Matrix Isolation of 3,4-Benzocyclodeca-3,7,9-triene-1,5-diyne

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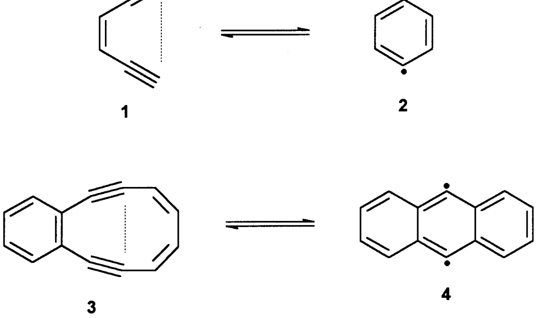
Received December 18, 1997

Keywords: Bergman cyclization / Matrix isolation / Ab initio calculations / Flash pyrolysis / [10]Annulenes

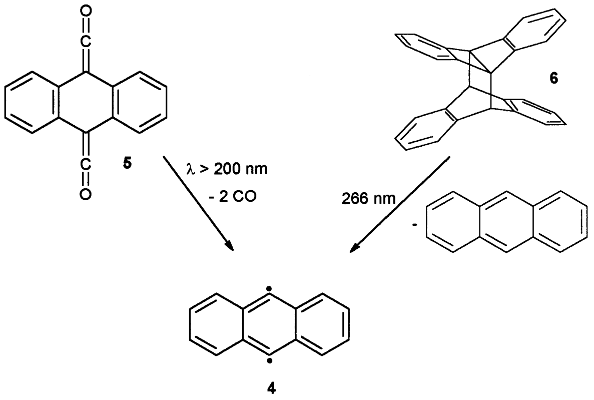
3,4-Benzocyclodeca-3,7,9-triene-1,5-diyne (3) has been synthesized from two different precursors and characterized by means of matrix-isolation spectroscopy. Energies, structures and IR spectra of the product, the intermediate 9,10-didehydroanthracene (4), and of the transition state of the Bergman cyclization 3 → 4 have been calculated at the B3LYP/6-31G* level of theory.

The Bergman cyclization of hexa-1,3-diyn-3-ene (**1**) and related enediynes to give diradicals such as *p*-benzyne (**2**) has attracted much attention during recent years.[1] The activation barrier for the cycloaromatization of **1** was determined as 28.2 kcal/mol and the reaction enthalpy as 8.5 kcal/mol.[2] For cyclic enediynes, it was shown that the thermal stability of the structure correlates with the distance between the two triple bonds. The distance between the two terminal carbon atoms was determined to be 4.12 Å in **1**, but only 3.01 Å in the 10-membered ring system **3**.[1] As a consequence, **1** is stable at room temperature, whereas early attempts by Masamune et al.[3] to synthesize **3** in solution failed, resulting only in the isolation of products derived from 9,10-didehydroanthracene (**4**).



The matrix isolation and spectroscopic characterization of dehydroanthracene **4** was published by Chapman et al. in 1976.[4] UV irradiation (λ > 200 nm) of bis(ketene) **5** in organic glasses produced a reactive intermediate with a series of UV/Vis absorptions in the range of 256−449 nm, attributable to **4**. Irradiation of **5** in solid argon resulted in the formation of CO and **4**, showing IR absorptions at 710 and 760 cm^{-1} (Scheme 1).

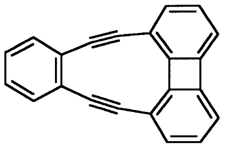
Scheme 1



Recently, Schottelius and Chen investigated the photochemistry of **6** by means of trapping experiments in solution as well as by laser-flash photolysis (LFP).[5] Two transient species were observed in acetonitrile, a fast transient with a lifetime of 2.6 μs ($\lambda_{max} \approx$ 295 nm), and a slow transient with a lifetime of 1.0 ms ($\lambda_{max} \approx$ 335 nm). Based on kinetic data, quenching studies, and ab initio calculations, these species were assigned as **4** and **3**, respectively. According to the ab initio calculations [CAS(6×6)/6-31G* and CASPT2N/6-31G*], **3** and **4** are close in energy. Since the LFP experiments revealed that **3** was formed from **4** in an exothermic reaction, and that at room temperature no reaction of **3** back to **4** was observed within the time scale of the experiment, it was concluded that **3** lies at least 3−4 kcal/mol below **4**. An estimated activation barrier of 12−13 kcal/mol for ring closure of **3** accounts for the lifetime being of the order of milliseconds.

The only derivative of **3** that has been described in literature is 3,4-benzocyclodeca-3,7,9-triene-1,5-diyne (**10**).[6] In

10, the rigid bridged biphenylene moiety prevents the Bergman cyclization and formation of the highly reactive diradical **4**, and thus this compound is thermally stable even at room temperature. The aromatic planar all-*cis*-[10]annulene (**11**) would require bond angles of 144° at the sp^2 carbon atoms, which accounts for the fact that in solution only the more stable non-planar conformers were detected by NMR spectroscopy.[7] We report herein on the matrix isolation and spectroscopic identification of **3**, synthesized from two independent precursors.



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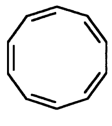


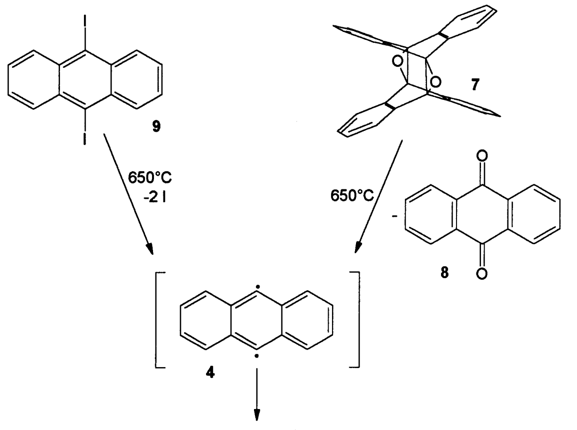
11

Results and Discussion

Synthesis and Characterization of 3

Flash-vacuum pyrolysis (FVP) of epoxide **7**[8] at 650°C with subsequent trapping in argon at 10 K resulted in the complete fragmentation of the starting material (Scheme 2). Anthraquinone was easily identified in the product mixture by comparison of the IR spectrum with that of authentic matrix-isolated material.[9] Strong IR absorptions not attributable to anthraquinone were additionally found at 1519, 758, and 712 cm^{-1}.

Scheme 2



The IR spectra of **3** and **4** were calculated at the B3LYP/6-31G* level of theory (Tables 1 and 2).[10][11] According to these calculations, singlet and triplet **4** should exhibit IR absorptions distinct from those of **3**. However, since the level of theory used in these calculations (B3LYP/6-31G*) is not adequate for describing a singlet diradical, the computed vibrational energies of singlet **4** are probably somewhat less reliable than the values for **3**. The insufficient consideration of correlation should have little effect on stretching and bending vibrations mainly localized at the terminal rings of the anthracene skeleton, but should be large for the in-plane (B_{1u}) deformation, particularly the vibration at 537 cm^{-1}. Despite this uncertainty, by comparison of the experimental with the calculated spectra, diradical **4** could clearly be ruled out as one of the products trapped in the matrix. On the other hand, there is a good agreement between a set of IR absorptions and the calculated spectrum of enediyne **3** (Table 1, Figure 1). Characteristic of the cyclodeca-1,3,7-triene-5,9-diyne moiety of **3** are the ring-deformation modes at 493 (in-plane), 512 (out-of-plane), and 712 cm^{-1} (out-of-plane), which are predicted by theory to within 4, 18 and 2 cm^{-1}, respectively.

Table 1. IR-spectroscopic data of compound **3**

Mode	$\tilde{\nu}$ [cm^{-1}][a] (exp.)	I_{rel}[b] (exp.)	$\tilde{\nu}$ [cm^{-1}][c] (calcd.)	I_{rel}[b] (calcd.)	Description[d]	Sym.
13	493	20	489	22	10-ring δ ip	A_1
14	512	13	530	10	10-ring δ oop	B_1
18	616	14	612	13	ring δ ip	B_2
20	712	53	710	60	10-ring δ oop	B_1
23	758	100	745	100	6-ring δ oop	B_1
34	1043	10	1035	7	ring ip	A_1
45	1464	19	1458	8	ring ip	B_2
47	1519	54	1516	43	ring ip	A_1
56	3040–3095	br.	3056	94	10-ring ν C–H	A_1
58			3082	13	6-ring ν C–H	A_1
59			3093	29	6-ring ν C–H	B_2
60			3098	41	6-ring ν C–H	A_1

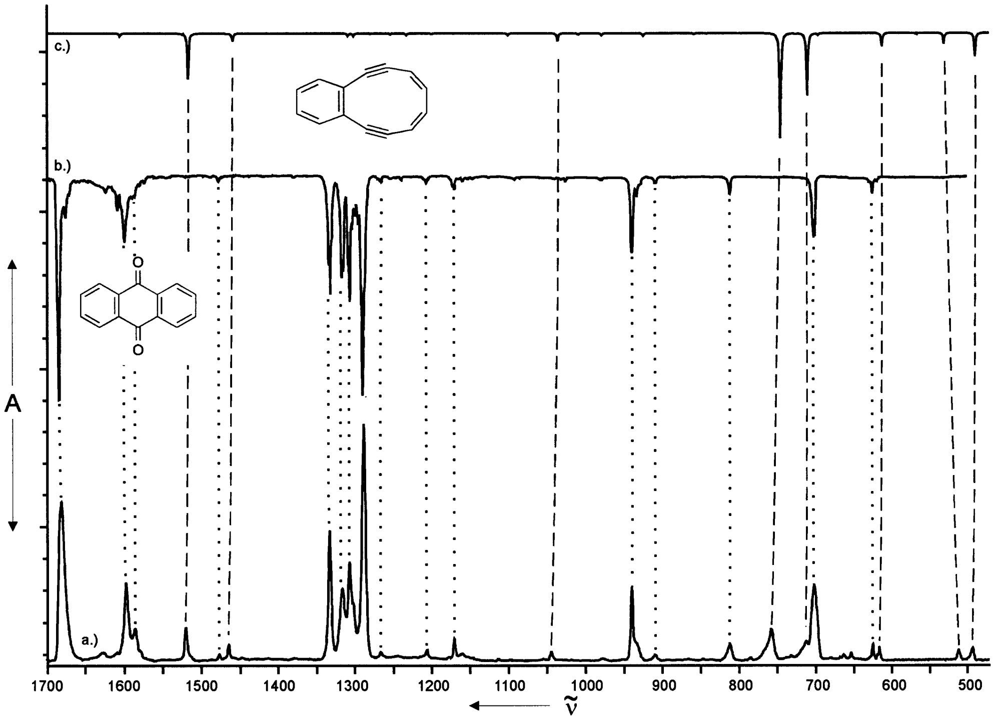
[a] Argon at 10 K. – [b] Relative intensities (based on the strongest absorption). – [c] Calculated at the B3LYP/6-31G* level of theory; IR bands with a relative intensity $I_{rel} > 5$ are listed; the assignment is tentative and is based on band positions and intensities. – [d] Approximate description.

Table 2. B3LYP/6-31G*-calculated frequencies of singlet and triplet **4**, scaled with 0.963[12][23]

	S-4			T-4	
Sym.	$\tilde{\nu}$ [cm^{-1}]	I [km/mol]	Sym.	$\tilde{\nu}$ [cm^{-1}]	I [km/mol]
B_{3u}	88.5	2.2	B_{3u}	83.0	2.0
B_{1u}	227.8	6.2	B_{1u}	218.3	2.5
B_{3u}	378.0	4.8	B_{3u}	376.0	3.7
B_{2u}	459.4	2.7	B_{3u}	483.6	1.6
B_{1u}	518.0	137.8	B_{2u}	587.8	4.5
B_{3u}	571.3	8.9	B_{1u}	630.2	1.7
B_{3u}	744.2	103.1	B_{3u}	734.5	102.7
B_{1u}	770.8	62.4	B_{2u}	991.6	6.4
B_{3u}	923.2	1.9	B_{1u}	1120.9	3.0
B_{2u}	948.4	2.6	B_{1u}	1211.0	3.8
B_{1u}	1066.0	60.5	B_{1u}	1276.7	0.8
B_{2u}	1072.7	5.5	B_{2u}	1319.8	8.1
B_{1u}	1242.6	2.1	B_{2u}	1428.0	1.8
B_{2u}	1317.7	0.9	B_{1u}	1439.5	2.8
B_{1u}	1454.9	1.0	B_{2u}	1522.4	3.8
B_{2u}	1584.0	8.4	B_{1u}	1616.5	5.7
B_{1u}	1618.6	9.0	B_{2u}	3075.8	2.7
B_{2u}	3086.1	25.3	B_{1u}	3086.4	49.8
B_{1u}	3102.1	18.8	B_{2u}	3093.9	68.0
B_{2u}	3105.3	33.5			

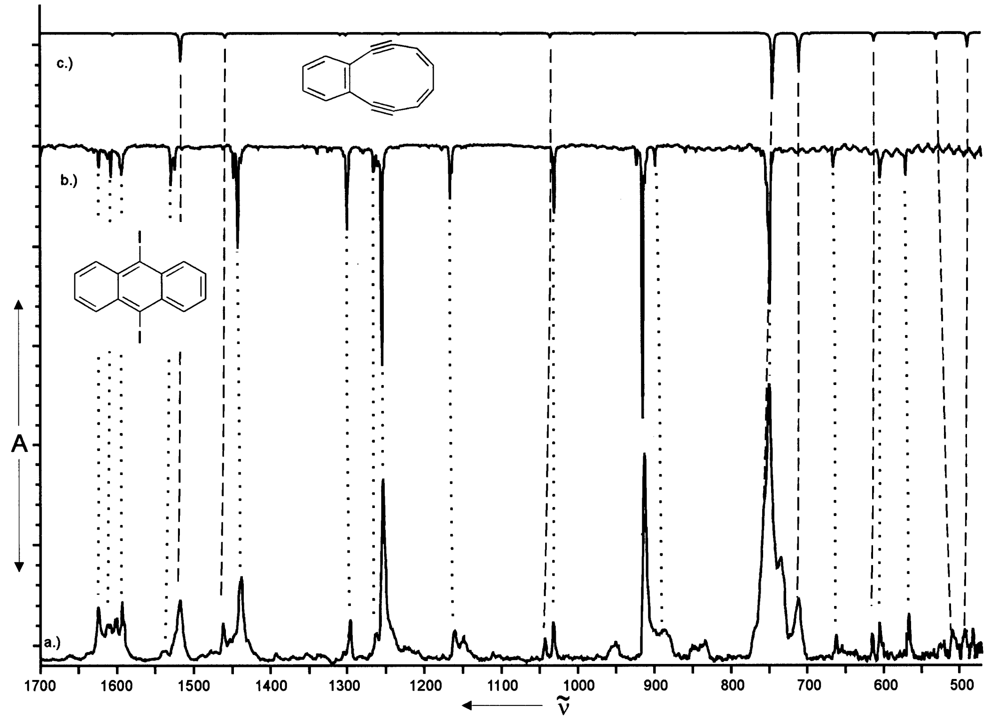
In order to further corroborate the characterization of **3**, 9,10-diiodoanthracene (**9**) was pyrolysed under similar conditions as an independent precursor. FVP of **9** at 650°C produced the same set of IR absorptions as assigned to **3**

Figure 1. (a) IR spectrum of the products of a flash-vacuum pyrolysis of **7** (Ar, 10 K); (b) IR spectrum of **8** (Ar, 10 K); (c) calculated spectrum of **3** (B3LYP/6-31G*; scaled)



(Figure 2). However, at this temperature the decomposition of **9** is still incomplete, and thus the yield of **3** is lower than that with **7** as the precursor (Scheme 2). Attempts to synthesize **3** or **4** by irradiation of matrix-isolated **9** failed, since **9** proved to be stable even towards prolonged UV irradiation. This is explained by the rapid in-cage recombination of the radical pair formed on photolysis of matrix-isolated **9**.

Figure 2. (a) IR spectrum of the products of a flash-vacuum pyrolysis of **9** (Ar, 10 K); (b) IR spectrum of **9** (Ar, 10 K); (c) calculated spectrum of **3** (B3LYP/6-31G*; scaled)



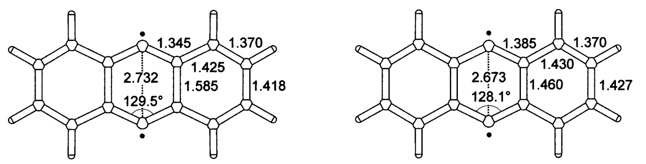
Calculation of the 4 → 3 Rearrangement

Species with considerable diradical character such as **4** are notoriously difficult to describe using single-reference ab initio and DFT methods. Unfortunately, adequate consideration of correlation in systems as large as **4** is prohibitive. We used the B3LYP hybrid functional[10][11] and a 6-31G* basis set for our theoretical treatment of the Bergman system **4** → **3**, because this method is known to perform well in predicting vibrational frequencies of closed-shell structures[12] (see above), and because it is superior to most ab initio perturbation methods (e.g. MP2) in treating correlation. Errors in calculated kinetic and particularly thermodynamic energies of the system **4** → **3** due to inadequate consideration of correlation are estimated by comparing theoretical (B3LYP/6-31G*) and experimental data of the parent system **2** → **1**. In the latter system, activation and reaction enthalpies were experimentally determined within error limits of only 0.5−1.0 kcal/mol ($\Delta H^{\ddagger} = 28.2 \pm 0.5$ kcal/mol, $\Delta H^{\circ} = 8.5 \pm 1.0$ kcal/mol[2][13][14]). Table 3 gives the relative energies of **1**, [**1** → **2**]‡, **2**, **3**, [**3** → **4**]‡ and **4**, while Figure 3 depicts the structures of **3**, [**3** → **4**]‡ and **4**. Stationary points were characterized by normal-coordinate analysis and the B3LYP energies include zero-point contributions.

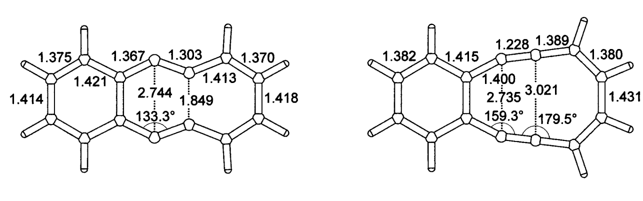
Table 3. Calculated relative energies of the Bergman cyclizations 1 → 2 and 3 → 4

	1	TS [1 → 2]‡	S-2	T-2
E_{rel} (B3LYP/6-31G* + ZPE)	0.0	30.6	20.9	7.8
E_{rel} (experimental)[2][13]	0.0	28.2	8.5	–
error	0.0	2.4	12.4	–
	3	TS [3 → 4]‡	S-4	T-4
E_{rel} (B3LYP/6-31G* + ZPE)	0.0	20.3	19.8	7.9
corrected relative energies	0.0	ca. 18	6−8	–

Figure 3. Calculated (B3LYP/6-31G*) structures of **3**, [**3** → **4**]‡ and **4**



4 singlet **4 triplet**

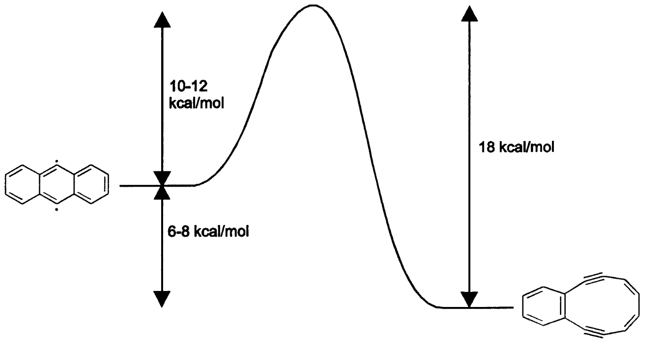


[4 → 3]‡
transition state

3

The computed activation barrier of **1** → **2** is in good agreement with the experimental value (error: 2.4 kcal/mol). Both the enediyne and the transition structure are almost pure closed-shell systems and are well described by DFT.[14] However, as expected, the error in the reaction enthalpy is large (12.4 kcal/mol) due to the high diradical character of **2**.[15] In a first approximation, we assume that the error is of similar magnitude in **2** and **4**, since the π systems of the annelated benzene rings in **4** are orthogonal with respect to the in-plane "radical" orbitals. On the basis of the above data we estimate enediyne **3** to be 6−8 kcal/mol more stable than diradical **4**. The theoretically determined activation enthalpy of only 10−12 kcal/mol and the exothermic reaction enthalpy for the retro-Bergman cyclization **4** → **3** are consistent with the exclusive formation of **3** as the product of the FVP experiments (Figure 4).

Figure 4. Calculated (B3LYP/6-31G*) corrected relative energies of the Bergman cyclization **3** → **4**



Based on the estimated activation barrier of 18 kcal/mol and an activation entropy of −3.7 cal mol^{-1} K^{-1} (B3LYP/6-31G*) for the Bergman cyclization leading back to the aromatic diradical **4**, the half-life of **3** should be of the order of a few seconds at 20°C. Thus, in accordance with the LFP experiments,[5] enediyne **3** is predicted to be unstable at room temperature.

This also explains the failure of the synthesis of **3** attempted by Masamune.[3] Under various reaction conditions anthracene was obtained as the principal product. The formation of 9,10-dideuterated anthracene in deuterated solvents clearly indicated the ring-closure to **4**, which was subsequently trapped by the solvent. In our hands, preparative-scale pyrolysis of **7** and work-up at room temperature did not produce **3** either, but rather anthracene and polymeric material.

This work was financially supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie.*

Experimental Section

Matrix Spectroscopy: Matrix-isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by co-deposition of a large excess of argon (Messer-Griesheim, 99.9999%, approximately 0.15 mmol/min) and the trapped species onto a cold CsI window. To obtain optically clear matrices, the cold window was maintained at 30 K during deposition, and the matrix was subsequently cooled to 10 K. − Pyrolyses were carried out in a quartz tube placed 3 cm in front of the cold window. In order to obtain short contact times, a heating zone of only 3 cm in length was used. A large excess of argon and the precursor were passed through the pyrolysis zone and the products were directly trapped on top of the cold window at 10 K. − Infrared spectra were recorded using a Bruker IFS-66 FT-IR spectrometer with a standard resolution of 1 cm^{-1} in the range 400−4000 cm^{-1}. Irradiations were carried out by means of Osram HBO 500 W/2 mercury high-pressure arc lamps in Oriel housings equipped with quartz optics or a Gräntzel mercury low-pressure lamp (254 nm). IR radiation from the arc lamp was absorbed by a 10-cm path of water. Schott cut-off filters were used (50% transmission at the wavelength specified) in combination with dichroic mirrors.

Tetradehydrodiepoxydianthracene **7**: A solution of 191.1 mg (1.136 mmol) of *m*-chloroperbenzoic acid in 100 ml of dichloromethane was added dropwise to a solution of 200 mg (0.568 mmol) of tetradehydrodianthracene[21] in 200 ml of dichloromethane. The mixture was stirred for 30 min at room temp. and then the solvent was evaporated. The yellowish residue was washed with dichloromethane and recrystallized from toluene. Yield: 161.4 g (74%), m.p. 312−314°C. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.13 (dd, *J* = 3.1, 3.1 Hz, 8 H, CH, arom.), 6.91 (dd, *J* = 3.1, 3.1 Hz, 8 H, CH, arom.). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 139.9 (C, arom.), 126.4 (CH, arom.), 122 (CH, arom.), 70.2 (C−O). − MS (70 eV); *m/z* (%): 385 (24), 384 [M^+] (76), 176 (100). − $C_{28}H_{16}O_2$ (384.13): calcd. C 95.42, H 4.58; found C 95.31, H 4.51. − IR (Ar, 10 K): $\tilde{\nu}$ = 456 (6), 483 (8), 603 (4), 626 (19), 654 (71), 704 (75), 727 (3), 743 (5), 753 (25), 784 (100), 865 (19), 905 (11), 913 (24), 935 (31), 950 (6), 1032 (4), 1139 (5), 1160 (3), 1217 (2), 1338 (14), 1348 (9), 1364 (12), 1369 (8), 1375 (7), 1425 (5), 1448 (27), 1452 (15), 1462 (20), 1467 (6), 1952 (5), 3064 (12), 3081 (6) cm^{-1} (rel. intensity).

9,10-Diiodoanthracene (**9**): Diiodide **9** was synthesized according to a procedure described by Duerr, Chung and Czarnik.[22] − IR (Ar, 10 K): $\tilde{\nu}$ = 572 (11), 606 (12), 667 (9), 750 (60), 754 (15), 900 (8), 913 (14), 916 (100), 924 (8), 1031 (25), 1165 (10), 1167 (20), 1255 (80), 1261 (8), 1266 (10), 1301 (31), 1439 (6), 1443 (38), 1449 (12), 1525 (9), 1529 (15), 1612 (5), 3044 (2), 3056 (3), 3079 (4), 3095 (8) cm^{-1} (rel. intensity).

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[9] IR bands of anthraquinone (Ar, 10 K): $\tilde{\nu}$ = 625 (7), 702 (33), 812 (8), 908 (3), 933 (4), 939 (33), 1159 (2), 1170 (6), 1207 (3), 1266 (2), 1289 (96), 1306 (43), 1316 (46), 1332 (56), 1477 (3), 1597 (28), 1681 (100), 1707 (1), 1725 (2), 1969 (1), 3079 (4) cm^{-1} (rel. intensity).

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[14] High level ab initio calculations[16][17][18][19] are in good agreement with experimental data ($\Delta H^{\neq}$ = 28.5 kcal/mol, $\Delta H°$ = 8.0 kcal/mol).[16]

[15] According to a CASSCF(8,8) calculation, the weightings of the two configurations of the bonding and antibonding combination of the two in-plane ("radical") π orbitals are 0.53 and 0.32. This is close to a pure diradical system in which both configurations would have an equal contribution.[20]

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