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Radicals

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Isolation and Characterization of the Triradical 1,3,5-Trimethylenebenzene**

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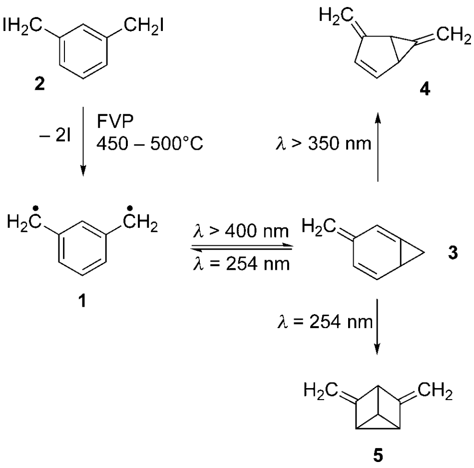
Organic high-spin molecules[1,2] can serve as model compounds for the design of organic magnetic materials.[3,4] The most frequently used coupling unit to achieve ferromagnetic coupling between π radical centers is the *m*-phenylene group. Thus, 1,3-dimethylenebenzene (*m*-xylylene) **1** was shown to have a robust triplet ground state.[5,6] The spectroscopic properties, structure, and photochemistry of **1** was recently investigated using matrix isolation spectroscopy.[7] Prerequisite for these studies was the observation that high yields of **1** are obtained by flash vacuum pyrolysis (FVP) of 1,3-bis(iodomethyl)benzene **2** at 450 °C and subsequent trapping of the products in argon at 10 K (Scheme 1).

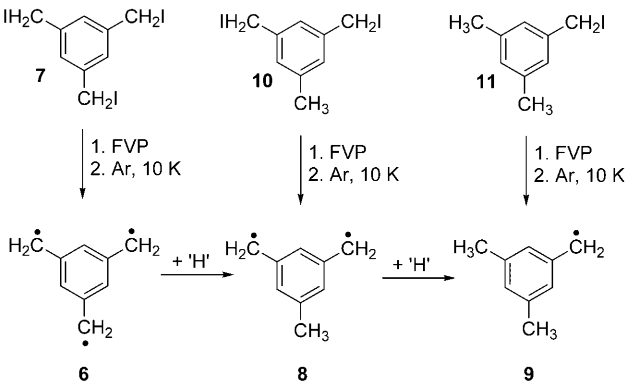


Scheme 1. Synthesis and photochemistry of *m*-xylylene **1**.

Most notably is the photochemistry of diradical **1**. Near-UV irradiation rapidly yields the highly strained polycyclic hydrocarbons **3**–**5**, which are all thermodynamically less stable than diradical **1**, in photostationary equilibria with **1**. However, because these hydrocarbons show only weak or no absorption in the near-UV region, they can be obtained in high photostationary yields, depending on the wavelength of the irradiating light.

1,3,5-Trimethylenebenzene **6** (see Scheme 2 for the structure) forms the basis of a number of organic high-spin polyradicals, and several derivatives of **6** have been described in literature. The first attempt to synthesize a derivative of **6** was reported in 1937 by Leo.[8] In contrast, the parent triradical **6** has only been investigated by negative-ion photoelectron spectroscopy in the gas phase and by theoretical methods. Hammad and Wenthold measured the heat of formation of triradical **6** by collision induced dissociation of the biradical anion 5-chloromethyl-*m*-xylylene.[9] It was shown that the interaction between the radical centers in **6** is very small, and therefore the heat of formation can be reliably estimated by simple bond additivity. The doublet – quartet energy gap has been calculated to 12–14 kcal mol^{-1} by various theoretical methods.[10,11] Herein we describe the first isolation and spectroscopic characterization of the elusive triradical **6** by using the matrix isolation technique.

Flash vacuum pyrolysis of 1,3,5-tris(iodomethyl)benzene **7** with subsequent trapping of the products in argon at 10 K (Scheme 2) allowed us to obtain IR, UV/Vis, and EPR spectra of the pyrolysis products. The IR spectrum obtained after pyrolysis of **7** at 480 °C shows three intense bands at 614.7, 727.3, and 814.7 cm^{-1} as well as several weak bands assigned to triradical **6** (Figure 1, Table 1). The assignment has been confirmed by partial deuteration and by comparison with calculations at various levels of theory (see the Supporting Information). With a sufficiently large basis set, DFT and MP2 calculations show only moderate spin contaminations and predict very similar IR spectra. Therefore, here we only



Scheme 2. Synthesis of 1,3,5-trimethylenebenzene **6** and by-products through flash vacuum pyrolysis.

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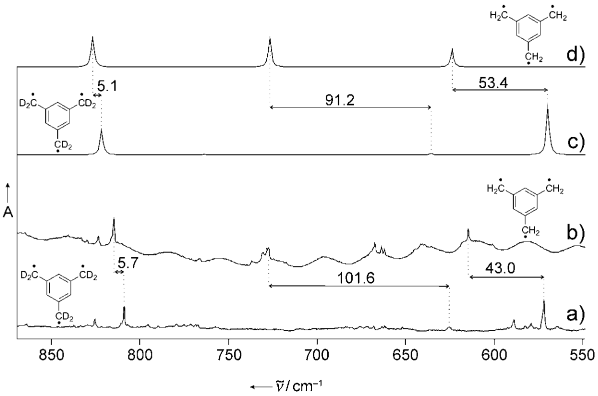

Figure 1. IR spectra obtained after FVP at 480 °C and subsequent trapping of the products in argon at 10 K. a) FVP of [D_6]-**7**. b) FVP of **7**. c) IR spectrum of quartet [D_6]-**6** calculated at the UB3LYP/6-311+G(d,p) level of theory. d) IR spectrum of quartet **6** calculated at the UB3LYP/6-311+G(d,p) level of theory.

Table 1: IR spectroscopic data of triradical **6** and [D_6]-**6**.

Mode ν	Sym.	**6**, exp.[a]	**6**, calcd[b]	[D_6]-**6**, exp.[a]	[D_6]-**6**, calcd[b]	Assignment
14	A_2''	614.7 (75)	624.1 (58)	571.7 (100)	570.7 (100)	C^3–H oop def
16	A_2''	727.3 (65)	727.4 (96)	625.7 (1)	636.2 (3)	C^1–H_2 oop def
21	A_2''	814.7 (100)	827.9 (99)	809.0 (60)	822.8 (53)	C^3–H oop def
22	E′	926.3 (2)	936.3 (2)	–[c]	764.8 (1)	C^1–H_2 rock
28	E′	–[c]	1214.9 (0)	1058.0 (5)	1081.1 (3)	C^1–H_2 scis, C^3–H ip def
35	E′	1462.6 (5)	1490.2 (7)	1246.3 (1)	1270.1 (4)	C^1–H_2 scis, C^1=C^2 str
38	E′	1478.3 (5)	1512.5 (8)	1481.3 (5)	1509.4 (4)	C^1=C^2 str, C^1–H_2 scis
41	E′	3018.9 (10)	3145.3 (12)	2214.9 (5)	2284.0 (5)	sym C^1–H_2 str
43	E′	3038.0 (10)	3167.8 (18)	3039.4 (5)	3167.7 (15)	C^3–H str
47	E′	3111.6 (10)	3241.7 (13)	–[c]	2416.5 (6)	asym C^1–H_2 str

[a] Argon, 10 K. Values in parentheses are the signal intensities. [b] UB3LYP/6-311+G(d,p). Values in parentheses are the signal intensities. [c] Not assigned owing to overlap with a strong neighboring signal. asym = asymmetric, def = deformation, ip = in plane, oop = out of plane, rock = rocking, scis = scissoring, str = stretch, sym = symmetric.

discuss the results from calculations at the UB3LYP/6-311+G(d,p) level of theory.

The three most intense bands of **6** are the A_2'' symmetrical out of plane (oop) C–H deformation modes ν_{14}, ν_{16}, and ν_{21} of the methylene groups and the ring hydrogen atoms (Figure 2, Table 1). If the precursor is deuterated at all methylene positions ([D_6]-**7**), only two very strong absorptions are observed in the spectrum (ν_{14} and ν_{21}), whereas ν_{16} is now very weak.

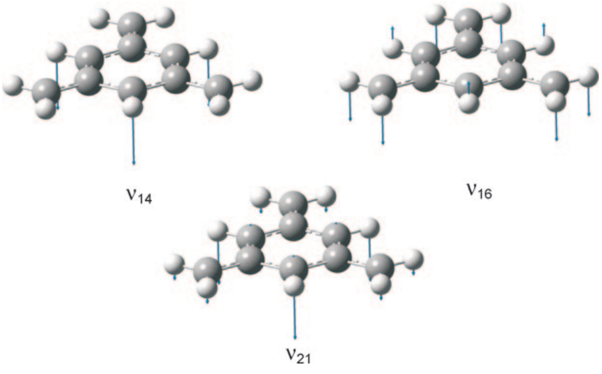

Figure 2. A_2'' symmetrical out of plane vibrations of **6**.

The vibration ν_{21} at 814.7 cm^{-1} is described best as a symmetrical ring C–H oop deformation mode with only small contributions from the methylene groups. Consequently, deuteration of the methylene groups results in a deuterium isotopic shift of only −5.7 cm^{-1}, in good agreement with the calculations (−5.1 cm^{-1}).

The vibration ν_{16} at 727.3 cm^{-1} shows the largest deuterium isotopic shift (−101.6 cm^{-1}) and the largest change in intensity on deuteration. Deuteration of the methylene groups results in a drastic reduction of the intensity of this band to approximately 3 % of the original value. The reason for this is the out of phase movement of the methylene hydrogen atoms with respect to the ring hydrogen atoms. This results in [D_6]-**6** in a fortuitous cancellation of the dipole moment contributions of the C–H and the C–D movements and thus drastically reduced IR intensity. Both the isotopic shift and the reduced intensity are reproduced by the calculations. Vibration ν_{14} at 614.7 cm^{-1} shows a deuterium shift of −43.0 cm^{-1} (calculated shift: −53.4 cm^{-1}).

Minor products of the FVP of **7** detected by IR spectroscopy in solid argon are 3,5-dimethylbenzylradical **9** and triplet 5-methyl-*m*-xylylene **8** (Scheme 2). For comparison of the IR spectra these products were independently synthesized and matrix-isolated by FVP of 1,3-bis(iodomethyl)-5-methyl-benzene **10** and 3,5-dimethylbenzyliodide **11**, respectively (see the Supporting Information).

The UV/Vis spectrum of an argon matrix at 10 K obtained after FVP of **7** shows absorptions from several species (see the Supporting Information). A weak band at 292.3 nm and parts of a broad and intense band around 232.4 nm are assigned to triplet diradical **8**, while the weak transition at 260.9 nm and the very weak transition at 318.5 nm are assigned to radical **9**—these results are in good accordance with the fluorescence excitation and absorption bands of benzylradicals.[12–15] Two remaining weak bands at 367 nm and 254.9 nm might belong to **6**, however, we cannot exclude the possibility that these bands are caused by an unknown impurity. Nguyen and co-workers calculated for **6** the first electronic transition to 354 nm by MS-CASPT2 theory, which would be in good agreement with the 367 nm band.[16]

Further evidence for the formation of triradical **6** comes from EPR spectroscopy where **6** could be generated by either FVP of **7** with subsequent trapping of the products in argon at 5 K or by photolysis of matrix-isolated **7** at 5 K (Figure 3). Matrices containing **6** show a centrosymmetric five-line EPR spectrum centered at 3427 G. At 5 K the spectrum is persistent for days without any change. A half-field signal at

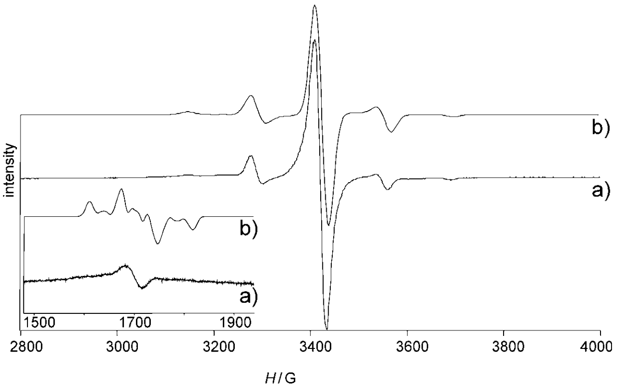

Figure 3. a) EPR spectrum obtained after irradiation of matrix isolated **7** with 308 nm. b) Simulated quartet EPR spectrum using $|D/hc| = 0.0128\ \mathrm{cm}^{-1}$, $|E/hc| = 0\ \mathrm{cm}^{-1}$, $g = 2.0023$, $\mu = 9.60067$ GHz. Inset: half-field signal.

1708 G and a very weak signal at 1130 G corresponding to a $\Delta m_s = \pm 3$ transition appear together with the main signals at $g = 2$. The five lines in the spectrum can be assigned to the z and xy signals of a randomly oriented quartet molecule with a threefold or higher axis of symmetry. Similar EPR spectra have been observed for other quartet molecules with high symmetry and have been predicted by theory.[17–24] The simulation of a quartet state ($S = 3/2$) with the zero-field-splitting (zfs) parameters $|D/hc| = 0.0128\ \mathrm{cm}^{-1}$ and $|E/hc| = 0\ \mathrm{cm}^{-1}$ gives the best agreement with the experimental spectrum. The experimental spectrum cannot be simulated with a triplet state, which rules out the possibility that the half-field signal belongs to a triplet species. Triplet diradical **8** has been independently synthesized and characterized by EPR spectroscopy. As expected, its zfs parameters $|D/hc| = 0.0111\ \mathrm{cm}^{-1}$ and $|E/hc| \leq 0.0009\ \mathrm{cm}^{-1}$ are very similar to that of triplet *m*-xylylene **1** (see the Supporting Information).

UV photolysis (308 nm) of matrix-isolated **7** produces a clean EPR spectrum of **6** (Figure 3). Interestingly, other paramagnetic intermediates (radicals or diradicals formed by loss of one or two of the three iodine atoms) are not formed in detectable amounts during initial photolysis of **7**. Under the same conditions the IR spectrum shows no apparent photochemistry of **7**. Obviously, the recombination of the radical pairs produced by cleavage of the C–I bonds is very efficient, and thus the yield of **6** obtained by photolysis of **7** is too low for detection by IR spectroscopy.

In contrast to the highly photolabile diradical **1**, triradical **6** is rather photostable. Prolonged UV irradiation results in a very slow degradation of **6**. The IR spectrum of the photoproducts of **6** show a number of broad, low intensity bands that could not be assigned. The slow photochemistry of **6** is remarkable since under the same conditions **1** rearranges in clean reactions to the strained hydrocarbons **3**, **4**, and **5**.[7]

In summary, we were able to synthesize trimethylenebenzene **6** by FVP of triiodide **7**. The matrix IR and EPR spectra clearly prove that **6** is a highly symmetrical triradical with a quartet ground state. This is in accordance with earlier theoretical studies that predicted a large quartet–doublet splitting. The photostability makes derivatives of **6** interesting building blocks of organic magnets.

Experimental Section

Synthesis: 1,3,5-tris(bromomethyl-d_2)benzene was synthesized according to the literature starting from trimethyl-1,3,5-benzenetricarboxylate.[25]

Synthesis of 1,3,5-tris(iodomethyl-d_2)benzene [D_6]-**7**: 1,3,5-tris-(bromomethyl-d_2)benzene (0.363 g, 1 mmol) was dissolved in 10 mL of dry acetone. To this solution NaI (2.248 g, 15 mmol) was added and the mixture stirred for 3 h at RT. The suspension was filtered and after removal of the solvent a yellow-white solid remained. This solid was further purified by column chromatography on silica gel using *n*-hexane as the eluent to give the product in 85% yield. IR (KBr): $\tilde{\nu} =$ 2271, 2263, 1593, 1436, 1183, 1070, 951, 909, 852, 830, 694, 512, 499 cm^{-1}; HRMS(EI): *m/z* calcd for [$C_9H_3D_6$]: 503.8215; found: 503.8211.

Matrix isolation: Matrix isolation experiments were performed by standard techniques[26] using a closed-cycle helium cryostat and a CsI spectroscopic window cooled to 10 K. FTIR spectra were recorded with a standard resolution of 0.5 cm^{-1}, using a liquid-nitrogen-cooled MCT detector in the range 400–4000 cm^{-1}. X-band EPR spectra were recorded from a sample deposited on an oxygen-free high-conductivity copper rod (75 mm length, 2 mm diameter) cooled with a closed-cycle cryostat to 4 K. UV/vis spectra were recorded in the spectroscopic range of 800 to 200 nm with a standard resolution of 0.1 nm, using a Varian UV/Vis NIR spectrophotometer from a sample deposited on a sapphire window cooled to 10 K by a closed-cycle cryostat. Flash vacuum pyrolysis was carried out by slowly subliming **7** through a 7 cm quartz tube heated electrically with a tantalum wire.

Broadband irradiation was carried out with mercury high-pressure arc lamps in housings equipped with quartz optics and dichroic mirrors in combination with cutoff filters (50% transmission at the wavelength specified). For 254 nm irradiation a low-pressure mercury arc lamp was used. An excimer laser (XeCl) was used for 308 nm photolysis.

Computational Methods: Optimized geometries and vibrational frequencies of all species were calculated at the B3LYP[27–29] level of theory employing the 6-311+G(d,p) polarized valence-triple-ξ basis set.[30,31] Tight convergence criteria were used throughout. A spin-unrestricted formalism was used for all high-spin systems and for singlet biradicals, whenever instability[32] was observed. All calculation were carried out with Gaussian 03.[33]

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