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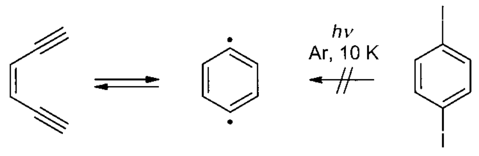
[22] **9**: ESI-MS (positive-ion mode), m/z (%): 1210.3 (15) $[(M+2Na^+)/2]$, 1207.3 (10) $[(M+H^++K^+)/2]$, 1199.3 (40) $[(M+H^++Na^+)/2]$, 1188.3 (100) $[(M+2H^+)/2]$; ^1H NMR (COSY, 400 MHz, D_2O): $\delta = 4.85$ (d, 1H, $J_{H\text{-}1,H\text{-}2} = 3.0$ Hz; H1), 4.66–4.58 (m, 1H; E^{α}), 4.58–4.53 (m, 1H; $1 \times P^{\alpha}$), 4.53–4.47 (m, 2H; $1 \times S^{\alpha}$, $1 \times T^{\alpha}$), 4.46–4.39 (m, 3H, $J_{H\text{-}1',H\text{-}2'} = 7.9$ Hz; H1′, $2 \times S^{\alpha}$), 4.39–4.09 (m, 12H; H4, A^{α} {4.31}, L^{α} {4.29}, $1 \times P^{\alpha}$ {4.36}, Q^{α} {4.36}, $4 \times T^{\alpha}$, $3 \times T^{\beta}$ {4.26}), 4.18–4.09 (m, 3H; H2, $1 \times T^{\beta}$, $1 \times V^{\alpha}$), 4.09–3.89 (m, 6H; H3 {4.00}, H3′ {4.00}, H4′, H9″a, $1 \times T^{\beta}$ {4.05}, $1 \times V^{\alpha}$), 3.88–3.71 (m, 10H; G^{α}, S^{β}, $2 \times P^{\delta}$), (3.88–3.71 (m, 2H), 3.71–3.49 (m, 12H)] (H4″ {3.60}, H5, H5′, H5″, H6a, H6b, H6′a, H6′b, H6″, H7″, H8″, H9″b, $2 \times P^{\delta}$), 3.49–3.41 (m, 1H; H2′), 2.70 (dd, 1H; $J_{H3''eq,H3''ax} = 12.3$, $J_{H3''eq,H4''} = 3.7$ Hz; $H3''_{eq}$), 2.46–2.38 (m, 2H; E^{γ}), 2.29 (t, 2H, $J_{Q\beta,Q\gamma} = 7.5$ Hz; Q^{γ}), (2.25–2.12 (m, 1H), 2.08–1.89 (m, 12H)) (E^{β}a {2.02}, P^{β}, P^{γ}, Q^{β} {2.02, 1.90}, V^{β}), 2.00, 1.96, 1.94 (3 × s, 9H; CH_3CO), 1.89–1.78 (m, 1H; E^{β}b), 1.71 (t, 1H, $J_{H3''eq,H3''ax} = J_{H3''ax,H4''} = 12.0$ Hz; H3″ax), 1.64–1.47 (m, 3H; L^{β}, L^{γ}), 1.31 (d, 3H, $J_{A\alpha,A\beta} = 7.0$ Hz; A^{β}), (1.26 (d, 3H, $J_{T\beta,T\gamma} = 5.9$ Hz), 1.20 (d, 3H, $J_{T\beta,T\gamma} = 6.4$ Hz), 1.18–1.08 (m, 9H)) (T^{γ}), 0.88 (m, 12H; V^{γ}), 0.83 (d, 6H, $J_{L\gamma,L\delta} = 5.9$ Hz; L^{δ}); ^{13}C NMR (100.6 MHz, D_2O): $\delta = 177.8$, 177.0, 176.6, 174.6, 173.3, 173.2, 172.7, 171.9, 171.7, 171.4, 170.9, 170.8 (C=O), 104.6 (C1′), 99.0 (C2″), 77.4, 75.8, 74.9, 73.0, 71.8, 71.1, 68.9, 68.8, 68.4, 68.3, 67.3, 67.0, 66.9 (C2′, C3, C3′, C4, C4′, C4″, C5, C5′, C6″, C7″, C8″, T^{β}), 62.8 (C9″), 61.4, 61.2, 61.0 (C6, C6′, S^{β}), 60.5, 59.5, 59.3, 59.1, 57.2, 55.7, 55.4, 52.9, 52.6, 51.9, 50.9, 49.8 (C2, C5″, A^{α}, E^{α}, L^{α}, P^{α}, Q^{α}, S^{α}, T^{α}, V^{α}), 48.5, 48.0 (P^{δ}), 42.3 (G^{α}), 39.7 (L^{β}), 39.5 (C3″), 31.2 (Q^{γ}), 30.4, 30.2 (V^{β}), 29.7, 29.4 (E^{γ}, P^{β}) 27.0, 25.8, 24.7 (E^{β}, Q^{β}, P^{γ}), 24.5, 22.2, 21.8, 21.1, 18.9, 18.8, 18.5, 18.2, 17.8, 17.7 ($\mathit{C}H_3CO$, L^{γ}, L^{δ}, T^{γ}, V^{γ}), 16.6 (A^{β}); the signal for C1 could not be assigned.

Matrix Isolation of Perfluorinated *p*-Benzyne[**]

Hans H. Wenk, Andreas Balster, Wolfram Sander,* David A. Hrovat, and Weston T. Borden

The thermal cyclization of enediynes **1** to produce *p*-benzyne (*p*-didehydrobenzene) and its derivatives **2** (Bergman cyclization)[1] is the key step for the biological activity of the enediyne antibiotics.[2] During the past few years this reaction and the proposed intermediates have thus been the target of a large number of synthetic,[3–11] spectroscopic,[12–16] and theoretical[17–21] studies.[22] The heat of formation of 1,4-didehydrobenzene (**2a**) was determined by Roth et al. to be 138.0 ± 1.0 kcal mol^{-1}, which results in a reaction enthalpy for the cyclization of **1a**→**2a** of 8.5 ± 1.0 kcal mol^{-1}.[23] The activation barrier for the ring-closure of **1a** was determined to be 28.7 ± 0.5 kcal mol^{-1}. A singlet ground state was predicted for **2a**, and a singlet–triplet splitting ΔE_{ST} of -3.8 ± 0.5 kcal mol^{-1} was measured by Squires et al. using negative-ion photoelectron spectroscopy (NIPES).[14] Recently the matrix isolation and characterization of **2a** by IR spectroscopy was reported from our laboratory.[15]



1a **2a** **3a**

The experimental data available for *p*-didehydrobenzene (**2a**) has contributed to the understanding of the biological activity of calicheamicin-type antitumor drugs. The challenge is now to modify the diradicals **2** in order to control their reactivity.[24] However, so far all attempts to isolate and characterize derivatives of benzyne **2a** failed.

Density functional theory (DFT) and CASSCF calculations indicate that 1,4-didehydro-2,3,5,6-tetrafluorobenzene (**2b**) should be a suitable target for synthesis and isolation in low-temperature matrices. The fluorine substituents at the terminal acetylenic positions result in a large destabilization of 1,3,4,6-tetrafluoro-hex-3-ene-1,5-diyne (**1b**) with respect to *p*-benzyne **2b**, and the cyclization of **1b** is estimated to be exothermic by 7.9 kcal mol^{-1} (UB3LYP/6-311++G(d,p)). The barrier for the ring-opening of **2b** is calculated to be 37.5 kcal mol^{-1}, almost twice that of **2a** (19.8 ± 1 kcal mol^{-1}).[23]

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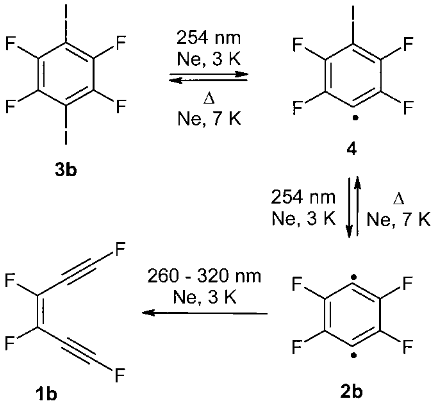
A readily available photochemical precursor of **2b** should be 1,4-diiodo-2,3,5,6-tetrafluorobenzene (**3b**). The photolysis of iodobenzenes results in the cleavage of the C–I bond, leading to the formation of phenyl radicals and iodine atoms. However, under the conditions of matrix isolation the radicals generally can not escape the matrix cage; therefore, the yield of radicals is very much limited by rapid in-cage recombinations. Thus, UV irradiation ($\lambda = 254$ nm) of **3b** in argon at temperatures as low as 3 K does not produce the 4-iodo-2,3,5,6-tetrafluorophenyl radical **4** in quantities large enough for IR spectroscopic detection. Only the more sensitive and specific EPR spectroscopy indicates the formation of traces of radicals.



Surprisingly, the irradiation (254 nm) of **3b** in neon at 3 K results in the rapid formation in moderate yields of a new compound with strong IR absorptions at 1471, 1188, 942, 834, and 693 cm^{-1}. By comparison with the IR spectrum calculated at the UB3LYP[25] level of theory, using the 6-311G(d,p) basis set, this new compound was identified as phenyl radical **4** (Figure 1, Table 1). Apparently, under these conditions the radical pairs are separated by neon atoms.[16b] Warming the matrix for several minutes to 7.5 K results in the recombination of **4** and the iodine atom, reforming the starting compound **3b**.

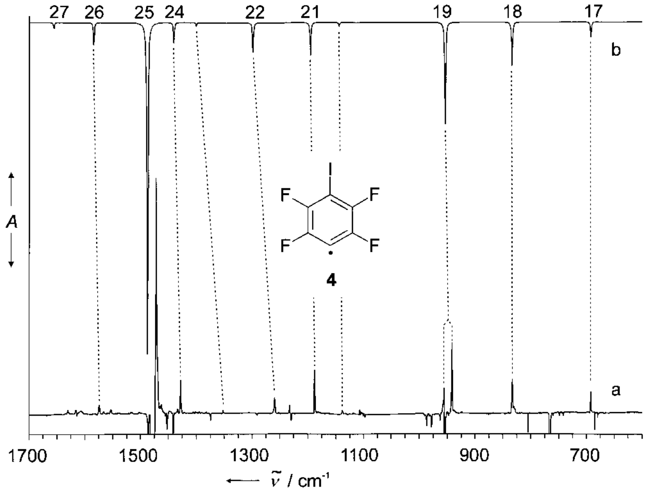


Figure 1. Photochemistry of **3b** in solid neon at 3 K. a) Difference spectrum. Bands pointing upwards arise during 10 min irradiation with 254 nm. b) Calculated spectrum (UB3LYP/6-311G(d,p), unscaled) of radical **4**.

Table 1. IR spectroscopic data of 4-iodo-2,3,5,6-tetrafluorophenyl radical (**4**).

Mode	Symmetry	$\tilde{\nu}_{exp}$[a] [cm^{-1}]	$I_{rel,exp}$[b]	$\tilde{\nu}_{calcd}$[c] [cm^{-1}]	$I_{rel,calcd}$
17	b_2	692.9	0.09	693.2	0.05
18	a_1	833.6	0.14	834.1	0.13
19	b_2	941.9	0.29	954.3	0.31
		956.0	0.11		
20	b_2	1138.4	0.01	1144.8	0.01
21	a_1	1188.1	0.18	1195.1	0.10
22	b_2	1259.4	0.04	1298.1	0.09
23	a_1	1352.2	0.01	1400.2	0.01
24	a_1	1428.3	0.13	1440.9	0.06
25	b_2	1471.7	1.00	1487.2	1.00
26	a_1	1574.4	0.03	1584.8	0.07

[a] Neon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the B3LYP/6-311G(d,p)[29] level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

Prolonged 254 nm irradiation of **3b** and **4** at 3 K produces another compound, A, which has its strongest IR absorptions at 1516, 1507, 1117, and 925 cm^{-1}. Warming the matrix to 7.5 K causes all the IR absorptions assigned to radical **4** and to compound A to decrease and results in formation of **3b** (Figure 2). Compound A is photolabile and UV irradiation in the range 260–320 nm gives an additional compound, B, which has its strongest IR absorption at 2337 cm^{-1}. Compound B was clearly identified as enediyne **1b** by comparison of the experimental with the DFT calculated IR spectrum (Figure 3, Table 2).

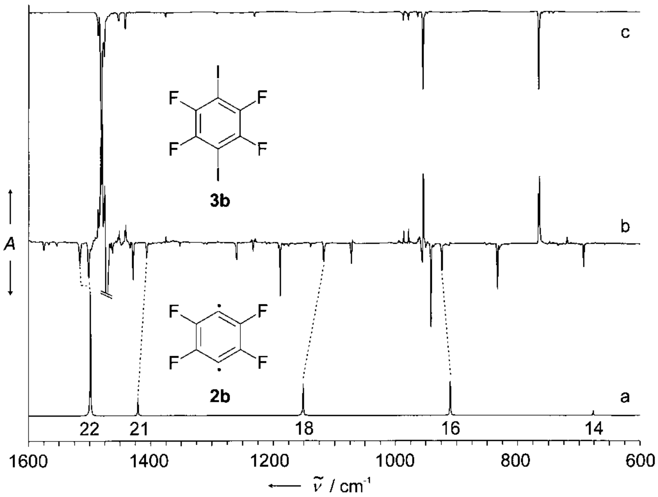


Figure 2. Thermal reactions of the products formed by 254 nm irradiation (3 h) of **3b** in a neon matrix at 3 K. a) Calculated spectrum (CASSCF(8,8)/cc-pVDZ, scaled by 0.91) of singlet **2b**. b) Difference spectrum. Bands pointing upwards appear, bands pointing downwards disappear upon annealing (7.5 K, 10 min). Bands marked with dotted lines are assigned to **2b**, other bands belong to radical **4**. c) IR spectrum of diiodotetrafluorobenzene (**3b**) matrix isolated in solid neon at 3 K.

Both the thermal reaction with iodine atoms to reform **3b** and the photochemical formation of **1b** strongly suggest that compound A should be assigned the structure of *p*-benzyne

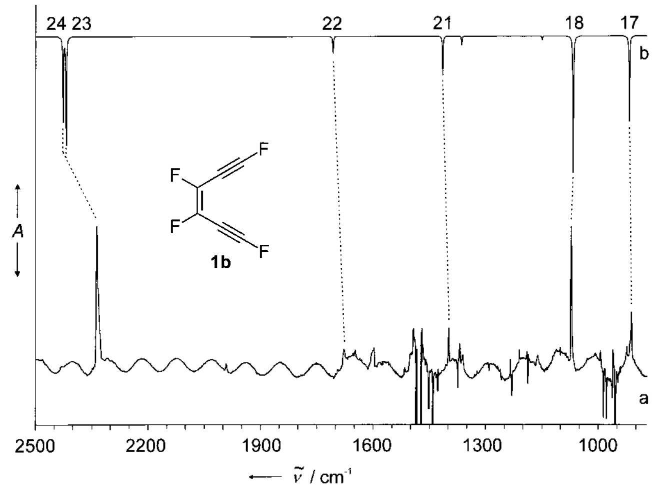


Figure 3. Photochemistry of diradical **2b**. a) Difference spectrum. Bands pointing upwards appear upon broad band irradiation (260–320 nm) of the products formed by 254 nm irradiation (3 h) of **3b** in solid neon at 3 K. Bands marked with dotted lines are assigned to enediyne **1b**. b) Calculated IR spectrum (B3LYP/6-311++G(d,p), unscaled) of **1b**.

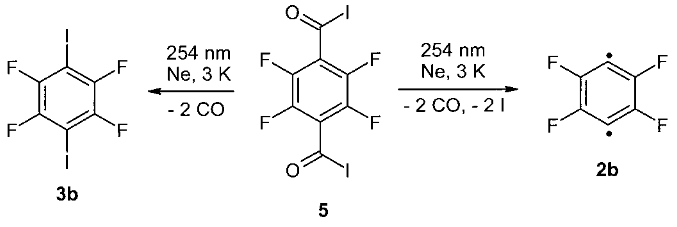
Table 2. IR spectroscopic data of 1,3,4,6-tetrafluorohex-3-ene-1,5-diyne (**1b**).

Mode	Symmetry	$\tilde{\nu}_{exp}$[a] [cm^{-1}]	$I_{rel,exp}$[b]	$\tilde{\nu}_{calcd}$[c] [cm^{-1}]	$I_{rel,calcd}$
14	a_1	–	–	576.3	0.01
15	b_2	–	–	591.4	0.00
16	a_2	–	–	680.0	0.00
17	b_2	912.5	0.32	918.3	0.62
18	a_1	1072.1	0.98	1067.3	1.00
19	b_2	–	–	1150.6	0.03
20	a_1	–	–	1363.0	0.07
21	b_2	1398.5	0.25	1414.1	0.28
22	a_1	1678.0	0.09	1707.0	0.13
23	a_1	2337.3	1.00	2418.6	0.79
24	b_2			2426.5	0.61

[a] Neon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the B3LYP/6-311++G(d,p)[29] level of theory. Band positions are unscaled. The assignment is tentative and is based on band positions and intensities.

2b. Thus, our experiments find that the UV irradiation of **3b** in neon at 3 K results in the stepwise loss of two iodine atoms to give **2b**, which at slightly longer wavelength irradiation ring-opens to **1b**.

p-Benzyne **2b** could be independently generated by irradiation (254 nm, neon, 3 K) of 2,3,5,6-tetrafluoroterephthaloyl diiodide (**5**). The photochemistry of the diiodide is quite complex, and it is not clear, whether **2b** is directly formed from **5** or the photodecarbonylation first yields **3b**, which in subsequent photochemical steps loses iodine atoms to give **4** and **2b**.



The assignment of **2b** was confirmed by (8/8)CASSCF calculations, which nicely reproduce the experimental IR spectrum (Figure 2, Table 3). The only major deviation is the splitting of the very strong b_{2u} symmetrical ν(C–F) stretching vibration into two components at 1516 and 1502 cm^{-1} in the experimental spectrum.

Table 3. IR spectroscopic data of singlet 1,4-didehydro-2,3,5,6-tetrafluorobenzene (**2b**).

Mode	Symmetry	$\tilde{\nu}_{exp}$[a] [cm^{-1}]	$I_{rel,exp}$[b]	$\tilde{\nu}_{calcd}$[c] [cm^{-1}]	$I_{rel,calcd}$
14	b_{1u}	–	–	677	0.04
15	a_g	–	–	690	0.00
16	b_{2u}	924.6	0.59	911	0.28
17	b_{3g}	–	–	1148	0.00
18	b_{1u}	1117.3	0.44	1151	0.26
19	b_{2u}	–	–	1154	0.03
20	a_g	–	–	1360	0.00
21	b_{1u}	1406.6	0.37	1421	0.15
22	b_{2u}	1501.7 1516.1	0.5 0.5	1499	1.00
23	a_g	–	–	1560	0.00
24	b_{3g}	–	–	1610	0.00

[a] Neon, 3 K. [b] Relative intensities based on the sum of the components of the strongest absorption (mode 22). [c] Calculated at the CASSCF(8,8)/cc-pVDZ level of theory. Band positions are scaled by a factor of 0.91. The assignment is tentative and is based on band positions and intensities.

UB3LYP/6-311++G(d,p) DFT calculations predict a near degeneracy of the lowest lying triplet and singlet states of **2b**, as do (8/8)CASSCF and CASPT2/cc-pVDZ ab initio calculations. The singlet is computed to be the ground state with $\Delta E_{ST} = -0.1$, -1.5, and -0.5 kcal mol^{-1}, respectively, at these levels of theory. The singlet ground state found for unsubstituted *p*-benzyne (**2a**)[14] results from the through-bond stabilization of the molecular orbital (MO), formed from the antisymmetrical combination of the nonbonding atomic orbitals (AOs), relative to the MO formed from the symmetrical combination.[26] However, the fluorine substituents in **2b** stabilize the MO formed from the symmetrical combination of the nonbonding AOs more than the MO formed from the antisymmetrical combination. Consequently, these two nonbonding MOs are much closer to being degenerate in fluorocarbon **2b** than in hydrocarbon **2a**, and this results in the magnitude of ΔE_{ST} being predicted to be considerably smaller in **2b** than in **2a**.

Since the calculated IR spectra for the singlet and triplet states of **2b** are virtually identical at both the UB3LYP and CASSCF levels of theory, we are not able to determine the ground state multiplicity from the IR data. Experimental identification of the ground state of **2b** will have to await our developing the capability to obtain EPR spectra at 3 K in neon matrices.

Experimental Section

Matrix isolation experiments were performed by standard techniques 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. Argon matrices for EPR spectroscopy were deposited on a sapphire rod at 15 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}. EPR spectra were measured with a Bruker Elexsys E500 spectrometer. Irradiations were carried out with a Gräntzel low-pressure mercury lamp (254 nm) and an Osram HBO 500 W/2 high-pressure mercury arc lamp in an Oriel housing with quartz optics and a dichroic mirror (260 – 320 nm). 1,4-Diiodotetrafluorobenzene was purchased from Aldrich and used as supplied. DFT and CASSCF calculations were performed with the Gaussian 98 suite of programs.[27] CASPT2 calculations were carried out with MOLCAS.[28]

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Terminal Borylene Complexes as a Source for the Borylene $B{-}N(SiMe_3)_2$: Alternative Synthesis and Structure of $[(OC)_5Cr{=}B{=}N(SiMe_3)_2]$**

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The generation of hypovalent borylenes $B{-}R$—the boron analogues to carbenes CR_2—usually requires drastic conditions: the classical method involves the reduction of boron trihalides at temperatures above 2000 °C,[1] and alternatively, the silylborylene $B{-}SiPh_3$ can be obtained photochemically at $-196\,^{\circ}C$ from $RB(SiPh_3)_2$ (R = Me, 2,4,6-$Me_3C_6H_2$ (Mes)) in hydrocarbon matrices.[2] The reductive[3] or photochemical[4] generation of species $B{-}R$ in condensed phase might be assumed from the nature of the corresponding trapping products. There is, however, no direct proof for the intermediacy of borylenes—in particular, the $MeBBr_2/2\,C_8K$ system as a source for $B{-}Me$ appears questionable.[5]

Already in 1973 borylene complexes were recognised to be a potentially useful source for borylenes in cases where gaseous species cannot be used.[1b] Since 1995 we have reported on both bridged[6] and terminal[7] borylene complexes of the type $[L_xM{-}B(R){-}ML_x]$ and $[L_xM{=}BR]$, respectively, thus demonstrating the possibility of stabilizing borylenes $B{-}R$ in the coordination sphere of a transition metal. Related species, however, showing boron in higher coordination number were also reported recently.[8] As the synthesis of borylene complexes is mainly restricted to salt elimination reactions,[6, 7, 8b] we began to investigate compounds of the type $[L_xM{=}BR]$ as possible sources for $B{-}R$ with borylene transfer reactions between different metal centers to provide an alternative synthetic route for this novel class of compounds.

In an initial experiment the photochemically induced transfer of the aminoborylene $BN(SiMe_3)_2$ from $[(OC)_5W{=}B{=}N(SiMe_3)_2]$ (**1**)[7] to $[Cr(CO)_6]$ was investigated, since the expected chromium–borylene complex $[(OC)_5Cr{=}B{=}N(SiMe_3)_2]$ (**2**) was already obtained by a different method and known to be stable under the chosen conditions.[7] Compound **1** was irradiated at $-30\,^{\circ}C$ in toluene in the presence of three equivalents of $[Cr(CO)_6]$. After 12 h

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