Dehydroarenes

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Trifluoro-1,3,5-tridehydrobenzene**

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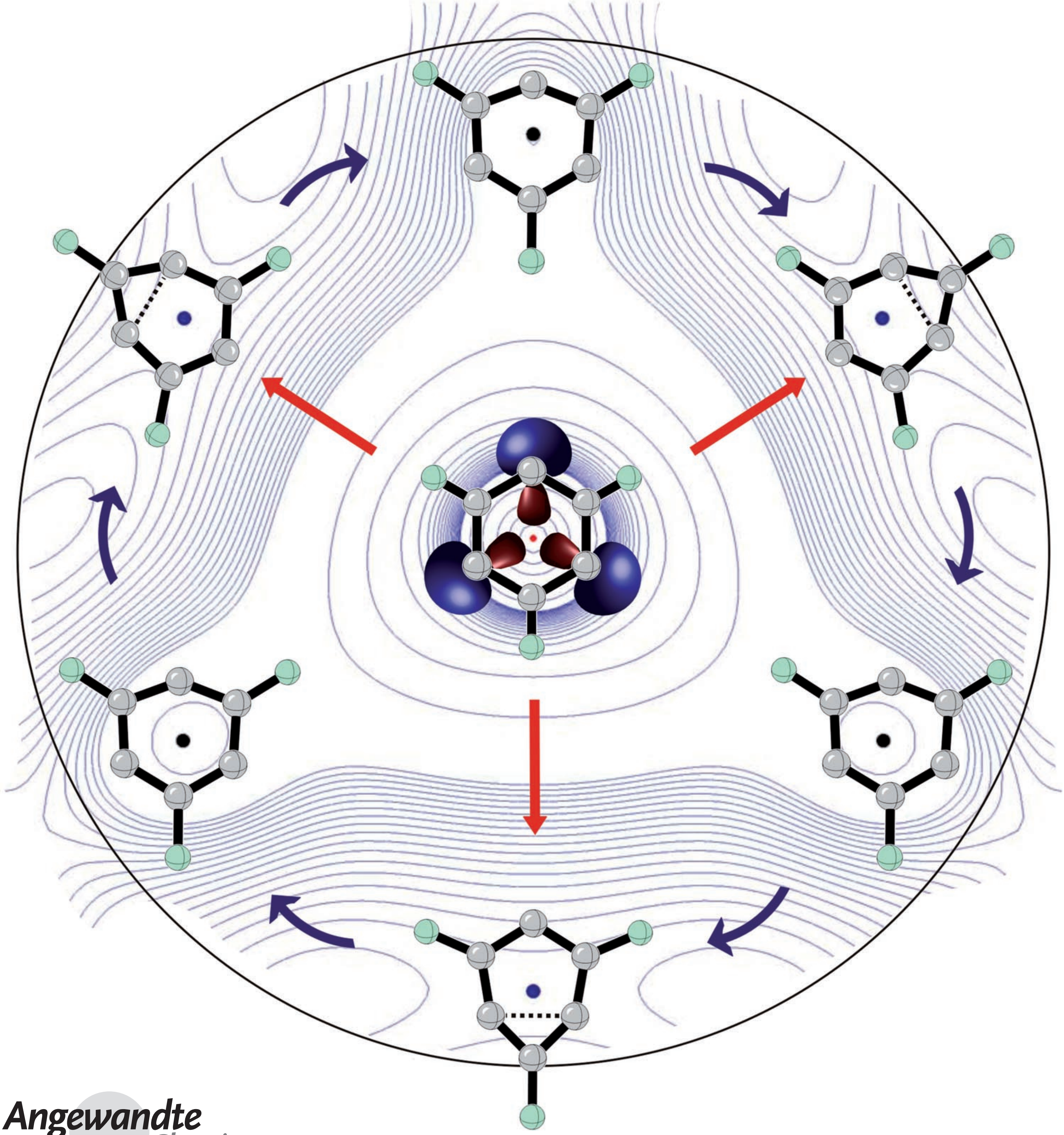

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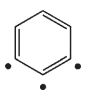
Triradicals[1] combine high reactivity with complex electronic structures, and therefore their investigation poses special challenges to experiment and theory. Tridehydrobenzenes **1**–**3**, formally derived from benzene by removal of three hydrogen atoms, are prototypes of this class of reactive intermediates and have been subject to recent experimental and computational studies.[2–4]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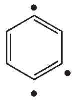
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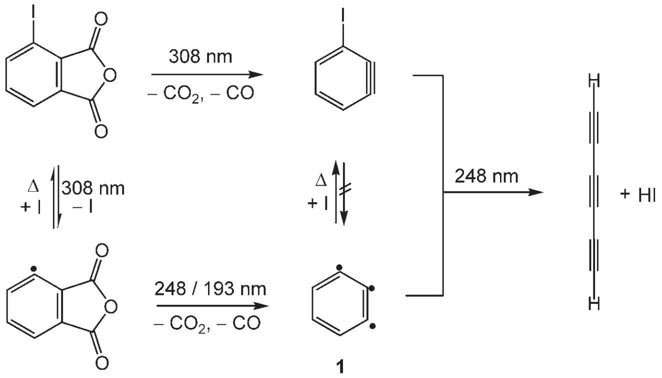

Scheme 1. Formation and subsequent reactions of 1,2,3-tridehydrobenzene (**1**).

According to calculations by Krylov and co-workers, **2** and **3** are less stable than **1** by 3 and 17 kcal mol^{-1}, respectively.[2] All three systems are predicted to exhibit doublet ground states, indicative of bonding interactions between the formally unpaired electrons. The adiabatic doublet-quartet splittings have been calculated to be 49, 41, and 28 kcal mol^{-1} for **1**, **2**, and **3**, respectively. These values show that coupling of the unpaired spins is most effective in **1**, in which all three radical centers are adjacent, and weakest in **3**.[2]

Recently, we described the isolation and IR spectroscopic characterization of 1,2,3-tridehydrobenzene (**1**) in a cryogenic neon matrix at 3 K.[3] Consecutive photolysis of 3-iodophthalic anhydride with 308 and 248 nm laser light led to the formation of **1**, which could clearly be identified by subsequent trapping with iodine atoms upon annealing the matrix at 8 K (Scheme 1). The most significant finding was the identification of a bicyclic $^2A_1$ ground state for **1**, while previous computations assumed a monocyclic $^2B_2$ ground state for that molecule. According to high-level computations, the former is adiabatically only 1–2 kcal mol^{-1} lower in energy. On the basis of a comparison of calculated and measured IR data, the $^2B_2$ state could undoubtedly be discarded in favor of a more bicyclic geometry with a weakly bonding distance of 170 pm between the formal radical centers at C1 and C3.[3]

The existence of two low-lying doublet states is readily understood by considering the frontier molecular orbitals shown schematically in Figure 1 a. At small C1–C3 distances, the singly occupied molecular orbital (SOMO) is of a_1 symmetry, whereas at larger distances the antibonding b_2 orbital drops below in energy. For 1,3,5-tridehydrobenzene (**3**), a similar situation can be envisaged (Figure 1 b). In D_{3h} symmetry, the two doublet states arising from occupation of either the a_1 or b_2 orbital are degenerate (symmetry labels in C_{2v}). The degeneracy is lifted by a Jahn–Teller distortion to either the $^2A_1$ or $^2B_2$ state. Similar to **1**, both doublet states are close in energy, the latter being 3–4 kcal mol^{-1} less stable.[2] In contrast to **1**, however, the $^2B_2$ isomer of **3** does not correspond to a minimum on the C_6H_3 potential energy surface (PES), but is instead predicted to be a transition state for interconversion of equivalent $^2A_1$ minima.[2a]

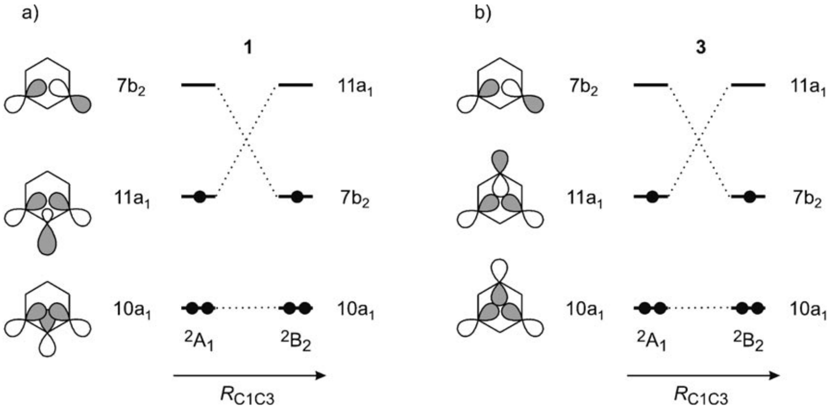

Figure 1. Frontier molecular orbitals in the two lowest electronic states of a) **1** and b) **3**.

Thermochemical data for **3** were determined in the gas phase by Wenthold and co-workers.[4] According to these measurements, the heat of formation of the triradical is (179 ± 4.6) kcal mol^{-1}, which leads to the bond dissociation energies (BDEs) given in Scheme 2 for successive hydrogen removal from benzene.

The similarity of the first and third BDEs indicates that **3** is most appropriately described as a *meta*-benzyne[5,6] moiety

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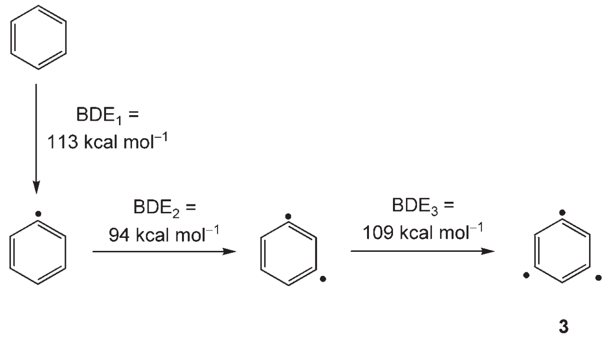
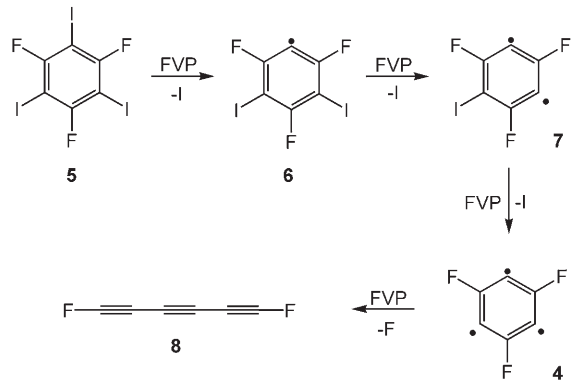


Scheme 2. Successive hydrogen removal from benzene to 1,3,5-tridehydrobenzene (**3**) and corresponding bond dissociation energies (BDEs).

that interacts only weakly with the third radical center on the opposite side of the ring.[4] This finding is in full agreement with the calculated $^2A_1$ ground state of **3**. However, given the similar energy of the two lowest doublet states of **3**, and taking into account that several computational methods predict the $^2B_2$ state to be a second minimum instead of a transition state (see below), more direct information about the ground-state properties of **3** and its derivatives is desirable.

Herein, we describe the matrix isolation and IR spectroscopic characterization of trifluoro-1,3,5-tridehydrobenzene (**4**), a simple derivative of triradical **3**. Fluorine substitution often leads to kinetic stabilization of reactive species that are otherwise too reactive to be isolated even under low-temperature conditions.[7] A suitable precursor of **4** is 1,3,5-triiodo-2,4,6-trifluorobenzene (**5**), which has three labile C–I bonds that on UV photolysis or flash vacuum pyrolysis (FVP) should be cleaved to produce the corresponding mono-, di-, and triradicals **6**, **7**, and **4**, respectively (Scheme 3).



Scheme 3. Formation of triradical **4** from 1,3,5-triiodo-2,4,6-trifluorobenzene (**5**).

The photochemistry of trifluorotriiodobenzene **5** in neon at 3 K has been described previously.[8] Irradiation at 248 nm (KrF excimer laser) or 254 nm (low-pressure mercury arc lamp) produced the expected phenyl radical **6** and *meta*-benzyne **7** that were identified by comparison of their matrix IR spectra with density functional theory (DFT) calculations. As the radicals **6** and **7** are formed in proximity to iodine atoms in the same matrix cage, warming of the matrix from 3 K to 7.5 K results in a recombination of the radicals and iodine atoms to yield back the precursor **5**. Unfortunately, derivative **7** turned out to be photostable, and even upon prolonged irradiation no evidence for the formation of **4** could be obtained in these experiments.[8]

Alternatively, pyrolysis of **5** in the gas phase with subsequent trapping of the products in a cryogenic matrix could also lead to the elusive triradical **4**. In a similar way, a number of didehydroarenes were synthesized by FVP of aryl diiodocompounds.[6f,g] A drawback of this method is the fragmentation of fluorinated aromatic compounds that contain radical centers. In these experiments, complex mixtures of small fluorinated molecules (CF_2, CF_3, CF_4, C_2F_3, etc.) are observed.[9] The mechanism of this fragmentation is not yet clear and currently under investigation in our laboratory.

The FVP of **5** was investigated at temperatures between 500 and 750 °C (Figure 2 and Figure S1 in the Supporting Information). The thermal decomposition of **5** begins at temperatures above 600 °C. However, even above 700 °C the product mixture still contains undecomposed precursor **5**. Apart from impurities (CO, CO_2, H_2O) common in pyrolysis experiments, significant amounts of fragments (especially CF_2, CF_3, and CF_4) are observed under these conditions (Figure S1 in the Supporting Information). At higher temperatures, the concentration of the fragments increases and several additional compounds are found. Two of those are readily identified as phenyl radical **6**, produced in very low yields, and didehydrobenzene **7**. This observation is in line

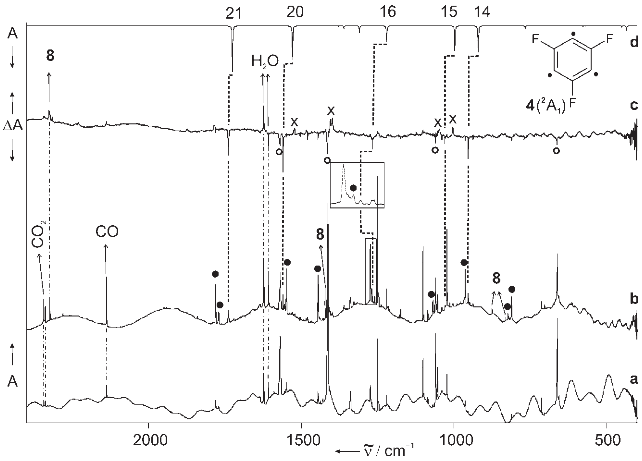
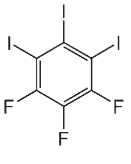


Figure 2. FVP of trifluorotriiodobenzene **5**. a) IR spectrum of a matrix (Ar, 3 K) containing the FVP products (675 °C) of **5**. b) IR spectrum of a matrix containing the FVP products (725 °C) of **5**. Absorptions of *meta*-benzyne **7** are labeled by dots. c) Difference spectrum: Bands pointing downwards decrease, and bands pointing upwards increase in intensity upon irradiation with a low-pressure mercury lamp of a matrix containing the FVP products (725 °C) of **5**. Absorptions of monoradical **6** are labeled with crosses; the strongest absorptions of **5** are labeled with circles. d) Calculated vibrational spectrum (UBLYP/cc-pVTZ) of triradical **4** in its $^2A_1$ ground state. Note that most of the unassigned peaks belong to low-molecular-weight fragmentation products such as SiF_4, CF_4, CF_3, CF_2 etc. Assignments of these by-products are provided in the Supporting Information.

with previous FVP studies of aromatic diiodo compounds,[6f,g] where the concentrations of the monoradicals are generally low compared to that of the diradicals. This indicates a higher thermal lability of the C–I bond in monoradicals compared to the diiodo compounds.[10] A third species with characteristic absorptions at 831, 875, 1422, and 2324 $\mathrm{cm^{-1}}$ is identified as difluorohexatriyne **8**.[11] The formation of **8** clearly indicates that the cleavage of C–F bonds occurs at least to some degree in the FVP experiments. These three molecules were identified by comparison of the matrix IR spectra with data from the literature and DFT calculations.

A number of additional IR signals at 954, 1030, 1266, 1560, and 1738 $\mathrm{cm^{-1}}$ were assigned to a new species **A**. These signals appear only at high temperatures of the FVP (above 700 °C) and show always the same relative intensity, as expected for a single compound. Species **A** proved to be photolabile, and on UV irradiation (254 nm) all IR absorptions assigned to **A** decrease in intensity. Simultaneously, all IR bands of **5** (remaining precursor after FVP) decrease in intensity as previously reported.[8] The products formed during photolysis are phenyl radical **6** and hexatriyne **8**. As photolysis of **5** results in the formation of **6** but not in **8**, the hexatriyne must be a product of the photolysis of **A**.

By comparison of these five IR absorptions with DFT calculations (BLYP and B3LYP), compound **A** is identified as trifluoro-1,3,5-tridehydrobenzene **4** in its $^2A_1$ state (Table 1). A high-spin quartet state can clearly be excluded based on the poor agreement with the computed vibrational spectrum.[12] To gain additional support for this assignment, we also investigated the photo- and thermochemistry of the isomeric triiodobenzenes **9** and **10** under identical FVP conditions. Whereas several common products could be identified after FVP of **9**, **10**, and **5** (fragments such as CF_2 and CF_3), only **5** produced monoradical **6**, diradical **7**, and triradical **4**, which confirms the assignment of **4**.



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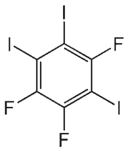

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To investigate the effect of fluorine substitution on the molecular and electronic structure of tridehydrobenzene **3**, extensive quantum chemical computations were carried out employing density functional theory (DFT) as well as ab initio methods.[13] Structures of **3** and **4** obtained at the UB3LYP, UBLYP,[14] and RO-CCSD(T)[15] level, and PES scans along the C1–C3 distance coordinate[16] are shown in Figure 3. For both systems, the three methods give rather similar results regarding the structure and energetic separation of the two lowest doublet states. In agreement with previous calculations,[2] **3** is found to have a $^2A_1$ ground state with a C1–C3 separation almost identical to *meta*-benzyne,[5,6] whereas the $^2B_2$ excited state is 2–3 $\mathrm{kcal\,mol^{-1}}$ higher in energy. Interestingly, the B3LYP method (in contrast to BLYP) predicts the latter to be a minimum rather than a transition state that is 1.4 $\mathrm{kcal\,mol^{-1}}$ less stable than the $^2A_1$ ground state. Despite several attempts, no additional stationary point could be localized in this region of the B3LYP PES. In particular, no transition state for the interconversion of both isomers could be found.

Fluorination has only a small effect on the equilibrium geometry and relative stability of both states. This finding is in contrast to *meta*-benzyne, where fluorination leads to for-

Table 1: IR spectroscopic data of matrix-isolated trifluoro-1,3,5-tridehydrobenzene **4** ($^2A_1$). Calculated data for the low-spin ($^2A_1$, $^2B_2$) states and high-spin quartet state[12] are given for comparison.

	Ar, 3 K		4 ($^2A_1$)			4 ($^2B_2$)[c]			4 ($^4A''$)		
Mode	$\tilde{\nu}_{exp}$ [$\mathrm{cm^{-1}}$][a]	$I_{exp,rel}$	Sym.	$\tilde{\nu}_{calcd}$ [$\mathrm{cm^{-1}}$][a]	I_{calcd} [$\mathrm{km\,mol^{-1}}$][b]	Sym.	$\tilde{\nu}_{calcd}$ [$\mathrm{cm^{-1}}$][a]	I_{calcd} [$\mathrm{km\,mol^{-1}}$][b]	Sym.	$\tilde{\nu}_{calcd}$ [$\mathrm{cm^{-1}}$][a]	I_{calcd} [$\mathrm{km\,mol^{-1}}$][b]
1			*b*1	163.0	0 (0)	*b*2	310.2*i*	36 (12)	*a''*	122.2	31 (6)
2			*b*1	250.5	1 (0)	*b*1	125.2	0 (0)	*a'*	122.4	0 (0)
3			*b*2	271.3	1 (0)	*a*2	247.9	0 (0)	*a'*	184.9	2 (0)
4			*a*1	286.6	0 (0)	*b*1	270.8	1 (0)	*a''*	297.3	22 (5)
5			*a*2	323.1	0 (0)	*a*1	279.2	0 (0)	*a'*	307.5	0 (0)
6			*a*1	379.9	1 (0)	*b*2	309.7	2 (0)	*a''*	330.3	4 (1)
7			*b*2	435.0	29 (9)	*a*1	484.3	9 (2)	*a'*	471.0	1 (0)
8			*b*1	451.7	8 (2)	*b*1	484.4	14 (4)	*a''*	549.2	2 (0)
9			*a*1	546.4	0 (0)	*a*2	502.5	0 (0)	*a'*	555.2	0 (0)
10			*a*2	556.0	0 (0)	*a*1	568.0	0 (0)	*a''*	598.9	0 (0)
11			*b*2	569.3	3 (0)	*b*1	573.1	7 (2)	*a'*	612.5	2 (0)
12			*b*1	578.7	7 (2)	*b*2	573.6	0 (0)	*a'*	651.7	13 (3)
13			*a*1	767.0	17 (5)	*a*1	808.6	7 (2)	*a'*	872.8	0 (0)
14	**954**	**60**	***b*2**	**921.7**	**193 (57)**	*b*2	976.2	173 (57)	*a'*	976.3	60 (13)
15	**1030**	**30**	***a*1**	**997.6**	**183 (54)**	*a*1	1016.0	166 (55)	*a''*	985.8	18 (4)
16	**1266**	**40**	***b*2**	**1221.8**	**117 (35)**	*a*1	1291.3	99 (33)	*a''*	1021.9	477 (100)
17			*a*1	1310.6	54 (16)	*b*2	1325.4	90 (30)	*a'*	1171.7	332 (70)
18			*b*2	1361.3	17 (5)	*b*2	1413.1	1 (0)	*a''*	1275.7	124 (26)
19			*a*1	1378.0	3 (0)	*a*1	1427.7	0 (0)	*a'*	1299.1	32 (7)
20	**1560**	**70**	***b*2**	**1530.0**	**246 (73)**	*a*1	1572.6	297 (100)	*a''*	1426.6	211 (44)
21	**1738**	**100**	***a*1**	**1726.6**	**336 (100)**	*b*2	1690.6	262 (88)	*a'*	1525.2	186 (39)

[a] UBLYP/cc-pVTZ. [b] Relative intensities are given in parenthesis. [c] Contains imaginary frequency.

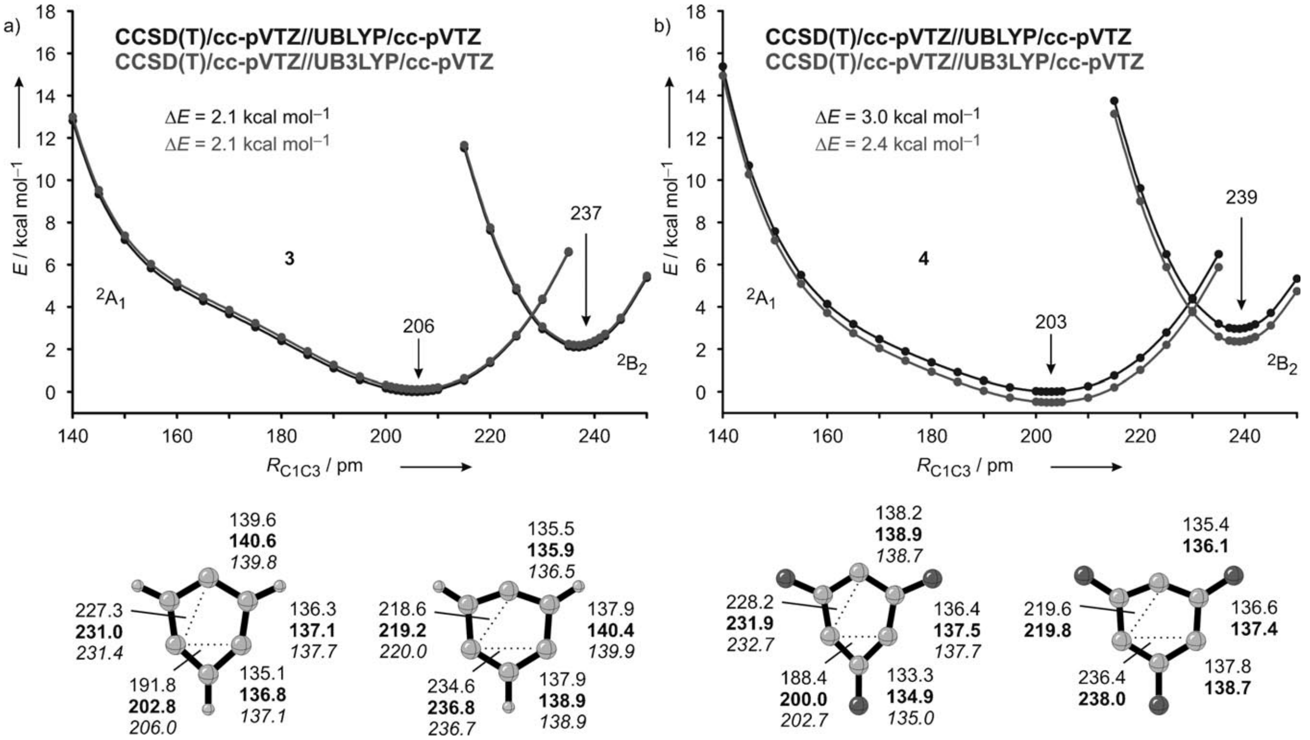

Figure 3. Energy as a function of the distance of radical centers C1 and C3 in a) **3** and b) **4**. Selected C–C bond lengths of stationary points are given in pm (normal print: UB3LYP/cc-pVTZ; bold: UBLYP/cc-pVTZ; italics: RO-CCSD(T)/cc-pVTZ). Note that the PES scans yield two-dimensional cuts through a Jahn–Teller triple-cone potential, where the three equivalent $^2B_2$ states are transition states for the interconversion of three equivalent $^2A_1$ minima. This interconversion corresponds to a pseudorotation around the cone apex.

mation of a bicyclic structure and, accordingly, to a significant increase in the singlet–triplet splitting.[8] This effect has been rationalized in terms of eclipsing strain of the three adjacent fluorine atoms in tetrafluoro-*m*-benzyne, rather than by electronic effects of the substituents.[8c] In line with this interpretation, a similar effect is not found for fluorination of **3**, because no steric interaction exists between the fluorine atoms in **4**. However, a thorough investigation of substituent effects in aromatic bi- and triradicals seems to be necessary to fully understand the interplay of electronic and steric factors influencing the ground- and excited-state properties of these intermediates.[17]

Analogous to **3**, the B3LYP functional predicts the $^2B_2$ state to be a minimum on the C_6F_3 PES. The vibrational spectra calculated at the B3LYP level for both states of **4** are similar. To allow for a more quantitative comparison with the experimental IR spectrum, anharmonic corrections to harmonic vibrational frequencies for both isomers were calculated perturbatively (Table S1 in the Supporting Information). Surprisingly, a low-frequency vibrational mode of *b*2 symmetry becomes imaginary in the fundamental IR spectrum of the $^2B_2$ state of **4**, corresponding to a change of 380 cm^{-1} (from 100 cm^{-1} in the harmonic approximation to 283*i* cm^{-1} with inclusion of anharmonicity effects). Thus, in agreement with the BLYP calculations, only the three equivalent $^2A_1$ states of **4** correspond to minimum-energy structures, whereas the three equivalent $^2B_2$ states are transition states for their mutual interconversion.

In summary, trifluoro-1,3,5-tridehydrobenzene (**4**) was generated by FVP of trifluorotriiodobenzene (**5**) at temperatures above 700 °C. Despite the formation of several side products and low-molecular-weight fragments, the IR absorptions of triradical **4** can readily be assigned on the basis of their photolability upon irradiation at 254 nm. The measured IR spectrum is in good agreement with the vibrational spectrum calculated at the BLYP level for the $^2A_1$ ground state of **4**. Fluorination of **3** has only a marginal effect on the structures and relative stabilities of the two lowest doublet states. According to high-level calculations, the $^2B_2$ states of both **3** and **4** are transition states for the interconversion of degenerate $^2A_1$ minima lying 2–3 kcal mol^{-1} above the $^2A_1$ ground states. A detailed investigation aimed at a deeper understanding of substituent effects in aromatic bi- and triradicals is currently in progress in our laboratories.

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[12] Similar to the triplet state of tetrafluoro-*m*-didehydrobenzene,[8] both DFT methods yield a C_s-symmetric structure for the lowest quartet state of **4**, deviating slightly from planarity. At the BLYP level, the $^{4}A''$ state of **4** is adiabatically 24.9 kcal mol^{-1} higher in energy than the $^{2}A_1$ ground state.

[13] a) DFT calculations were carried out with Gaussian 03: Gaussian 03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**. b) Ab initio computations were carried out with Molpro 2000.1: H.-J. Werner, P. J. Knowles, *Molpro 2000.1*, Birmingham, **1999**.

[14] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; c) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[15] CCSD(T) calculations employed the partially spin-restricted open-shell coupled cluster (RHF-RCCSD(T)) program: a) P. J. Knowles, C. Hampel, H.-J. Werner, *J. Chem. Phys.* **1993**, *99*, 5219; b) P. J. Knowles, C. Hampel, H.-J. Werner, *J. Chem. Phys.* **2000**, *112*, 3106.

[16] Distances of two of the radical centers have been frozen and all other coordinates optimized at the DFT level within the constraint to C_{2v} symmetry. Subsequently, CCSD(T) calculations have been carried out on the geometries obtained from these calculations.

[17] For **1**, which already has a rather bicyclic structure,[3] fluorination leads to a stabilization of the $^{2}B_2$ state which becomes the ground state of trifluoro-1,2,3-tridehydrobenzene, without changing the structure of either state significantly. On the basis of steric effects alone, the opposite tendency would be expected. Thus, electronic effects are likely to play an important role here as well.

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