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p-Benzyne**

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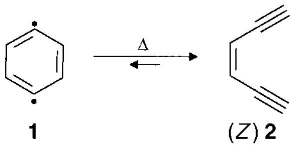
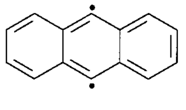
Dedicated to Professor Dr. Günther Maier
on the occasion of his 66th birthday

Since the discovery of the enediyne antibiotics there has been great interest in *p*-benzyne (1,4-didehydrobenzene, **1**) and its derivatives.[1–3] Compound **1** is formed as a reactive intermediate at very low stationary concentrations in the rearrangement of (*Z*)-3-hexene-1,5-diyne [(*Z*)-**2**],[4–6] and can be trapped in the gas phase with O_2 or NO.[7] Roth et al. determined the heat of formation of **1** from the kinetics of these trapping reactions to be 138.0 ± 1 kcal mol^{-1} (which means it is 8.5 kcal mol^{-1} less stable than (*Z*)-**2**), and the barrier toward ring opening to be 19.8 kcal mol^{-1}.[7]



1 (*Z*) **2**



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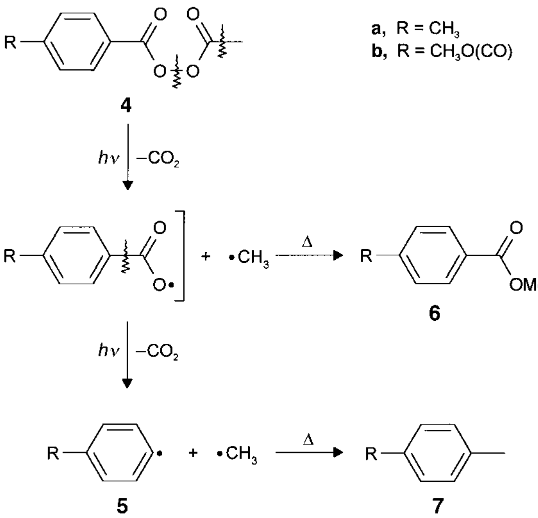
Although several attempts at the synthesis of **1** from *p*-substituted benzene derivatives are reported in the literature,[8, 9] the only derivative of **1** so far characterized spectroscopically, at low temperature, is 9,10-didehydroanthracene (**3**).[10] Squires et al. determined thermochemical data for **1** through collision-induced dissociation of the *p*-chlorophenyl anion in the gas phase in a quadrupole mass spectrometer.[11, 12] These data ($\Delta H_f^\circ = 137 \pm 3$ kcal mol^{-1}) are in excellent agreement with the values reported by Roth et al.[7] and with theoretical data from ab initio calculations at the CCSD(T)[13, 14] and CASSCF/CASPT2[15] levels of theory. Thus, both experiment and theory predict **1** to lie in an energy well sufficiently deep to permit, in principle, its isolation at low temperature. Here we report a matrix isolation and IR spectroscopic characterization of *p*-benzyne (**1**).

Acyl peroxides of type **4** were first used by Pacansky et al.[16, 17] for the matrix isolation of radicals, and were recently utilized for the generation of the phenyl radical[18] and the synthesis of *m*-benzyne.[17] Upon irradiation, **4** decomposes to an aryl radical **5**, CO_2, and a second radical, which in the case of acetyl peroxides is a methyl radical (Scheme 1). As long as the temperature of the matrix is kept low enough to prevent the diffusion of small molecules, the two radical fragments are separated by two CO_2 molecules, but at higher temperatures the radicals react rapidly to give **6** and **7**.



Scheme 1. Photolysis of **4a**, **b** in argon at 10 K.

Similarly, diacetylterephthaloyl diperoxide (**8**)[19] should yield **1**, CO_2, and methyl radicals (Scheme 2). Vacuum flash pyrolysis of **8** at temperatures between 300 and 600 °C and trapping of the products in argon at 10 K resulted in the formation of *Z* enediyne **2** and CO_2 as the main products, together with a small amount of dimethyl terephthalate (**6b**).

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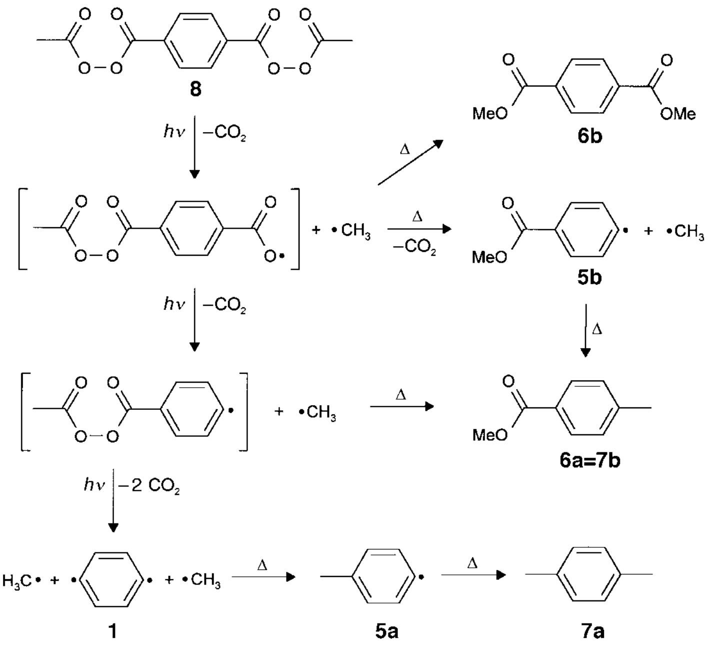


Scheme 2. Photolysis of **8** in argon at 10 K.

At higher pyrolysis temperatures (*Z*)-**2** is partially isomerized to (*E*)-**2**. No other products were observed, nor were IR absorption bands that could be attributed to **1**. This suggests that **1** is formed during pyrolysis of **8** but is not stable toward ring opening at the temperatures necessary for fragmentation of the peroxide. The fact that the Bergman rearrangement[4] is rapid under these conditions was readily demonstrated by vacuum flash pyrolysis of (*Z*)-[1,6-D_2]hex-3-en-1,5-diine at 300–500 °C, which resulted in an equilibrium mixture of the [1,6-D_2] and [3,4-D_2] isotopomers. Again, the *E* isomer was a secondary product formed only at temperatures above 800 °C.

The radicals expected to be formed upon photolysis of **8** are *p*-benzyne (**1**), the methyl radical, the *p*-tolyl radical (**5a**), and the 4-(methoxycarbonyl)phenyl radical (**5b**, Scheme 2). To obtain reference spectra of **5a**, **b** the photochemistry of acyl peroxides **4a**, **b**[19] was first investigated under matrix conditions.

Photolysis ($\lambda = 254$ nm, Scheme 1) of matrix-isolated acetyl 4-methylbenzoyl peroxide (**4a**) yielded CO_2, methyl *p*-toluate (**6a**), methyl radical, and a new species with strong IR absorption bands at 1450, 1029, 767, and 452 cm^{-1}. The two latter species disappeared when the matrix was annealed at 30 K, and *p*-xylene (**7a**) was formed. This thermal reaction and the similarity of the observed IR absorption bands to those of the phenyl radical[17] strongly suggest that the new species is the *p*-tolyl radical (**5a**).

Photolysis ($\lambda = 248$ nm) of acetyl 4-(methoxycarbonyl)benzoyl peroxide (**4b**) produced CO_2, dimethyl terephthalate (**6b**), methyl radical, and the 4-(methoxycarbonyl)phenyl radical (**5b**) with strong bands at 1438, 1372, and 739 cm^{-1}. Because of the strong carbonyl absorption of ester **6b** at 1740 cm^{-1} the carbonyl absorption of **5b** could not be clearly observed. When the matrix was annealed at 40 K the methyl radicals reacted with **5b** to produce methyl *p*-toluate (**7b** = **6a**).

The main products of photolysis ($\lambda = 254$ nm) of **8** were dimethyl terephthalate (**6b**) and CO_2 (Scheme 2). Other products were the methyl radical, radical **5b**, and small amounts of the *p*-tolyl radical (**5a**). Annealing of the matrix at 40 K reduced the number of these radicals. IR absorption bands of medium to low intensity at 1445, 980, 814, 725, and 691 cm^{-1} also disappeared when the matrix was warmed; however, it was not possible to assign these to any of the known compounds (Figure 1).

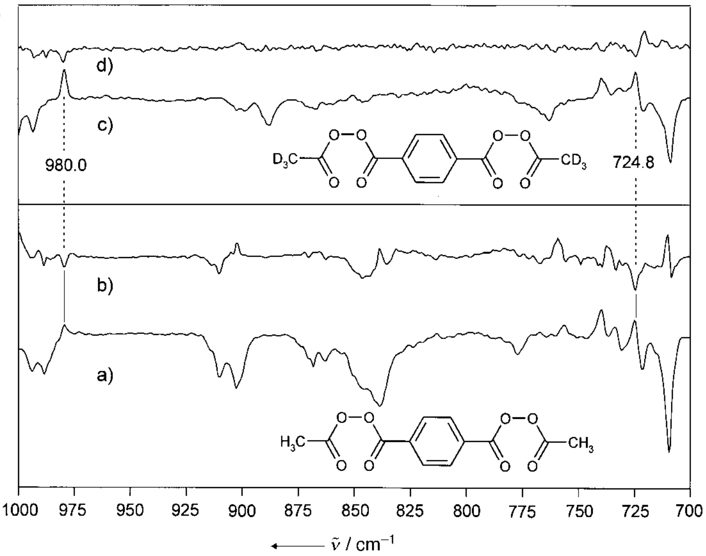
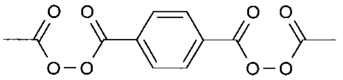
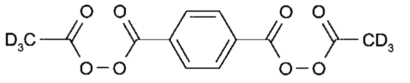


Figure 1. Difference IR absorption spectra after photolysis (254 nm, 10 K) of **8** (a) and [D_6]**8** (c) as well as spectra after subsequent annealing at 40 °C (b and d). After irradiation, no bands remain for the starting material, only those of the photolysis products are observed. Upon disappearance of the bands for the radicals and **1**, bands for unknown products appear.

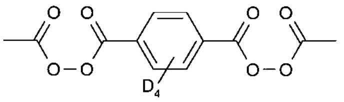
Irradiation of matrix-isolated [D_6]**8** (with perdeuterated acetyl groups) again resulted in formation of a set of IR absorption bands for a thermolabile species. The bands at 980 and 725 cm^{-1} were the only ones that did not exhibit isotopic shifts (Figure 1) and therefore cannot be associated with a compound that contains methyl groups. It is tempting to assign these vibrations to *p*-benzyne (**1**). To obtain a third isotopomer of **8** the benzene ring was perdeuterated to give [D_4]**8**. Photolysis of [D_4]**8** under the same conditions did not result in absorption bands at 980 and 725 cm^{-1}. Instead, a very weak absorption appeared at 767 cm^{-1}, which was tentatively assigned to [D_4]**1**.



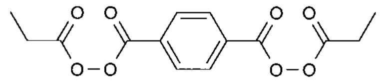
8



[D_6]**8**



[D_4]**8**

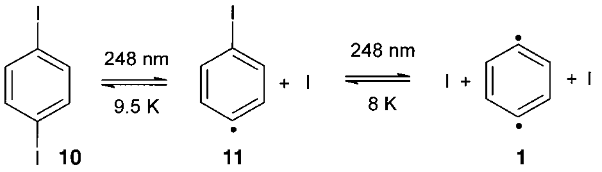


9

Irradiation ($\lambda = 254$ nm) of matrix-isolated dipropionyl terephthaloyl peroxide (**9**) produced CO_2, diethyl terephthalate, ethyl radicals,[20] and small amounts of the 4-(ethoxycarbonyl)phenyl radical, identified by the similarity of its IR spectrum to that of the methyl derivative **5b**. When the matrix was annealed, all the absorption bands assigned to the radicals decreased in intensity. Again, the bands at 980 and 725 cm^{-1} assigned to **1** became apparent during photolysis and disappeared after the matrix was annealed; therefore, the photochemistry of **9** is completely analogous to that of **8**.

Iodobenzenes are independent precursors of radicals and didehydrobenzenes. Indeed, irradiation of matrix-isolated 1,2-diiodobenzene produces *o*-benzyne.[21] Since the C–I bond energy is about 65 $kcal\,mol^{-1}$ and aromatic iodides begin to absorb UV light at 270 nm, 248- or 254-nm irradiation provides direct energetic access to radicals.[22] From our earlier work with the phenyl radical we concluded on the basis of photoorientation and polarization measurements that partial in-plane rotation of the ring is necessary to permit the formation from iodobenzene of radical pairs that do not immediately recombine.

Neon matrices (at 6 K) provide unique viscosity conditions that allow rupture of the first C–I bond and subsequent partial rotation of the ring, which in the photolysis of 1,4-diiodobenzene (**10**) leads to radical **11**.[23] A small fraction of **11** is converted into **1** by the subsequent absorption of photons. The observed set of IR absorption bands is exceedingly weak ($A \approx 10^{-3}$) but reproducible, and it corresponds well with results obtained from the photolysis of peroxides. These bands disappear from the spectra after annealing at about 8 K, while facile recombination of monoradical **11** with iodine atoms to form **10** is observed at 9.5 K. It is impossible to decide whether a small fraction of **10** originates from recombination of iodine atoms with **1**. The frequencies of the observed bands are very probably affected by the proximity of heavy iodine atoms, whereas the intensities may be distorted by nonlinearity in the detector response to such extremely weak signals.



To provide further support for this assignment, the vibrational spectrum of **1** was calculated at different levels of theory ranging from MP2 through MP4 to GVB, CCSD, CCSD(T), and density functional theory (DFT) with the B3LYP functional. Most of these descriptions turned out to be insufficient because of the multireference character of **1** and the necessity of providing a reasonable description of both static and dynamic electron correlation in **1**. Useful descriptions were obtained only at the CCSD(T)[24] and B3LYP[25, 26] levels of theory. Basis sets ranging from 6-31G(d,p) to 6-311+G(3df,3pd)[27] were utilized; in the first case the size of the basis set was limited by the available computer capacity. All calculations were carried out with the programs ACES[28] and GAUSSIAN 94.[29]

In Table 1, scaled B3LYP vibrational frequencies and corresponding IR intensities calculated for the harmonic approximation are compared with the observed IR bands. Calculations predict that the IR spectrum of **1** should be characterized by four relatively strong bands: the b_{3u}-symmetric ring torsion mode (boat conformation, out-of-plane) at 427 (entry 2), the b_{3u}-symmetric CH wagging mode at 728 (entry 7), the b_{1u}-symmetric ring deformation mode at 886 (entry 9), and the b_{1u}-symmetric C–C stretching and C-C-H bending mode at 1005 cm^{-1} (entry 12). In addition, four rather weak bands should appear at 1008 (entry 13, probably masked by entry 12), 1182 (entry 15), 1335 (entry 17), and 1384 cm^{-1} (entry 19). Of these bands, all but the weak bands 13 and 17 could be identified in the recorded IR spectra, with differences from the calculated frequencies of only 3 to at most 30 cm^{-1}. The agreement for the intense bands 12 and 7 is particularly satisfying.

Table 1. Calculated IR frequencies $\tilde{\nu}$ [cm^{-1}] and intensities I [$km\,mol^{-1}$] for **1** and [D_4]**1** at the UB3LYP/6-311+G(3d1f,3p1d) level.[a]

Entry	Sym.		**1**		$\tilde{\nu}_{exp.}$		[D_4]**1**	
		$\tilde{\nu}$	I	$\tilde{\nu}_{scaled}$[b]	for **10/8**	$\tilde{\nu}$	I	$\tilde{\nu}_{scaled}$[b]
1	a_u	414	0	396	–/–	360	0	345
2	b_{3u}	445	20	427	435 (w)/–	392	26	376
3	b_{3g}	577	0	554	–/–	557	0	535
4	b_{2g}	614	0	589	–/–	544	0	523
5	a_g	625	0	600	–/–	603	0	579
6	b_{1g}	731	0	702	–/–	568	0	546
7	b_{3u}	758	76	728	721 (s)/725 (s)	625	24	600
8	b_{2g}	915	0	876	–/–	760	0	729
9	b_{1u}	923	18	886	918 (w)/–	806	20	774 (767)
10	a_u	947	0	909	–/–	772	0	741
11	a_g	1021	0	980	–/–	849	0	815
12	b_{1u}	1047	17	1005	976 (w)/980 (s)	911	6	875
13	b_{2u}	1050	3	1008	–/–	798	0	766
14	a_g	1151	0	1105	–/–	990	0	950
15	b_{2u}	1231	5	1182	1207 (w)/–	1149	1	1103
16	b_{3g}	1279	0	1228	–/–	977	0	938
17	b_{2u}	1391	5	1335	1331 (w)/–	1361	<1	1306
18	a_g	1394	0	1338	–/–	1369	0	1315
19	b_{1u}	1442	2	1384	1403 (w)/–	1320	1	1267
20	b_{3g}	1633	0	1568	–/–	1614	0	1549
21	b_{1u}	3173	1	3046	–/–	2340	1	2246
22	b_{3g}	3175	0	3048	–/–	2339	0	2245
23	b_{2u}	3189	3	3061	–/–	2357	2	2263
24	a_g	3190	0	3062	–/–	2360	0	2266

[a] The experimentally determined values were obtained by irradiation of **10** (first value) and **8** (second value). Relative intensities are indicated in parentheses, as is the only detected band for [D_4]**1**. UB3LYP/6-311+G (3d1f, 3p1d) geometry: $R(\cdot CC) = 1.366$, $R(CC) = 1.419$, $R(\cdot C \cdot C) = 2.664$, $R(CH) = 1.082$ Å; $\measuredangle(C \cdot CC) = 125.8$, $\measuredangle(\cdot CCC) = 117.2$, $\measuredangle(\cdot CCH) = 123.4°$. [b] Scaling factor 0.96.

Upon perdeuteration of **1** the IR spectrum changes significantly (Table 1). Of the six bands calculated for [D_4]**1** in the region 700 to 1500 cm^{-1} with weak (entries 15, 17, and 19), strong (entries 9 and 12), or very strong intensity (entry 7), all but band 9 are considerably weaker than in the non-deuterated case. According to our calculations, it should be nearly impossible to observe modes 12, 15, 17 (also not observed for **1**), or 19. The band corresponding to the b_{3u}-symmetric motion (entry 7) should have a reduced intensity of 24 $km\,mol^{-1}$, but its frequency is shifted to 600 cm^{-1} (into a region in which the IR spectrum could not be recorded). The only detectable IR band of [D$_4$]**1** in the region 700 – 1500 cm^{-1} is predicted to fall at 774 cm^{-1} and should belong to the b_{1u}-symmetric mode 9 (masked in the case of **1** by IR absorption of other compounds, Table 1). This is in agreement with the fact that the only IR band observed for [D$_4$]**1** in the region 700 – 1500 cm^{-1} is at 767 cm^{-1}.

We were thus able to prepare in a matrix from two precursors a thermolabile species with IR absorption at 435, 721/725, 976/980, 1207, and 1403 cm^{-1}. These IR bands are in agreement with calculated frequencies for *p*-benzyne (**1**). The IR spectrum of [D$_4$]**1** is characterized by a single intense IR absorption (767 cm^{-1}) between 700 and 1500 cm^{-1}. The Bergman rearrangement is very rapid in the gas phase, and for this reason **1** is converted completely into ring-opened enediyne (*Z*)-**2**.

Experimental Section

General procedure for the synthesis of acyl peroxides: a solution of the acyl chloride (5 mmol for the synthesis of **4**, 10 mmol for **8**) in $CHCl_3$ (20 mL) and pyridine (12 mmol in 20 mL of $CHCl_3$) was added within one hour at − 10 °C to a suspension of the corresponding peroxy- or diperoxyacid (5 mmol) in $CHCl_3$ (100 mL) and stirred at this temperature for 2 h. The cold solution was filtered and washed with water (30 mL), 10% HCl (30 mL), and a saturated solution of $NaHCO_3$ (2 × 30 mL). The $CHCl_3$ solution was dried over Na_2SO_4, and solvent was removed in vacuo at 15 °C. The peroxides were obtained in 40 – 80% yield as crystalline material of generally high purity and, if necessary, purified by preparative HPLC (SiO_2, $CH_2Cl_2/CHCl_3$). Compounds **4a**,[30] **8**,[31] and **11**[31] were identified by comparison with literature data.

4b: M.p. 95 °C; IR (KBr): $\tilde{\nu} = 3106$ (vw), 2961 (vw), 1814 (w), 1814 (m), 1771 (vs), 1723 (vs), 1578 (w), 1503 (vw), 1440 (m), 1408 (m), 1368 (w), 1288 (vs), 1229 (s), 1154 (m), 1110 (s), 1034 (vs), 1010 (vs), 958 (vw), 894 (w), 870 (w), 836 (w), 823 (w), 787 (vw), 720 (vs), 668 (m), 643 (w), 584 cm^{-} (vw); UV/Vis (EtOH): λ_{max} (lgε) = 208 (3.45), 244 (4.12), 286 nm (3.16); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.09$ (dd, $J = 27.2$, 8.4 Hz, 4 H), 3.93 (s, 3 H), 2.26 (s, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 166.0$ (s, C=O), 165.8 (s, C=O), 162.2 (s, C=O), 135.1 (s), 129.9 (d), 129.7 (d), 129.3 (s), 52.6 (q), 16.6 (q); MS (70 eV): *m*/*z* (%): 238 (3) [M^+], 207 (4), 180 (13), 164 (10), 163 (100), 149 (36), 135 (13), 121 (8), 104 (14), 103 (10), 77 (9), 76 (17), 75 (9), 65 (11), 50 (15), 45 (7), 44 (11), 43 (27), 39 (6), 28 (6); HR-MS: calcd for $C_{11}H_{10}O_6$ 238.0477, found 238.0472.

8: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.11$ (s, 4 H), 2.27 (s, 6 H); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 164.9$, 160.8, 129.6, 129.0, 15.6; MS (70 eV): *m*/*z* (%): 282 (2) [M^+], 207 (87), 191 (5), 166 (15), 149 (100), 135 (9), 121 (16), 104 (53), 76 (31), 65 (20), 60 (17), 50 (32), 44 (60), 43 (95).

[D$_6$]8: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.11$ (s); ^{13}C NMR (200MHz, $CDCl_3$): $\delta = 164.9$, 160.8, 129.6, 129.0, 15.6; MS (70 eV): *m*/*z* (%): 288 (1) [M^+], 210 (61), 194 (16), 166 (15), 149 (100), 138 (7), 121 (12), 104 (39), 76 (22), 65 (17), 63 (12), 50 (24), 46 (85), 44 (57).

[D$_4$]8: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.27$ (s); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 164.9$, 160.8, 129.6, 129.0, 15.6; MS (70 eV) *m*/*z* (%): 286 (3) [M^+], 211 (100), 170 (16), 153 (58), 139 (11), 125 (13), 108 (54), 80 (28), 69 (17), 60 (16), 52 (27), 44 (57), 43 (66).

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