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Vibrational Spectrum of *m*-Benzyne: A Matrix Isolation and Computational Study[†]

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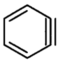
Abstract: *m*-Benzyne (**2**) was generated in low-temperature matrices and IR spectroscopically characterized from four different precursors. To assign the IR absorptions, the perdeuterated derivative **2**-d_4 was also investigated. By comparison with CCSD(T) calculations all vibrations between 200 and 2500 cm^{-1} with a predicted relative intensity >2% could be assigned. All experimental and theoretical results are in accordance with a biradicaloid structure for **2**, while there is no evidence for a bicyclic closed-shell structure. While benzyne **2** is stable under the conditions of matrix isolation at low temperature, flash vacuum pyrolysis at high temperatures or UV irradiation results in the rearrangement to *cis*-enediyne. A mechanism involving ring opening accompanied by hydrogen migration is proposed.

Introduction

The didehydrobenzenes **1**−**3** (benzynes) are important reactive intermediates that have also found multiple applications in synthesis.[1] The heat of formations $\Delta H_{f,298}$ of **1**−**3** were determined by Squires et al. to be 105.1 ± 3.2, 121.9 ± 3.1, and 137.8 ± 2.9 kcal/mol, respectively,[2] the latter value being in excellent agreement with the measurement of Roth and coworkers.[3] Among these species *m*-benzyne (**2**) is the least investigated derivative.[1a,4] The radical centers in **2** are coupled substantially by through-space and through-bond interactions[5] which lead to a singlet−triplet splitting of 21.0 ± 0.3 kcal/mol.[6] Thus, the reactivity of **2** is expected to reflect both biradicaloid and closed shell character.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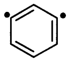
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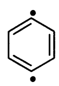
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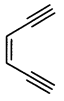
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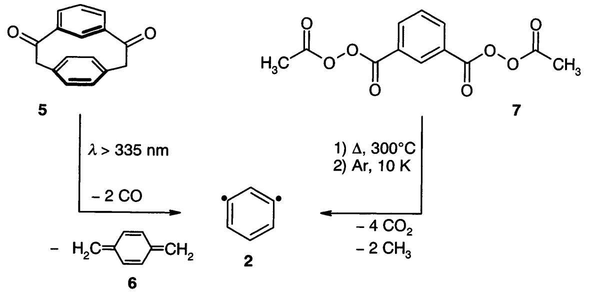
During the past years we developed several precursors of **2** and derivatives that are suitable for generating *m*-benzynes in low-temperature matrices (Scheme 1).[7] UV photolysis of matrix-isolated [2.2]metaparacyclophanediketone (**5**) leads to the formation of *p*-xylylene (**6**), CO, and **2**. Isophthaloyl diacetyl peroxide (**7**), on the other hand, is a thermal precursor that on

Scheme 1



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[*] To whom correspondence should be addressed.

[†] Dedicated to Prof. Waldemar Adam on the occasion of his 65th birthday.

[‡] Ruhr−Universität.

[§] Göteborg University.

(1) (a) Sander, W. *Acc. Chem. Res.* **1999**, *32*, 669. (b) Kauffman, T.; Wirthwein, R. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 20. (c) Hoffman, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967.

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(3) Roth, W. R.; Hopf, H.; Horn, C. *Chem. Ber.* **1994**, *127*, 1765.

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(5) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499.

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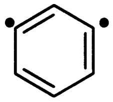
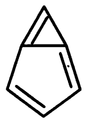
flash vacuum pyrolysis (FVP) at 300 °C yields methyl radicals, CO_2, and again **2**.[7d]

The structure of **2**—monocyclic biradical **2a** vs *anti*-Bredt olefin **2b**—has not yet been discussed in depth on the basis of experimental data.[8] On the basis of B3LYP calculations, Hess recently argued that our IR spectrum published in 1996 might well be interpreted in favor of a bicyclic structure (bicyclo[3.1.0]hexatriene (**2b**)).[4i,j,9] It should be emphasized, however, that Hess assigned several absorptions in the experimental spectrum leading to a pattern similar to that calculated at the B3LYP level for **2b**. Here we will show that this assignment is not backed by experimental evidence and that the theoretical level used by this author is not suitable for describing the biradicaloid structure **2a**.[9]


2a


2b

Another interesting point is the thermal or photochemical rearrangement of **2** to give *cis*-enediyne **4**.[10] This rearrangement requires a change of the CH connectivity and thus involves the migration of a hydrogen atom. The hydrogen migration in benzynes **1** and **2** to give **3** has recently been postulated by Zewail et al.[11] The three isomeric benzynes **1**−**3** were generated by femtosecond photolysis of 1,2-, 1,3-, and 1,4-dibromobenzene, respectively. Femtosecond time-resolved mass spectrometry revealed that both CBr bonds are broken within less than 100 fs. The benzyne molecules then decay with a lifetime of around 400 ps. From the similar lifetimes of all three benzynes it was concluded that **1** and **2** rearrange to **3**, which subsequently ring opens to **4**.[11] In this paper we show that **2** indeed rearranges to **4**, both thermally and photochemically; however, for this rearrangement the hydrogen migration in **2** to give **3** as the primary precursor of **4** is not necessary.

Results and Discussion

Matrix Isolation of *m*-Benzyne (2). Four different precursors of **2** were investigated in our laboratory: cyclophane **5** as a photochemical precursor and peroxide **7**, 1,3-diiodobenzene (**8**), and 1,3-dinitrobenzene (**9**) as thermal precursors. The photochemical precursor yields **2** by UV irradiation of **4** in solid argon or neon at temperatures between 3 and 12 K. Byproducts of this photolysis are CO and **6**, which are formed in the same matrix cage. Since this might result in secondary thermal reactions and in shifts of the IR absorptions, independent thermal sources of **2** were developed. FVP of the thermal precursors with subsequent trapping of the products in low-temperature matrices with a large excess of an inert gas should produce **2** and the byproducts in separate matrix cages and thus minimize unwanted intermolecular interactions.

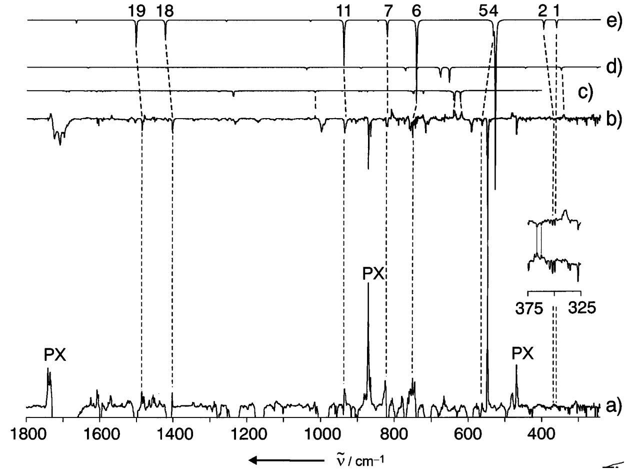
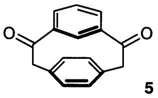


Figure 1. IR spectra showing the photochemical formation and decay of *m*-benzyne (**2**). (a) Difference spectrum showing the photochemistry of cyclophane (**5**) on 335 nm irradiation. Bands pointing upward are assigned to **2** and *p*-xylylene (**6**). (b) Difference spectrum showing the photochemistry of the same matrix after photolysis at 305 nm. (c) IR spectrum of an independently sythesized sample of *cis*-**4**. (d) BLYP/6-311G(d,p) calculated spectrum of *cis*-**4**. (e) Vibrational spectrum of **2** calculated at the CCSD-(T)/6-311G(2d,2p) level of theory.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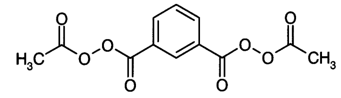
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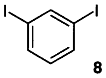
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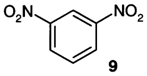
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Broad-band irradiation of **5**, matrix isolated in argon at 10 K, for several hours with $\lambda > 335$ nm (Hg high-pressure arc lamp in combination with a cutoff filter) results in the decrease of the IR absorptions of **5** and formation of **2**, CO, and **6**, as has been described before (Figure 1).[7d] If the monochromatic light of a low-pressure mercury arc lamp ($\lambda = 254$ nm) is used to irradiate **5**, additional absorptions at 1833, 1127, 693, and 677 cm^{-1} were observed which reach a maximum intensity after several hours of irradiation. These absorptions disappear on broad-band irradiation with $\lambda > 305$ nm. A strong IR absorption around 1830 cm^{-1} is characteristic of acyl radicals,[12] and it is thus tempting to assign the photolabile species the structure of biradical **10**. The 305 nm photolysis of mixtures of **5** and **10** yields the same products as the direct 305 nm photolysis of **5**; however, since the concentration of **10** (estimated from the IR intensities) is always low compared to that of **5**, it is not possible to directly follow the photochemistry of **10** (Scheme 2). Alternative intermediates that could explain the 1833 cm^{-1} absorption are the acylradicals **11** and **12**. Although these structures cannot be rigorously excluded, we expect them to be less stable than **10**.

The absorptions of **2** and **6** both disappear on prolonged irradiation with $\lambda > 305$ nm, which allows one to clearly assign

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(7) (a) Wenk, H. H.; Sander, W. *Chem. Eur. J.* **2001**, *7*, 1837. (b) Sander, W.; Exner, M. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2285. (c) Sander, W.; Bucher, G.; Wandel, H.; Kraka, E.; Cremer, D.; Sheldrick, W. S. *J. Am. Chem. Soc.* **1997**, *119*, 10660. (d) Marquardt, R.; Sander, W.; Kraka E. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 746. (e) Bucher, G.; Sander, W.; Kraka, E.; Cremer, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *35*, 746.

(8) Early trapping experiments have been interpreted in favor of a bicyclic structure bicyclo[3.1.0]hexatriene instead of a monocyclic biradical: (a) Washburn, W. N.; Zahler, R. *J. Am. Chem. Soc.* **1976**, *98*, 7827. (b) Washburn, W. N. *J. Am. Chem. Soc.* **1975**, *97*, 1615.

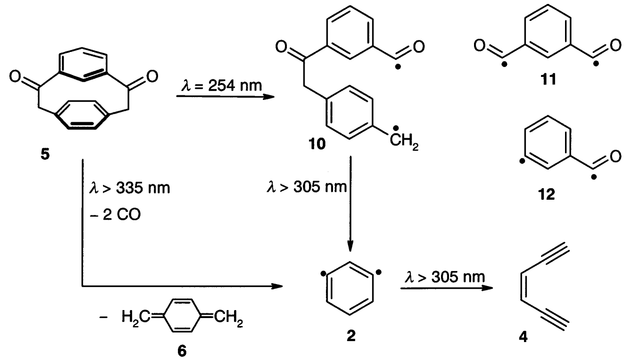
(9) For a detailed computational treatment of this point, see refs 4d,e.

(10) Sander, W.; Marquardt, R.; Bucher, G.; Wandel, H. *Pure Appl. Chem.* **1996**, *68*, 353.

(11) Diau, E. W. G.; Casanova, J.; Roberts, J. D.; Zewail, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 1376.

(12) See, for example: Neville, A. G.; Brown, C. E.; Rayner, D. M.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 1869.

Scheme 2



even weak IR absorptions of **2** (Figure 1). At least two products are formed; however, *cis*-**4** is the only product that could be unequivocally identified by comparison of the IR spectra with that of an independently synthesized sample. Since **6** in the absence of **2** is photochemically completely stable under the same irradiation conditions, the other photoproduct most likely is a reaction product between **2** and **6**. Due to its low yield, this product could not be identified. This result clearly demonstrates that **2** photochemically rearranges to **4** (Figure 1). The mechanism of this rearrangement is discussed below.

Aromatic diiodo compounds have been used both as thermal and photochemical precursors of biradicals.[13] Recently it was demonstrated that photolysis of 1,3-diiodo-2,4,5,6-tetrafluorobenzene, matrix isolated in neon at 3 K, produces 1,3-didehydro-2,4,5,6-tetrafluorobenzene (the perfluorinated *m*-benzyne) in reasonable yields via the corresponding monoradical.[7a] Interestingly, irradiation in argon at 10 K did not result in the loss of iodine atoms in amounts high enough to be detected by IR spectroscopy (traces of the radical could be observed by the more sensitive and selective EPR spectroscopy).

Photolysis of **8** in neon at 3 K produced a new set of bands that was assigned to the 3-iodo phenylradical **13** by comparison with the spectrum simulated at the UB3LYP/6-311G(d,p) level of theory. Prolonged irradiation at $\lambda = 254$ nm gave small amounts of **2**. In the IR spectrum the most intense absorption of **2** at 547 cm^{-1} was detected. Obviously, the loss of the second iodine atom in **13** is much less efficient than in the corresponding fluorinated radical. The influence of the matrix (neon vs argon), temperature, and fluorination on the product yields is not yet understood.

The FVP of **8** was investigated first by Fischer and Lossing in 1963 using mass spectrometry.[13] High temperatures (960 °C) were employed in these experiments, and only the enediynes *cis*-**4** and *trans*-**4** were detected in the mass spectra. Therefore, we reinvestigated the FVP of **8** carefully at various temperatures by trapping of the products of the FVP in solid argon at 10 K. The decomposition of **8** starts at 500 °C, producing small amounts of *cis*-**4** and *trans*-**4** as well as **13** and **2**. At 600 °C the decomposition of **8** is still not complete, but substantial amounts of all four products are detected. At temperatures above 650 °C decomposition of **8** is almost complete, but the yield of **2** is low, and apart from the enediynes additional fragmentation products were obtained. Figure 2 shows the spectrum of an argon matrix containing the products of the FVP of **8** at 600 °C. Annealing of the matrix up to 38 K does not result in significant changes in the IR spectrum, which indicates that molecular iodine is formed primarily in the gas phase or, more likely, during the deposition process of the matrix by recombination of iodine atoms (dark brown matrix).

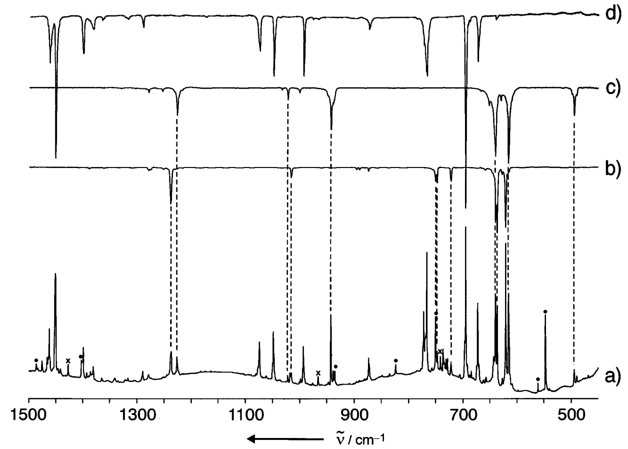
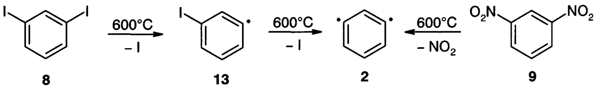


Figure 2. (a) IR spectrum of an argon matrix containing the FVP products of **8**. Bands denoted by circles belong to **2**; bands labeled by crosses are assigned to **13**. (b) IR spectrum of an independently sythesized sample of *cis*-**4**. (c) IR spectrum of an independently sythesized sample of *trans*-**4**. (d) IR spectrum of **8**.

Peroxide **7**, isolated in argon at 10 K, produces small amounts of **2** upon photolysis ($\lambda = 254$ nm), but a very complex product mixture is formed by in cage recombination reactions. FVP at 300 °C, however, allows the isolation of larger quantities of **2**. Other products that can be identified are CO_2 and methyl radicals. No enediynes **4** are formed under these conditions. Annealing the matrix at 35 K for several minutes causes all absorptions of **2** and CH_3 to decrease in intensity, which indicates reactions between the benzyne and CH_3 radicals as soon as the matrix is soft enough to allow diffusion of the trapped species. The disappearance of the IR bands of **2** during this annealing process again allows the assignment of even weak absorptions (see below).

Aromatic dinitro compounds have been reported to be suitable thermal precursors of biradicals.[14] FVP of **9** at 600 °C with subsequent trapping of the products in argon at 10 K produces **2** in low yields. All absorptions in the region 400−1600 cm^{-1} assigned to **2** by using the other precursors could also be detected. Only very small amounts of the enediynes are formed from this precursor, which may be due to the fact that the C−N bond is much stronger than the C−I bond, thus leaving less excess energy for fragmentation of **2** formed from **9** compared to **8**.



Ab Initio and DFT Calculations. The geometry and the vibrational spectrum of **2** were calculated at the CCSD(T) level of theory[15] using an augmented valence triple-ζ basis of the 6-311G(2d,2p) type.[16] Use of DFT turns out to be rather problematic in the case of **2**: Depending on the functional,

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(13) Fisher, I. P.; Lossing, F. P. *J. Am. Chem. Soc.* **1963**, *85*, 1018.

(14) (a) Grützmacher, H.-F.; Lohmann, J. *Liebigs Ann. Chem.* **1970**, *733*, 88. (b) Grützmacher, H.-F.; Lohmann, J. *Liebigs Ann. Chem.* **1975**, 2023.

(15) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

Table 1. IR Spectroscopic Data of *m*-Benzyne (**2**)

	argon, 10 K			BLYP 6-311++G(3df,3pd)			CCSD(T) 6-311G(2d,2p)				
vib[a]	$\tilde{\nu}$/cm^{-1}	I[b]	$\tilde{\nu}_i/\tilde{\nu}$[c]	$\tilde{\nu}$/cm^{-1}	I[b]	$\tilde{\nu}_i/\tilde{\nu}$[c]	$\tilde{\nu}$/cm^{-1}	I[b]	$\tilde{\nu}_i/\tilde{\nu}$[c]	sym	assignmt[d]
1	362			358	6	0.86	370	5	0.87	B1	oop ring deformn, sym (boat)
2	367			364	15	0.98	405	6	0.98	A1	ip ring deformn, sym
3				531	0	0.95	502	0	0.96	A2	
4	547	100	0.97	535	100	0.97	535	100	0.97	B2	ip ring deformn, asym
5	561	10	0.87	545	10	0.86	541	7	0.88	B1	oop ring deformn, asym (boat)
6	751	45	0.81	748	35	0.81	748	49	0.80	B1	C−H wag, 4 H, in phase
7	824	20	0.79	819	17	0.79	827	10	0.79	B1	C−H wag, 4 H, oop
8				818	0	0.80	831	0	0.79	A2	
9				824	2	0.97	852	1	0.97	A1	ip ring deformn, sym (breath)
10				938	0	0.82	933	0	0.81	B1	
11	936	25	0.83	914	22	0.82	944	27	0.82	B2	C−H bend, 2 H, in phase + C−C str
12				1029	1	0.79	1034	1	0.80	A1	
13				1075	0	0.74	1094	0	0.75	A1	
14				1091	0	0.91	1122	0	0.88	B2	
15				1207	1	0.78	1261	1	0.77	B2	
16				1271	0	0.86	1290	0	0.89	B2	
17				1364	0	0.98	1385	0	0.97	B2	
18	1402	15	0.93	1381	8	0.93	1425	12	0.93	A1	C−H bend, 2 H, in phase + C−C str. sym
19	1486	15	0.98	1468	8	0.97	1504	16	0.96	B2	C−H bend + C−C str
20				1680	0	0.98	1666	2	0.98	A1	
21				3064	26	0.74	3152	18	0.74	A1	C−H str, sym
22				3107	6	0.74	3192	7	0.74	A1	C−H str, asym
23				3112	11	0.74	3197	6	0.74	B2	C−H str + C−C str, sym
24				3124	4	0.75	3232	2	0.74	A1	C−H str, sym

[a] Number of the vibrational mode based on the CCSD(T) calculation. [b] Relative intensity based on the most intense absorption (100%). [c] Ratio of the frequencies of **2** vs **2**-d_4. [d] The assignment of experimental and calculated IR bands is based on comparison of band positions and relative intensities and is only tentative. oop = out of plane; ip = in plane.

strongly differing structures are obtained (the distances of the radical centers are as follows: CCSD(T)/6-311G(2d,2p), 2.101 Å; RBLYP/6-311++G(3df,3pd), 1.991 Å; RB3LYP/6-311++G-(3df,3pd), 1.606 Å).[9] The surprisingly good performance of BLYP[17a,b] in contrast to B3LYP[17c] to reproduce the structure and IR spectrum of *m*-benzyne[9] (and several derivatives thereof)[7b] has recently been explained by the self-interaction error of the B exchange functional, which mimics long-range (nondynamic) electron correlation, thus leading to fortuitous error cancellations for *m*-benzynes for the price of describing **2** as a bicyclic structure without any biradical character and an unusually long C1C3 bond.[18] The biradical character of **2** is not very large (19−32%), however,[4e,r] which has been explained by the strong σ-allylic interaction with the geminal C2H7-σ* antibonding orbital.[4e,5]

On the basis of the B3LYP results, it has been argued that **2** might exist in the form of the bicyclic structure **2b** rather than the biradical **2a**.[4i,j] However, reliable CCSD(T), CAS(8,8)-CISD+Q, and CASPT2 calculations refute this claim: The bicyclic structure does not exist; it is just a transient form of higher energy not occupying a stationary point on the potential energy surface.[9] Kraka and co-workers showed that apart from the quantum chemical evidence there is also chemical evidence that speaks against the existence of **2b**.[4d] In the current work, we now present spectroscopic evidence that clearly confirms that *m*-benzyne possesses the structure of biradical **2a** (Figure 3) rather than bicyclus **2b** contrary to claims made in the literature.

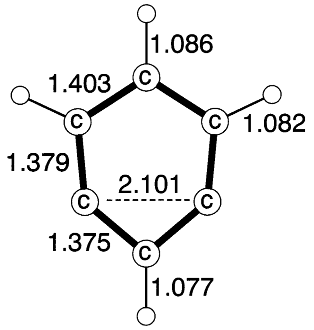

Figure 3. Structure of *m*-benzyne calculated at the CCSD(T)/6-311G-(2d,2p) level of theory.

Assignment of IR Vibrations and Implications on the Structure of 2. The assignment of IR bands to **2** in the experimental spectra is based on the following arguments: (i) The same set of IR absorptions is formed from four independent precursors **5** and **7**−**9** under different experimental conditions (matrix photolysis or FVP with subsequent matrix isolation). For each signal there is at least one spectrum in which the intensity of the respective absorption of **2a** is not obscured by partial overlap with other nearby signals of the precursor or byproducts. The highest yield of **2** was obtained by UV photolysis of **5**. (ii) The availability of four different precursors also allowed determination of the relative intensities of the IR absorptions with a reasonable accuracy. (iii) Photolysis of **2** produces **4**; thus all vibrations assigned to **2** decrease on subsequent photolysis. (iv) Annealing of a matrix containing **2** produced by FVP of **7** results in a decrease of all absorptions assigned to **2** and of the methyl radical, which is formed as a byproduct. This is presumably caused by the reaction of **2** with methyl radicals. (v) The assignment is further confirmed by

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(18) (a) Cremer, D. *Mol. Phys.* **2001**, *23*, 1899. (b) Polo, V.; Kraka, E.; Cremer, D. *Theor. Chem. Acc.* **2002**, *107*, 291. (c) Polo, V.; Gräfenstein, J.; Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **2002**, *352*, 469. (d) Cremer, D.; Filatov, M.; Polo, V.; Kraka, E.; Cremer, D. *Int. J. Mol. Sci.* **2002**, *3*, 604. (e) Polo, V.; Kraka, E.; Cremer, D. *Mol. Phys.* **2002**, *11*, 1771.

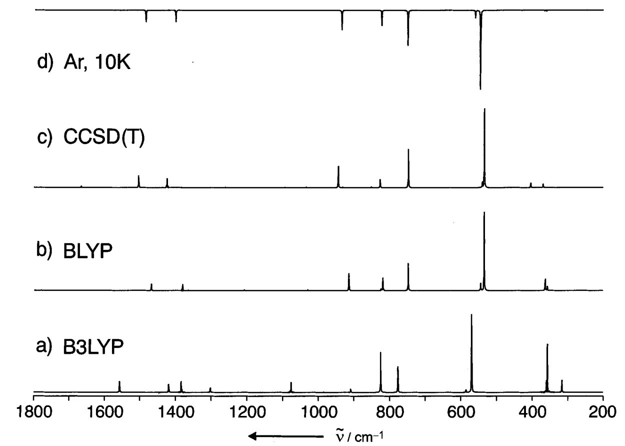

Figure 4. IR spectra of 2 calculated at the (a) B3LYP/6-311++G(3df,3pd), (b) BLYP/6-311++G(3df,3pd), and (c) CCSD(T)/6-311G(2d,2p) level of theory. (d) The experimental IR spectrum of **2** is shown schematically for comparison.

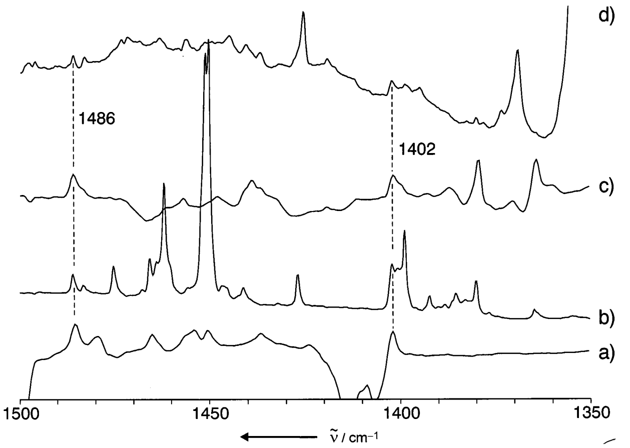

Figure 5. IR spectra of *m*-benzyne prepared from four different precursors. (a) Difference spectrum of **5** before and after 335 nm irradiation. Bands that form during photolysis are pointing upward. (b) IR spectrum of the FVP products of **8**. (c) Difference spectrum of the FVP products of **7** before and after annealing the matrix to 40 K. Bands pointing upward decrease in intensity upon annealing. (d) IR spectrum of the FVP products of **9**.

comparison of the experimental spectroscopic data with results from calculations. The frequencies, relative band intensities, and isotopic shifts on deuteriation (**2**-d_4) extracted from the experiments were compared to the data calculated at various levels of theory.

The frequencies and relative intensities of the IR absorptions that are unambiguously assigned to **2** are given in Table 1. This clearly reveals that the additional two peaks in the region 1200−1600 cm^{-1} of our original experimental spectrum[7d] that were assigned to **2** by Hess[4i] do not belong to **2**. The only bands that were not observed in our experiments are those predicted by the CCSD(T) calculation to be of zero or very low intensity ($\leq$2% of the strongest peak at 547 cm^{-1}).

In Figure 4, the B3LYP/6-311++G(3df,3pd) IR spectrum of **2b** is compared with the CCSD(T)/6-311G(2d,2p) and BLYP/6-311++G(3df,3pd) IR spectra of **2a**. If *m*-benzyne would adopt the bicyclic structure **2b**, it should possess the second strongest IR band at 344 cm^{-1} (Figure 4a) which involves 1,3 stretching and bending of the ring framework. However, the measured IR spectrum clearly reveals that there are just two IR bands below 500 cm^{-1} (362 and 367 cm^{-1}, Table 1, Figure 1), which due to their very low intensity can only tentatively be assigned to *m*-benzyne. This is in accordance with the prediction for the biradicaloid structure **2a** and disagrees with a bicyclic structure **2b**.

A characteristic feature of the IR spectrum of **2** is the strong absorption at 547 cm^{-1}, which exhibits only a small isotopic shift on deuteration (Table 1). CCSD(T)/6-311G(2d,2p) (535 cm^{-1}), CCSD(T)/6-31G(d,p) (545 cm^{-1}), and BLYP/6-311++G-(3df,3pd) (535 cm^{-1}) suggest this band to be due to the b_2-symmetrical in-plane ring-deformation mode no. 4. The weak absorption at 561 cm^{-1} can now be assigned to vibration no. 5 of **2** (Table 1, Figures 1 and 2). Signals at 751 (no. 6), 824 (no. 7), 936 (no. 11), 1402 (no. 18), and 1486 cm^{-1} (no. 19) are observed in the spectra of **2** produced from all four precursors (Figure 5). Band positions, relative intensities, and isotopic shifts nicely agree with the calculated data (Table 1). Other low-intensity peaks in the region between 700 and 1600 cm^{-1} are due to noise or byproducts and definitely do not belong to **2**.

A distinguishing feature between the IR spectra of **2a** and **2b** that was proposed by Hess[4i] is the number of intense bands in the region 1200−1600 cm^{-1} (Figures 4 and 5). For the bicyclic form four intense bands are predicted, while for the monocyclic biradical just two absorptions are calculated. Only two absorptions are found in the experimental spectrum of **2** (Table 1), again in accordance with the assignment of the biradicaloid structure **2a** rather than the bicyclic structure **2b** to our experimental data.

In agreement with all available facts, matrix-isolated **2** has the structure of biradical **2a**, while there is no evidence for the bicyclic structure **2b**. This is also in agreement with the conclusion from reliable high-level calculations (in contrast to B3LYP calculations) that only one minimum energy structure exists for *m*-benzyne with the equilibrium distance between the radical centers around 2.05 Å.[9]

Mechanism of the Rearrangement of Benzyne 2 to Enediyne 4. The pyrolysis of **2** to **4** can involve a variety of rearrangement and bond breaking processes. We considered five different reaction paths that are shown in Figure 6 (reaction and activation enthalpies in Figure 6 are all given relative to the enthalpy of **2**). The benzvalene mechanism (I) leads via an intermediate **14** possessing the benzvalene structure to biradical **3** which can open by a retro-Bergman cyclization to **4**. The latter process requires an activation energy of just 22.3 (activation enthalpy at 298 K: 20.2) kcal/mol,[19] which at 600 °C can be considered to be a relatively small barrier, and therefore it is not decisive for the feasibility of reaction path I. However, **14** does not represent a stationary point and rearranges via a capped annulene structure (C3 on top of a cyclopentadienylidene structure) to vinylidene **20**. The latter compound, however, can be formed from **2** in a more direct, less energy consuming manner (V in Figure 6; see below). Hence, path I can be excluded as a likely reaction path.

Also possible is a 1,2-carbon shift mechanism (II) which corresponds to an intramolecular retro-carbene rearrangement (see IIa) and leads to carbene **16**. Since carbene rearrangements are accompanied by the conversion of a single to a double bond, they are normally strongly exothermic and possess a low reaction barrier.[20] However, singlet carbene **16** is also a biradical

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[19] Gräfenstein, J.; Hjerpe, A. M.; Kraka, E.; Cremer, D. *J. Phys. Chem. A* **2000**, *104*, 1748. See also ref 3.

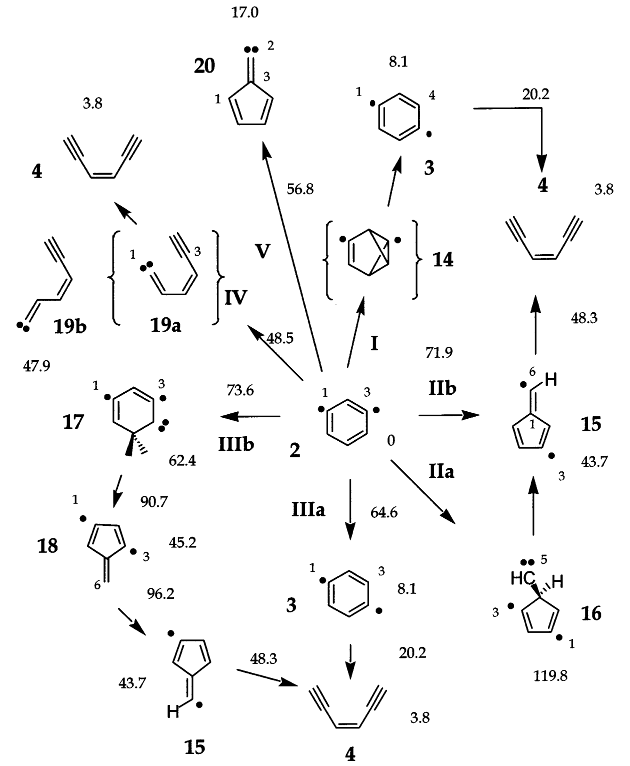

Figure 6. Reaction mechanism for the pyrolysis of **2**. Numbers in normal print represent B3LYP/6-31G(d,p) enthalpies at 298 K given in kilocalories per mole relative to the enthalpy of **2** where enthalpies connected with a reaction arrow correspond to activation enthalpies while enthalpies connected with a structure correspond to reaction enthalpies. Structures in parentheses were not found to occupy a stationary point. Small numbers indicate the numbering of the C atoms to follow rearrangements of the molecular framework.

and therefore represents a high-energy form (reaction enthalpy **2** → **16**: 119.8 kcal/mol), implying a reaction barrier of at least 120 kcal/mol.[21] Accordingly, reaction IIa will play no role even at 600 °C. However, there is the possibility that the formation of the highly unstable carbene **16** is avoided in mechanism IIb and biradicals such as **15** are generated. The relative energy of **15** is 44.8 kcal/mol (relative enthalpy: 43.7 kcal/mol) at the BS−UB3LYP/6-31G(d,p) level of theory. Ring opening of **15** to yield **4** was found to require 50.7 kcal/mol (activation enthalpy; 48.3 kcal/mol). However, the rearrangement from **2** to **15** is characterized by an activation energy of 74.9 kcal/mol (activation enthalpy: 71.9 kcal/mol); i.e., path IIb is not very likely even under pyrolysis conditions.

Reaction paths IIIa and IIIb belong to the [1,2]-hydrogen shift mechanism. Transfer of a H atom should lead to either **1** or **3**, where in the latter case again **4** can be formed via retro-Bergman cyclization. The [1,2]-H shift TS leading from **2** to **3** (reaction path IIIa) has a relative energy of 68.3 kcal/mol (activation enthalpy: 64.6 kcal/mol). Reaction IIIb, however, leads to an unusual carbene (**17**) that according to the calculated geometry possesses besides biradical also allene character thus increasing its ring strain. Reaction enthalpy and activation enthalpy are 62.4 and 73.6 kcal/mol, respectively. Subsequent rearrangement to biradical **18** (activation enthalpy: 90.7 kcal/mol) and the rearrangement from **18** to **15** (activation enthalpy: 96.2 kcal/mol) require too much energy to make path IIIb likely.

Mechanism IV involves a breaking of either C1C2 or C2C3, yielding vinylidene **19**, which by a [1,2]-H shift can rearrange to **4**. The investigation of IV revealed that the breaking of the C−C bond is already accompanied by a H shift so that **4** is formed in a one step mechanism requiring an activation energy of 51.9 kcal/mol (activation enthalpy: 48.5 kcal/mol). All attempts to find the all-cis vinylidene **19a** failed. Only the cis−trans form of **19b** could be located, which turned out to be 2 kcal/mol lower in energy (49.9 kcal/mol) than the TS of reaction path IV. Vinylidene **19b** rearranges with a small barrier (0.1 kcal/mol) to **4**, which after the inclusion of zero-point energy and thermal corrections vanishes; i.e., neither **19a** nor **19b** exist according to theory.

Reaction path V may be considered to start from a bicyclic form **2b**. Although it does not exist, it may be passed as a transient point during C1C2 bond cleavage accompanied by [1,2]-H shift. The product of this reaction, which possesses a reaction enthalpy of 17.0 kcal/mol and requires a relatively low activation enthalpy of 59.6 kcal/mol, is vinylidene **20**. Cleavage of the (formal) single bond C1C3 in **20** followed by a [1,5]-H shift can lead to **4**.

In summary, the most likely mechanism for the pyrolysis of **2** is reaction IV requiring an activation enthalpy of just 48.5 kcal/mol (B3LYP/6-31G(d,p)). Paths V (activation enthalpy: 59.6 kcal/mol), IIb (activation enthalpy: 71.9 kcal/mol), and IIIa (activation enthalpy: 64.6 kcal/mol) cannot be fully excluded but will not play an important role. All other paths considered in this work (Figure 6) are unlikely even at elevated temperatures.

Conclusions

m-Benzyne (**2**) was matrix isolated and spectroscopically characterized from four different precursors. A major problem for the generation of **2** in the gas phase is the rapid rearrangement to enediyne **4**. Only precursors that decompose at comparatively low temperatures allow production of **2** in quantities large enough for IR spectroscopic detection. The mechanism for this rearrangement, which requires ring opening accompanied by hydrogen migration, has been investigated by theoretical methods. The most reasonable reaction path starts with the ring opening of **2** to give vinylidene **19**. This vinylidene is highly labile and with a very low (or even absent) barrier rearranges to **4**. The rearrangement of **2** to **4** is also induced by UV irradiation; however, our experiments do not allow any distinction between a photochemical or a hot ground-state reaction.

The structure of **2**, biradicaloid **2a** vs bicyclic **2b**, was investigated both by spectroscopic means and by using high level ab initio calculations. The spectroscopic evidence collected in this work unequivocally confirms that **2** adopts the structure of biradical **2a**. This is in agreement with our first report and rejects all speculations that *m*-benzyne adopts the bicyclic structure **2b**. According to high-level calculations **2b** is not even a minimum on the C_6H_4 potential energy surface. However, there are considerable interactions between the formally unpaired electrons, and the energy required for reducing the distance between the radical centers from approximately 2 Å in the

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(21) The B3LYP activation enthalpy is 108.8 kcal/mol. However, due to the fact that the chemical processes of bond cleavage/bond formation in reaction **2** → **16** involve an odd number of electrons, the DFT description of the transition state suffers from a large self-interaction error, leading to a significant underestimation of the rection barrier.

equilibrium structure to 1.6 Å in the bicyclic structure is only a few kilocalories per mole.

Experimental Section

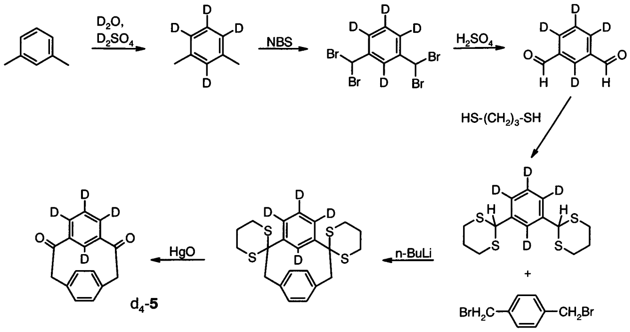
Matrix Isolation Spectroscopy. Matrix isolation experiments were performed by standard techniques with an APD DE-204SL and an APD DE-202 Displex closed cycle helium cryostat. Matrices were produced by co-deposition of the compound with a large excess of argon (Messer Griesheim, 99.9999%) on top of a cold CsI window with a rate of approximately 0.15 mmol/min. To obtain optically clear matrices, the spectroscopic window was retained at 30 K during deposition and subsequently cooled to 10 K. FVP experiments were carried out without additional heating of the spectroscopic window (temperature around 15 K).

Matrix infrared spectra were recorded by using a Bruker Equinox 55 FTIR spectrometer with a standard resolution of 0.5 cm^{-1} using a N_2(l) cooled MCT detector in the range of 500−4000 cm^{-1} and a Bruker IFS 66 FTIR spectrometer with the same resolution using a DTGS (FIR) detector in the range 250−500 cm^{-1}. Irradiations were carried out with use of Osram HBO 500 W/2 or Ushio USH-508SA mercury high-pressure arc lamps in Oriel housings equipped with quartz optics and dichroic mirrors (280−400 nm). IR irradiation from the lamps was absorbed by a 10-cm path of water. For broad-band irradiation Schott cutoff filters were used (50% transmission at the wavelength specified). For narrow-band irradiation a Gräntzel low-pressure mercury arc lamp (254 nm) was used.

Theoretical Methods. Three different levels of theory were applied. (i) First calculations were carried out with DFT using both the BLYP[17a,b] and the B3LYP[17c] functional and a variety of basis sets ranging from 6-31G(d,p) to 6-311G(d,p), 6-311G(2d,2p), and 6-311++G(3df,3pd).[16] Apart from this, Dunning's cc-pVDZ and cc-pVTZ basis sets [22] were used to verify the results. Geometries and the vibrational spectra were calculated to characterize stationary points and to determine IR spectra for comparison with experimental data. (ii) In the second step, restricted DFT (RDFT) results were checked for internal and external stability.[23] At large 1,3 distances (> 2.017 Å) the RB3LYP solution of **2a** turned out to become unstable, and a more stable broken symmetry (BS)-UB3LYP solution was found by mixing of HOMO and LUMO.[24] However, the BS−UDFT minimum of **2a** vanishes for larger basis sets, and even for the smaller basis sets it is separate by a barrier of just 0.03 kcal/mol from the more stable bicyclic form **2b**. The barrier vanishes when ZPE corrections are applied. Hence, for none of the B3LYP/basis set combinations used a true minimum was found for **2a**, which may be rationalized by the large S−T splitting of **2a** and strong T contamination of the UDFT description of **2a**. (iii) In the third step, geometry and the vibrational spectrum were calculated at the CCSD(T) level of theory[15] using the 6-311G(2d,2p) basis set.

Calculations were performed with Gaussian 98,[25] COLOGNE2000,[26] and a local version of the ACES II program.[27]

General Procedure. The [2.2]*m*,*p*-cyclophane **5** and its perdeuterated isotopomer **5**-d_4 were synthesized according to a modified procedure by Boekelheide et al.[28]



All solvents were distilled and dried before use. Column chromatography was carried out on ICN silica 32−63 (60 Å), preparative thin-layer chromatography on Merck precoated PLC plates (silica gel 60, F_{254}, 2 mm). NMR spectra were recorded on a Bruker DPX 200 or on a Bruker DRX 400; chemical shifts are given relative to TMS: d = doublet, t = triplet, and m = multiplet. Infrared spectra were recorded on a Perkin-Elmer 841 IR spectrometer in the range of 600−4000 cm^{-1} or FT-IR Bruker Equinox 55 and FT-IR Bruker IFS 66 in the range of 250−4000 cm^{-1}. MS data were obtained on a Varian MAT CH 5 and for high resolution on a VG AutoSpec at 70 e.V.

3,5-Bis(dibromomethyl)tetradeuteriobenzene. A mixture of tetradeutero-*m*-xylene (5.5 g, 50.0 mmol), NBS (*N*-bromosuccinimide) (53.4 g, 300.0 mmol), and AIBN (α,α′-azoisobutyronitrile) (0.5 g, 3.0 mmol) in CCl_4 (645 mL) was heated under reflux for 12 h and the succinimide filtered off. After removal of the solvent, the product crystallized in yellowish needles (17.5 g, 41.1 mmol, 86%): mp 93−94 °C; IR (cm^{-1}) 3005, 2365, 2336, 2285, 1721, 1428, 1371, 1224, 1213, 1195, 1146, 1054, 988, 976, 934, 842, 824, 808, 777, 716, 655, 610; ^{1}H NMR (200 MHz, $CDCl_3$) δ_H 6.63; ^{13}C NMR (50.33 MHz, $CDCl_3$) δ_C 142.14, 129.01, 39.55; MS (EI, 70 eV) (*m*/*z*, %) 429 (2.3) [M$^+$], 427 (8.8), 425 (14.4), 423 (10.2), 421 (2.8), 349 (29.4), 347 (91.8), 345 (100), 343 (37.9), 268 (27.5), 266 (56.6), 265 (30.5), 187 (9.8), 186 (14.5), 185 (13.4), 133 (28.2), 106 (65.5), 105 (40.4), 78 (20.7), 77 (21.8), 53 (53.1), 52 (26.5), 51 (26.1). Calcd: 425.738 800. Obsd: 425.741 309.

2,4,5,6-Tetradeuterioisophthalaldehyde. A 20.6 g amount of 3,5-bis(dibromomethyl)tetradeuteirobenzene (48.0 mmol) was added to 150 mL of H_2SO_4 (96%) at 110 °C. The bromine formed during the reaction was removed by a flow of argon. The reaction mixture was poured on crushed ice (1000 mL). The brownish solid precipitate was filtered off and dissolved in TBME (150 mL). The liquid layer was extracted with TBME (5 × 150 mL), neutralized, dried over $MgSO_4$, and evaporated. The residue was purified chromatographically (silica gel; CH_2Cl_2) to furnish 3.1 g (22.3 mmol, 46.4%) of a light yellow solid: mp 86−87 °C; IR (cm^{-1}) 3362, 2864, 1699, 1573, 1419, 1404, 1372, 1357, 1312, 1239, 1218, 1040, 1000, 935, 839, 777, 719, 650, 633; ^{1}H NMR (200 MHz, $CDCl_3$) δ_H 10.09; ^{13}C NMR (50.33 MHz, $CDCl_3$) δ_C 190.97, 136.83, 129.65; MS (EI, 70 eV) (*m*/*z*, %) 138 (76.7) [M$^+$], 137 (100), 136 (33.4), 109 (50.1), 108 (23.3), 81 (35.5), 80 (23.1), 78 (11.0), 54 (18.6), 53 (31.8), 52 (25.9), 51 (14.4), 29 (8.0). Calcd: 138.061 887. Obsd: 138.061 800.

Bis(1,3-propanedithioacetal) of 2,4,5,6-Tetra-deuterioisophthalaldehyde. A 3.9 g (28.0 mmol) amount of 2,4,5,6-tetradeuterioisophthalaldehyde was dissolved in 70 mL of acetic acid (99−100%). A 1.4 mL aliquot (5.3 mmol) of BF_3-Et_2O (45%) and 7.1 mL of propane-1,3-dithiol (44.4 mmol) were added dropwise under stirring at room

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temperature. After the mixture was stirred for another 11 days, the colorless precipitate was filtered off and dried in vacuo (7.48 g, 23.5 mmol, 84.2%): mp 126−127 °C; IR (cm^{-1}) 2934, 2899, 2826, 1737, 1579, 1423, 1381, 1342, 1276, 1252, 1224, 1184, 1116, 999, 949, 910, 873, 840, 808, 793, 742, 730, 693, 674, 650, 605; ^{1}H NMR (400 MHz, CDCl$_3$) δ_H 5.14 (s), 3.06−2.98 (m), 2.90−2.85 (m), 2.17−2.10 (m), 1.96−1.85 (m); ^{13}C NMR (100.66 MHz, CDCl$_3$) δ_C 139.98, 128.88, 51.09, 31.96, 25.05; MS (EI, 70 eV) (*m*/*z*, %) 318 (100) [M$^+$], 317 (50.0), 245 (15.4), 244 (65.5), 243 (36.2), 211 (15.7), 210 (15.4), 170 (53.6), 169 (53.9), 168 (15.9), 157 (16.5), 139 (12.6), 138 (13.4), 125 (12.6), 119 (15.2), 106 (91.7), 105 (31.8), 74 (39.8), 73 (31.7), 58 (15.2), 46 (21.0), 45 (41.2), 40 (22.0). Calcd: 318.054 245. Obsd: 318.053 200.

4,5,6,8-Tetradeuterio[2.2]metaparacyclophanebis(1,3-propanedithioketal). A 10 mL aliquot of a solution of *n*-butyllithium in hexane (1.6 N) was added under argon to a cooled (-32 °C) solution of 2,4,5,6-tetradeuterioisophthalaldehydebis(1,3-propanedithioacetal) (1.60 g, 5 mmol) in dry THF (250 mL), stirred for 1.5 h at the same temperature, and then pumped into a cooled (−32 °C) dropping funnel with an excess pressure of argon. This reddish brown solution of the dianion (−32 °C) and a solution of α,α′-dibromo-*p*-xylene (1.32 g, 5 mmol) in THF (250 mL, room temperature) were simultaneously added under high dilution conditions over a period of 6 h to refluxing THF (1000 mL). After removal of the solvent, the residue was absorbed on silica gel and separated from polymeric materials by eluation with CH$_2$Cl$_2$. Colorless crystals were obtained by using thin layer column chromatography (silica gel, CH$_2$Cl$_2$) (1.0 g, 2.5 mmol, 49%): DP > 220 °C; IR (cm^{-1}) 3035, 2902, 2352, 1882, 1725, 1593, 1501, 1424, 1357, 1327, 1275, 1243, 1200, 1117, 991, 934, 923, 904, 850, 835, 816, 798, 748, 729, 679, 665, 645, 617; ^{1}H NMR (400 MHz, CDCl$_3$) δ_H 7.32, 5.84, 3.46 (d), 2.75 (d), 2.89−2.37 (m), 1.97−1.85 (m); ^{13}C NMR (100.66 MHz, CDCl$_3$) δ_C 140.66, 134.55, 129.15, 128.62, 60.26, 53.55, 28.95, 27.44, 24.99; MS (EI, 70 eV) (*m*/*z*, %) 420 (29.4) [M$^+$], 419 (12.4), 318 (19.2), 317 (30.5), 316 (100.0), 315 (76.6), 314 (21.3), 283 (12.8), 242 (32.3), 241 (15.9), 168 (41.9), 167 (22.1), 158 (21.7), 149 (10.1), 124 (32.9), 123 (14.8), 121 (16.4), 120 (11.5), 86 (36.2), 84 (61.2), 49 (12.0), 47 (14.7), 41 (10.5), 36 (14.9). Calcd: 420.101 195. Obsd: 420.101 500.

4,5,6,8-Tetradeuterio[2.2]metaparacyclophane-2,9-dione-d4 (5). A solution of 4,5,6,8-tetradeuterio[2.2]*m*,*p*-cyclophanebis(1,3-propanedithioketal) (1.4 g, 3.4 mmol) in THF (50 mL) was added dropwise to a stirred slurry of 2.2 g (10.2 mmol) of mercury(II)oxide and 2.9 mL (10.3 mmol) of BF$_3$-Et$_2$O (45%) in THF/15% (25 mL) water at room temperature. The mixture was stirred for another 7.5 h at 40 °C after the complete addition. The cooled mixture was filtered off (Na$_2$SO$_4$, Celite, sand, silica gel) at room temperature and dried over MgSO$_4$. After removal of the solvent the cyclophane was purified by thin-layer chromatography (silica gel, CH$_2$Cl$_2$) to yield pale yellowish crystals (90 mg, 0.4 mmol, 11.0%): IR (10 K, cm^{-1}) 3032, 3016, 1889, 1709, 1691, 1570, 1541, 1505, 1413, 1405, 1371, 1338, 1315, 1287, 1273, 1216, 1137, 1103, 1022, 989, 939, 929, 904, 871, 854, 837, 830, 823, 812, 799, 788, 768, 759, 746, 732, 679, 668, 590, 587, 555, 490, 480, 422, 370, 294; ^{1}H NMR (200 MHz, CDCl$_3$) δ_H 7.04, 3.90; ^{13}C NMR (50.33 MHz, CDCl$_3$) δ_C 202.9, 141.02, 136.02, 132.60, 127.60, 52.57; MS (EI, 70 eV) (*m*/*z*, %) 240 (59.8) [M$^+$], 239 (26.5), 184 (36.6), 183 (22.2), 108 (100.0), 107 (46.6), 104 (11.6), 80 (78.9), 79 (36.4), 78 (14.6), 77 (12.6), 52 (23.0), 51 (11.5). Calcd: 240.108 837. Obsd: 240.110 300.

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Supporting Information Available: Figures 1S−6S detailing IR spectra of argon matrices at 10 K containing *m*-benzyne generated from three different precursors in the ranges 500−700, 700−900, 900−1100, 1100−1300, 1300−1500, and 1500−1650 cm^{-1} (PDF).This material is available free of charge via the Internet at http://pubs.acs.org.

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