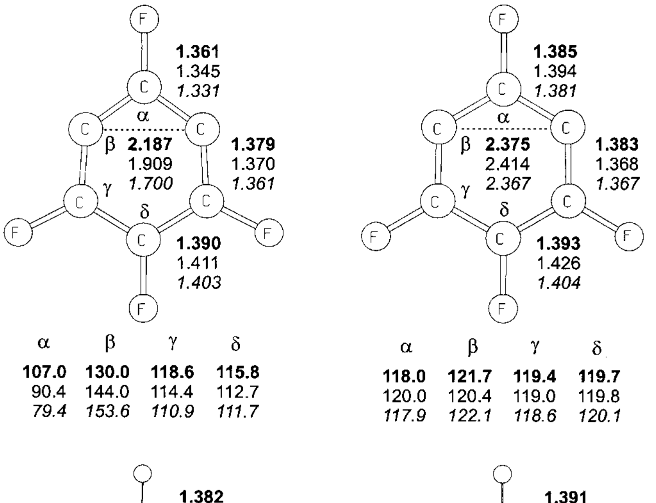


Figure 7. Calculated geometries of singlet (left) and triplet (right) *m*-didehydrobenzenes. C-C Bond lengths in Å, bond angles in degrees (bold: CASSCF(8,8)/cc-pVDZ; regular: BLYP/6-311++G(d,p); italic: B3LYP/6-311++G(d,p)).

A characteristic absorption at 1823.8 cm^{-1} (calculated at 1794.4 cm^{-1}) corresponds to an a_1 symmetrical ring stretching vibration (Figure 8, mode 24). The precursors **8** and **9** do not exhibit vibrations above 1700 cm^{-1}. An asymmetrical in-plane ring deformation mode with a large contribution of the radical centers (Figure 8, mode 10) has been shown to be characteristic of *m*-benzynes (547 cm^{-1} in **2**,[4] 543 cm^{-1} in 1,3-didehydro-5-fluorobenzene[15]). In tetrafluorobenzyne **5** this vibration is assigned to a weak absorption at 511 cm^{-1}. The splitting of modes 17, 19 and 24 into several components indicates matrix site effects, most likely interactions with the iodine atoms.

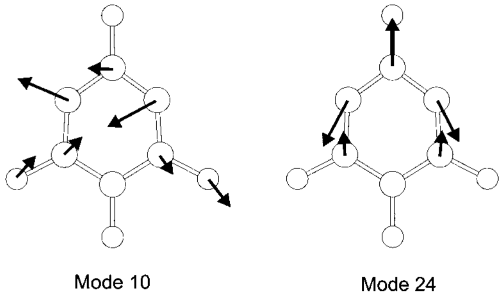


Figure 8. IR modes 10 and 24 of 1,3-didehydro-2,4,5,6-tetrafluorobenzene (**5**).

As a consequence of the multi-configuration character of *m*-benzynes the calculated geometries of **2** and **5** depend more on the level of theory than in the case of *o*-benzynes **1** and **4**. The CASSCF calculations, which include higher configurations, give a larger bond angle at C(2) and a longer C(1)–C(3) distance (Figure 7) than the DFT methods. While CASSCF and BLYP calculations give a shorter C(1)–C(3) distance for **5** than for **2**, B3LYP predicts this distance to be shorter in **2**. Despite this fact and the difference of 0.2 Å for *d*(C(1)–C(3)) between the two DFT methods the infrared spectra calculated by BLYP and B3LYP are very similar except for the blue-shift generally observed for B3LYP calculations. As for *o*-benzynes **1** and **4** an increase of the singlet–triplet splitting from the unsubstituted **2** to the tetrafluoro derivative **5** is predicted by all methods. For triplets T-**2** and T-**5**, which can be seen as models for noninteracting diradicals, *d*(C(1)–C(3)) is 0.343 and 0.505 Å longer than for singlets S-**2** and S-**5**, respectively. The differences between the computational methods are smaller for T-**2** and T-**5**.

Comparative calculations (BLYP/6-311++G(d,p)) of different fluorine-substituted *m*-benzynes indicate that the geometry is more sensitive to substitution in the 4- and 6- than in the 2- and 5-position. All calculated substituted *m*-benzynes have a shorter *d*(C(1)–C(3)) than unsubstituted **2**. The other C–C bonds are hardly affected by substitution with the difference compared to **2** lying well below 0.1 Å.

Conclusion

A general problem of the photochemical synthesis of radicals and other species of similar reactivity in rare gas matrices is the thermal in-cage recombination of the primarily formed radical pairs. Thus, while the photolysis of aryl and alkyl iodides in the gas phase yields the corresponding radicals in clean reactions, photolysis in argon matrices results in no net reaction. The radicals formed by cleavage of the C–I bond are trapped in the same matrix cage and thermally recombine back to the precursor molecule. This excludes many readily available precursors of radicals. To avoid the in-cage recombination, precursors have to be used that extrude highly stable molecules such as N_2, CO, or CO_2.

This approach was used for the synthesis of the perfluorinated *o*-benzyne **4**. Photolysis of tetrafluorophthalic anhydride **6** in an argon matrix produces CO, CO_2, and **4** in a clean reaction. This is completely analogous to the previously described synthesis of *o*-benzyne (**1**) from phthalic anhydride[5d] and demonstrates that phthalic anhydrides provide reliable photochemical precursors of *o*-benzynes. *o*-Benzynes are of comparatively low reactivity and react with CO only after photochemical activation. A reaction with CO_2 has not been observed.

m-Benzynes exhibit a higher radicaloid reactivity und thus more likely undergo secondary thermal reactions with other species trapped in the same matrix cage. In addition, cleavage of *m*-disubstituted benzenes produces in most cases radicals (if the substituents in *m*-position are not linked together as, for example, in metacyclophanes) and not stable molecules. This explains why the UV irradiation of 1,3-diiodobenzenes such as **8** in argon at 10 K does not result in any photochemistry. It is thus amazing that **8** is an excellent precursor of both the radical **9** and *m*-benzyne **5** if it is irradiated in solid neon at 3 K. An explanation of this could be that the radicals are formed with enough excess energy to leave the matrix cage in neon, but not in argon. A slight increase of the temperature of the neon matrices immediately results in radical recombination reactions. *o*-Benzyne **4** and *m*-benzyne **5** are the only C_6F_4 derivatives that have been isolated and spectroscopically characterized, so far. By combination of matrix IR spectroscopy with DFT calculations the IR spectra could be assigned.

The photochemistry of aryliodides in solid neon at very low temperatures is clearly distinct from that in argon. We are currently investigating the scope of this method for the generation of a variety of radicals.

Experimental Section

General: Tetrafluorophthalic anhydride was purchased from Aldrich and used as supplied. 1,3-Diiodotetrafluorobenzene was prepared by oxidative iodination of 1,3,4,5-tetrafluorobenzene according to a literature procedure by Neenan et al.[37]

Matrix isolation: Matrix isolation experiments were performed by standard techniques with a Sumitomo Heavy Industries RDK-408D closed cycle refrigerator (neon matrix experiments) or an APD CSW-202 Displex closed cycle cryostat (argon matrices). Matrices were produced by co-deposition of a large excess of rare gas (argon or neon, Messer-Griesheim, 99.9999%) and the trapped species on a cold CsI window. For argon matrices the cold window was retained at 30 K during deposition in order to obtain optically clear matrices and subsequently cooled to 9 K. Neon matrices were deposited at 3 K.

Infrared spectra were recorded with a Bruker IFS66 or Bruker Equinox 55 FTIR spectrometer with a standard resolution of 0.5 cm^{-1} in the range of 400–4000 cm^{-1}. Irradiations were carried out with a Gräntzel low pressure mercury lamp (254 nm) and Osram HBO 500 W/2 high-pressure mercury arc lamps in Oriel housings with quartz optics and a dichroic mirror (350–450 nm).

Theoretical methods: Calculations were performed with the GAUSSIAN98 suite of programs.[38] Geometries and vibrational spectra were calculated using the BLYP functional with a 6–311++G(d,p) basis set. For 3-iodotetrafluorophenyl radical **9** the CEP-31G(d) basis set was applied. Geometry optimizations of benzynes **1**, **2**, **4** and **5** were also performed at the B3LYP/6–311++G(d,p) and CASSCF(8,8)/cc-pVDZ level of theory (Table 5). The active space for the CAS calculation consisted of the π orbitals of the aromatic ring and the symmetric and antisymmetric combination of the σ orbitals at the radical centers.

Table 5. ΔE_{S-T} [kcal mol^{-1}] of unsubstituted and perfluorinated didehydrobenzenes.

	4	**1**	**5**	**2**
CASSCF(8,8)/cc-pVDZ	37.6	33.5	18.7	15.4
BLYP/6–311++G(d,p)	37.6	35.4	25.8	19.6
B3LYP/6–311++G(d,p)	36.3	31.3	23.7	14.4
exptl.[39]	–	37.6	–	21.0

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