

# 5-Fluoro- and 5-methyl-1,3-didehydrobenzene—a matrix isolation study

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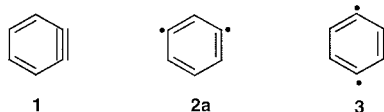
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The UV photolysis of [2.2]metaparacyclophanediones **4b** and **4c** leads to  $\alpha$ -cleavage and formation of CO, *p*-xylylene **5**, and *m*-benzenes **2b** and **c** with a fluorine or methyl substituent in the 5-position, respectively. The IR spectra of **2b** and **2c** were assigned by comparison with that of the parent *m*-benzynes **2a** and with spectra calculated at the BLYP/6-311G(d,p) level of theory. Both band positions and intensities of the experimental spectra are in excellent agreement with the DFT calculations. This method thus provides a reliable tool for the investigation of ground state properties of *m*-benzenes. The benzenes **2** exhibit a very strong IR absorption at  $545 \pm 2 \text{ cm}^{-1}$  which is almost not affected by the substituents and therefore can be used to identify *m*-benzenes in product mixtures.

## Introduction

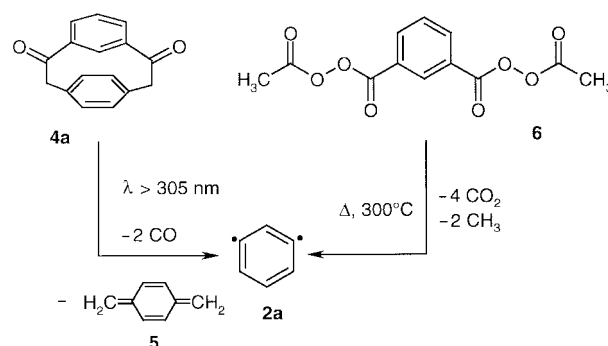
Dehydrobenzenes **1–3** are highly reactive intermediates of importance in organic synthesis<sup>1</sup> and to the biological activity of natural products<sup>2</sup> and have been investigated by trapping studies, gas phase spectroscopy, matrix isolation techniques and numerous theoretical methods.<sup>3,4</sup> The understanding of reaction mechanisms involving arynes as reactive intermediates has profited enormously by the accurate determination of the thermochemical properties of these species, including the singlet–triplet splittings ( $\Delta E_{\text{ST}}$ ), published by Robert Squires and co-workers.<sup>5–12</sup>



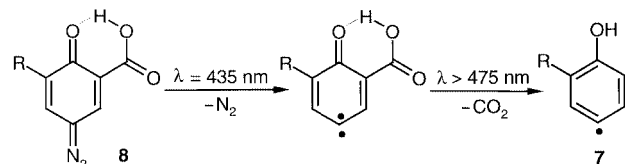
The properties of the benzenes **1–3** are determined by the amount of through bond and through space interaction of the in-plane  $\sigma$ -orbitals at the radical centers. While *o*-benzyne **1** is best described as a closed-shell molecule with  $\Delta E_{\text{ST}} = 37.5 \pm 0.3 \text{ kcal mol}^{-1}$ , *p*-benzyne **3** is a diradical with weakly coupled radical centers and a singlet–triplet splitting of only  $3.8 \pm 0.4 \text{ kcal mol}^{-1}$ . *m*-Benzyne **2a** shows intermediate properties with  $\Delta E_{\text{ST}} = 21.0 \pm 0.3 \text{ kcal mol}^{-1}$  and a heat of formation of  $121.9 \pm 3.1 \text{ kcal mol}^{-1}$ , half way between that of **1** ( $105.9 \pm 3.3 \text{ kcal mol}^{-1}$ ) and **3** ( $137.8 \pm 2.9 \text{ kcal mol}^{-1}$ ).<sup>12</sup> The stabilizing through-space interaction between the radical centers in **2a** is increased by a strong distortion of the benzene hexagon which reduces the distance between the radical centers from 2.4 Å (hexagon) to about 2.14 Å (CCSD(T) calculation)<sup>13</sup> and leads to the large singlet–triplet splitting. Consequently, the gas phase reactivity of a derivative of **2** resembles both that of the phenyl radical (although with reduced radical reactivity) and that of *o*-benzyne **1** (addition reactions).<sup>14</sup>

*m*-Benzyne **2a** was generated in argon matrices by two independent routes.<sup>15</sup> The UV photolysis of matrix-isolated (Ar, 10 K) [2.2]metaparacyclophane-2,9-dione **4a** resulted in fragmentation into *p*-xylylene **5**, CO, and benzyne **2a**. The flash vacuum pyrolysis of isophthaloyl diacetyl peroxide **6** produced CO<sub>2</sub>, methyl radicals, and again **2a**. Benzyne **2a** was identified by comparison of the experimental IR spectrum with *ab-initio* (CCSD(T)) and DFT (UB3LYP) calculations.

The only derivatives of **2** that have been matrix-isolated and spectroscopically characterized are 2,4-didehydrophenols **7**,



synthesized from quinone diazo compounds **8** via a carbene rearrangement.<sup>16,17</sup> The OH substitution in **7** causes only little change of the ring geometry compared to **2a**. The substitution results in a stabilization of the benzyne, however, somewhat less than the stabilization of benzene by OH substitution.<sup>17</sup>



The synthesis of matrix-isolated *m*-benzenes from **8** is restricted to dehydrophenols **7**, while the problem with peroxides of type **6** as precursors is the low volatility in combination with the rapid decomposition of the peroxides during deposition of the matrix from the gas phase. Derivatives of metaparacyclophanes **4** are thermally much more stable and thus should provide useful precursors for the synthesis of a variety of substituted *m*-benzenes. Here we describe the matrix isolation and spectroscopic characterization of two novel *m*-benzenes with a fluorine and a methyl substituent, respectively, in the 5-position.

## Results

### 5-Fluoro-1,3-didehydrobenzene **2b**

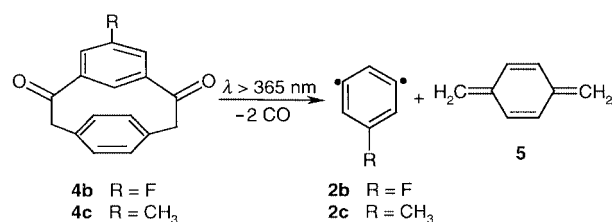
5-Fluoro[2.2]metaparacyclophane-2,9-dione **4b**, matrix-isolated in argon at 10 K, exhibits strong IR absorptions at 1727, 1695 (C=O str. vibrations), and 1296 (C–F str. vibration)  $\text{cm}^{-1}$ . The carbonyl region of **4b** is split to a complex pattern of IR bands,

**Table 1** IR Spectroscopic data of 5-fluoro-1,3-didehydrobenzene **2b**

No. <sup>c</sup>	Sym	Argon, 10 K <sup>a</sup>		BLYP/6-311G(d,p) <sup>b</sup>		Assignment <sup>e</sup>
		$\nu$	$I^d$	$\nu$	$I^d$	
22	a <sub>1</sub>			3121	3	C–H str., sym.
21	a <sub>1</sub>			1690	3	C–C str. + C–C bend., sym.
19	a <sub>1</sub>	1440	100	1402	100	C–F str. + C–H bend., sym.
15	a <sub>1</sub>	1184	46	1154	39	C–C str. + C–H bend. + C–F str., sym
13	b <sub>2</sub>	949	13	965	8	C–H bend. + C–C str.
12	a <sub>1</sub>	884	24	922	13	C–C bend., sym.
11	b <sub>1</sub>	810	18	802	17	C–H wag., o.o. phase
9	b <sub>1</sub>	767	9	747	14	C–H wag., o.o. phase
8	b <sub>1</sub>		6	614	1	C–C wag. + C–H wag., asym.
7	a <sub>1</sub>		6	603	3	C–C str. + C–H bend., sym.
6	b <sub>2</sub>	543	50	535	47	C–C rock. + C–C bend., asym.
4	b <sub>1</sub>	532	7	514	6	C–C wag. + C–H wag., asym.
2	a <sub>1</sub>			351	8	C–C bend., sym.

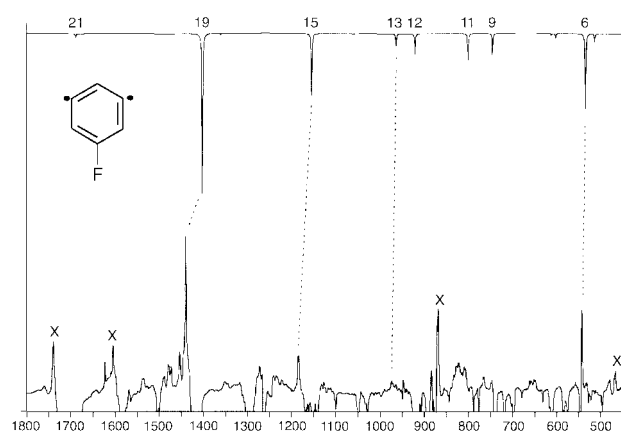
<sup>a</sup> IR spectroscopic data of **2b** obtained after 12 h irradiation ( $\lambda = 254$  nm) of **4b**, matrix-isolated in argon at 10 K. <sup>b</sup> Vibrational data of **2b** calculated at the BLYP/6-311G(d,p) level of theory. <sup>c</sup> Number of vibration according to the calculation. <sup>d</sup> Relative intensity based on the strongest peak (100%). <sup>e</sup> Assignment of calculated and experimental vibrations based on comparison of peak positions and intensities.

presumably due to Fermi resonances. Irradiation with  $\lambda > 285$  nm for 14 h results in a *ca.* 80% decrease of all absorptions of **4b** and formation of large amounts of CO (2137  $\text{cm}^{-1}$ ). The photolysis of **4b** is almost quantitative after 12 h with  $\lambda = 254$  nm irradiation, which indicates that the  $\alpha$ -cleavage is highly efficient under these conditions. Simultaneously, *p*-xylylene **5** with characteristic IR bands at 1740, 1605, 869, and 469  $\text{cm}^{-1}$  is formed. A novel compound with the strongest absorptions at 1440 and 543  $\text{cm}^{-1}$  is assigned to 5-fluoro-1,3-didehydrobenzene **2b** (Fig. 1, Table 1). The 543  $\text{cm}^{-1}$  absorption is very close to an intense absorption at 547  $\text{cm}^{-1}$  in the parent *m*-benzynes, which was assigned to the b<sub>1</sub> symmetrical ring deformation mode.<sup>15</sup> Fluorine substitution at C(5) obviously has only a minor influence on the position of this absorption.



A DFT calculation with the BLYP functional and the 6-311G(d,p) basis set nicely reproduces both band positions and relative intensities of the experimental spectrum (Table 1). Specifically, the b<sub>1</sub> symmetrical mode at 543  $\text{cm}^{-1}$  is reproduced within 8  $\text{cm}^{-1}$  (no scaling of vibrations applied). This vibration changes the bond angles—and thus the hybridization—at the radical centers C(1) and C(3), and therefore critically depends on the level of theory used for the calculation. The corresponding a<sub>1</sub> symmetrical mode is predicted to be of low intensity at 351  $\text{cm}^{-1}$  and not observed experimentally. The most intense absorption in the spectrum at 1440  $\text{cm}^{-1}$  is assigned to a combination of C(5)–F stretching with the symmetrical in plane bending of the C(4)–H and C(6)–H bonds. In fluorobenzene the C–F stretching vibration is found at 1496  $\text{cm}^{-1}$ .<sup>18</sup>

Since the photolysis of matrix-isolated cyclophane **4b** produces **2b**, **5**, and CO in close contact in the same matrix cage, a perturbation of the spectra might occur. However, compared to an independently synthesized and matrix-isolated sample, the IR bands of **5** are only slightly shifted and broadened. The good agreement of the experimental and calculated spectrum of **2b**, and the shape of the IR bands with comparatively narrow linewidths suggest that there is only a small perturbation of the spectrum of **2b**. For the parent *m*-benzynes **2a** this was confirmed by independent synthesis in the gas phase



**Fig. 1** Bottom: difference IR spectrum (in absorbance) showing the UV photochemistry of cyclophane **4b**. The IR absorptions of the photoproducts **5** and **2b** are pointing upwards. Top: IR spectrum of **2b** calculated at the BLYP/6-311G(d,p) level of theory (in absorbance). The peak numbers refer to Table 1.

with subsequent matrix isolation, which produces the same IR spectrum as the matrix photolysis of the cyclophane.<sup>15</sup>

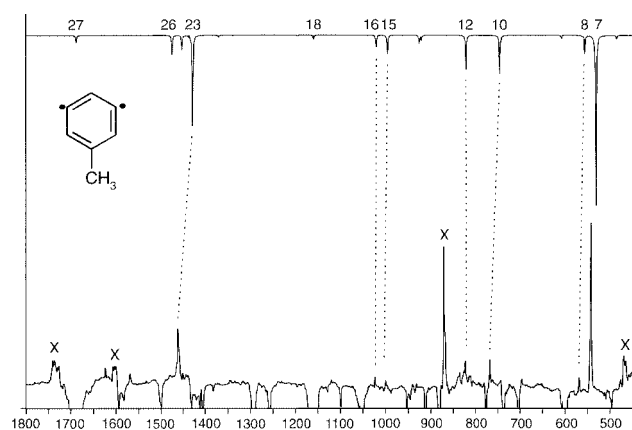
### 5-Methyl-1,3-didehydrobenzene **2c**

The methyl-substituted benzyne **2c** was synthesized analogously to the fluoro derivative **2b**. 5-Methyl[2.2]metaparacyclophane-2,9-dione **4c**, matrix-isolated in argon at 10 K, exhibits several intense IR absorptions between 1724 and 1689  $\text{cm}^{-1}$  in the carbonyl stretching region. UV photolysis of **4c** produces the expected fragmentation products CO and *p*-xylylene **5**, and a series of absorptions assigned to benzyne **2c** (Fig. 2). The most intense IR absorption of **2c** is the asymmetrical ring deformation mode at 543  $\text{cm}^{-1}$  at the same position as in **2b**, again close to the corresponding vibration of the parent benzyne **2a** (547  $\text{cm}^{-1}$ ) and in good agreement with calculations at the BLYP/6-311G(d,p) level of theory (531  $\text{cm}^{-1}$ , Table 2). The symmetrical ring deformation mode of **2c** is calculated as a weak absorption at 346  $\text{cm}^{-1}$  and due to experimental limitations not observed in the experimental spectrum. Similar to the 1440  $\text{cm}^{-1}$  absorption of **2b**, the IR spectrum of **2c** shows a medium intensity band at 1462  $\text{cm}^{-1}$ , assigned to a combination of C(5)–C(methyl) stretching and in plane C(4)–H and C(6)–H bending vibration. Due to the lower polarity of the C(2)–C(methyl) bond compared to the C(5)–F bond in **2c** this vibration is of lower intensity, while the band position is only slightly shifted.

**Table 2** IR Spectroscopic data of 5-methyl-1,3-didehydrobenzene **2c**

No. <sup>c</sup>	Sym	Argon, 10 K <sup>a</sup>		BLYP/6-311G(d,p) <sup>b</sup>		Assignment <sup>e</sup>
		$\nu$	$I^d$	$\nu$	$I^d$	
33	a'			3111	10	C–H str., sym.
32	a'			3089	7	C–H str., sym.
31	a''			3087	13	C–H str.
30	a''			3032	12	C–H str. (CH <sub>3</sub> )
29	a'			3004	15	C–H str. (CH <sub>3</sub> )
28	a'			2953	15	C–H str. (CH <sub>3</sub> ), sym.
27	a'			1689	4	C–C bend. + C–C str., sym.
26	a''	1570	16	1475	12	C–H twist (CH <sub>3</sub> )
25	a'	1533	11	1452	9	C–H bend. (CH <sub>3</sub> ) + C–H wag. (CH <sub>3</sub> )
23	a'	1462	42	1429	53	C–C bend. + C–C str., sym.
22	a'			1371	1	C–H wag. (CH <sub>3</sub> )
18	a'			1159	3	C–C str. + C–H bend., sym.
16	a'			1020	7	C–H twist (CH <sub>3</sub> )
15	a''	1000	13	996	11	C–H bend. (CH <sub>3</sub> ) + C–C str.
14	a''			925	5	C–H bend. (CH <sub>3</sub> ) + C–C str.
13	a'			921	3	C–C bend. + C–C str., sym.
12	a'	824	21	822	20	C–H wag., o.o. phase
10	a'	768	24	745	23	C–H wag., i. phase
9	a'			608	2	C–C str. + C–H bend., sym.
8	a'	570	13	556	11	C–C wag. + C–H wag., asym.
7	a''	543	100	531	100	C–C rock. + C–C bend., asym.
6	a''			528	2	C–C twist., asym.
5	a'			486	2	C–C wag. + C–H wag., asym.
4	a'			346	15	C–C bend., sym.
2	a'			176	2	C–C wag., sym.

<sup>a</sup> IR spectroscopic data of **2c** obtained after 22 h irradiation ( $\lambda = 365$  nm) of **4c**, matrix-isolated in argon at 10 K. <sup>b</sup> Vibrational data of **2c** calculated at the BLYP/6-311G(d,p) level of theory. <sup>c</sup> Number of vibration according to the calculation. <sup>d</sup> Relative intensity based on the strongest peak (100%). <sup>e</sup> Assignment of calculated and experimental vibrations based on comparison of peak positions and intensities.



**Fig. 2** Bottom: difference IR spectrum (in absorbance) showing the UV photochemistry of cyclophane **4c**. The IR absorptions of the photoproducts **5** and **2c** are pointing upwards. Top: IR spectrum of **2c** calculated at the BLYP/6-311G(d,p) level of theory (in absorbance). The peak numbers refer to Table 2.

## Discussion

The UV photolysis of cyclophanes **4** provides a useful method for the generation of matrix-isolated *m*-benzynes **2** in high yields and allows study of the influence of substituents on the properties of benzynes. One concern using this method is that **2** and the other fragments CO and *p*-xylylene **5** are formed in the same matrix cage which might cause perturbations of the spectra or even secondary thermal or photochemical reactions. However, such secondary reactions are not observed even with 254 nm irradiation and the experimental IR spectra are in good agreement with the calculated gas phase spectra, which excludes large interactions of species trapped in the same matrix cage.

DFT methods were used to calculate the geometries and IR spectroscopic data of the benzynes **2**. Recently Cramer demonstrated that—despite the single reference character of the DFT methods—open shell systems such as carbenes are reliably

described with the BLYP and BVWN5 functionals.<sup>19</sup> Kraka *et al.* used UB3LYP and CCSD(T) to calculate the geometry and the vibrational spectrum of *m*-benzyne **2a**.<sup>13</sup> The DFT results are close to the CCSD(T) calculations, as long as an unrestricted wave function (UB3LYP) is used, while B3LYP calculations yield the bicyclic isomer of **2a** with spectroscopic properties in disagreement with the experiment. In a recent computational study Cramer, Nash, and Squires demonstrated that thermochemical data of **2a** calculated at the BPW91/pVTZ level of theory come close to experimental data.<sup>20</sup> However, the C(1)–C(3) distance between the radical centers of 1.874 Å calculated with the BPW91 functional is significantly shorter than the CCSD(T) value of 2.178 Å. With a C(1)–C(3) distance of 2.00 Å the RBLYP structure is closer to the CCSD(T) results than the BPW91 structure and therefore this method was used throughout this paper.

The IR spectra calculated with the RBLYP functional are in excellent agreement with the experimental data. This method thus provides a reliable and, compared to CCSD(T) calculations, cost efficient method to compute ground state properties of *m*-benzynes. The spectra of **2** exhibit two characteristic vibrations: (i) the ring deformation mode at 543 cm<sup>-1</sup> in **2b** and **2c**, at 547 cm<sup>-1</sup> in **2a**, and at 519 cm<sup>-1</sup> in **7**. This vibration is obviously hardly affected by substitution at C(5), and even the OH group at C(4), adjacent to one of the radical centers, results in a red-shift of only less than 30 cm<sup>-1</sup>. Since this vibration is very strong, it can be used to identify *m*-benzynes in product mixtures. (ii) The second characteristic vibration is the combination of C(5)–X stretching with the symmetrical in plane bending of the C(4)–H and C(6)–H bonds. This vibration is weak in **2a** (1402 cm<sup>-1</sup>), strong in **2b** (1440 cm<sup>-1</sup>), and of medium intensity in **2c** (1462 cm<sup>-1</sup>).

A comparison of the calculated structures of **2a**, **2b** and **2c** reveals the small influence of substituents at C(5) on the ring structure (Fig. 3). Both the fluorine and the methyl group slightly decrease the C(1)–C(3) distance and the C(1)–C(2)–C(3) bond angle and thus increase the through bond interaction between the radical centers. The largest effect is, as expected,

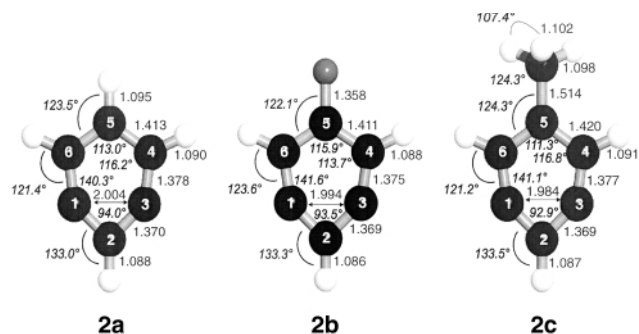


Fig. 3 Structures of *m*-benzynes **2a**, **2b**, and **2c** calculated at the BLYP/6-311G(d,p) level of theory.

observed in the local surroundings of the substituent. Thus, fluorine substitution leads to an increase of the C(4)–C(5)–C(6) bond angle, while methyl substitution has the opposite effect. The slightly negative charge located at the radical centers C(1) and C(3) results in a calculated dipole moment of 0.79 D in *m*-benzyne **2a**, which is reduced to 0.48 in **2b** and increased to 1.42 D in **2c**. Thus, the electron withdrawing fluorine substituent compensates the negative charge at the radical centers while the electron donating methyl group increases the overall charge polarization.

In conclusion, we were able to generate the *m*-benzynes **2b** and **2c** by UV photolysis of the corresponding cyclophanes **4b** and **4c**, a novel general route to substituted *m*-benzynes. The experimental IR spectra of **2b** and **2c** can be reproduced by DFT calculations, which reveals the reliability of these methods for the calculation of ground state properties of *m*-benzynes.

## Experimental

### Matrix isolation spectroscopy

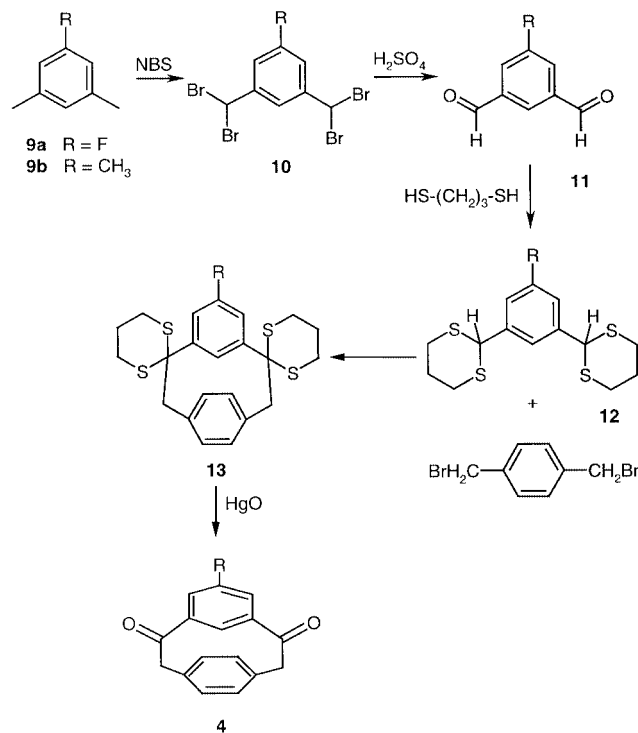
Matrix isolation experiments were performed by standard techniques with an APD DE-204SL and an APD DE-202 Displex closed cycle helium cryostat. Matrices were produced by deposition of argon (Linde, 99.9999%) on top of a CsI (IR) or sapphire (UV–vis) window with a rate of approximately 0.15 mmol min<sup>-1</sup>. To obtain optically clear matrices the spectroscopic window was retained at 30 K during deposition, and the matrix was subsequently cooled to 10 K. Matrix infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 1 or 0.5 cm<sup>-1</sup> in the range 400–4000 cm<sup>-1</sup>. UV–vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with a resolution of 2 nm. Irradiations were carried out with use of Osram HBO 500 W/2 or Ushio USH-508SA mercury high-pressure arc lamps in Oriol housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10 cm path of water. For broad-band irradiation Schott cut-off filters were used (50% transmission at the wavelength specified). For narrow-band irradiation interference filters in combination with dichroic mirrors (“cold mirrors”) or a Gräntzel low pressure mercury arc lamp (254 nm) were used.

### Calculations

Calculations were performed with the GAUSSIAN94 suite of programs.<sup>21</sup> Geometry optimizations and the calculations of vibrational spectra were performed with a DFT method using the RBLYP functional<sup>22,23</sup> and the 6-311G(d,p) valence triple zeta basis set.<sup>24</sup> The RBLYP wave functions have been tested to be stable with respect to becoming unrestricted.

### Synthesis of cyclophanes

The [2.2]metaparacyclophanes **4** were synthesized according to a modified procedure by Boekelheide *et al.*<sup>25</sup>



All solvents were distilled and dried before use. Flash column chromatography was carried out on ICN silica 32–63 (60 Å). NMR spectra were recorded on a Bruker DPX 200 instrument, chemical shifts in  $\delta$  relative to TMS, *J* in Hz, d = doublet, t = triplet, m = multiplet. Infrared spectra were recorded on a Perkin-Elmer 841 or Bruker IFS 66 IR Spectrometer in the range 4000–600 cm<sup>-1</sup>. MS data were obtained on a Varian MAT CH 5 instrument at 70 eV, high resolution mass data on a VG AutoSpec instrument at 70 eV.

### 3,5-Bis(dibromomethyl)fluorobenzene **10a**

A mixture of 1,3-dimethyl-5-fluorobenzene **9a** (10 ml, 80.7 mmol), NBS (*N*-bromosuccinimide) (86.13 g, 483.89 mmol) and AIBN (*α,α'*-azoisobutyronitrile) in CCl<sub>4</sub> (645 ml) was heated under reflux for 8 h and the succinimide filtered off. After removal of the solvent, a yellow oil remained (30.4 g, 86%).  $\nu/\text{cm}^{-1}$  3082, 3012, 1755, 1720, 1599, 1452, 1307, 1216, 1196, 1147, 993, 872, 788, 739, 700, 666, 642;  $\delta_{\text{H}}$ (200 MHz, CDCl<sub>3</sub>) 7.44 (t, *J* 1.63, 2 H), 7.29 (dd, *J* 1.63, *J* 8.66, 2 H), 6.56 (s, 1 H);  $\delta_{\text{C}}$ (50.33 MHz, CDCl<sub>3</sub>) 162.1 (d, *J* 236.2, CF), 144.2 (d, *J* 7.8, C<sub>q</sub>), 119.8 (d, *J* 2.9, CH), 115.7 (d, *J* 24.3, CH), 38.12 (CH); *m/z* 443–435 (M<sup>+</sup>), 363–357 (C<sub>8</sub>H<sub>5</sub>Br<sub>4</sub>F – Br), 283–279 (C<sub>8</sub>H<sub>5</sub>Br<sub>3</sub>F – Br), 202–200 (C<sub>8</sub>H<sub>5</sub>Br<sub>2</sub>F – Br), 120 (C<sub>8</sub>H<sub>5</sub>BrF – Br).

### 5-Fluoroisophthalaldehyde **11a**

30.4 g of **10a** (69.2 mmol) were heated in 150 ml conc. H<sub>2</sub>SO<sub>4</sub> (96%) to 110 °C, and the Br<sub>2</sub> formed during the reaction removed by a flow of Ar. The mixture was heated for another 2 h and the reaction mixture poured on ice (1 l). The product was extracted with TBME, neutralized and dried over MgSO<sub>4</sub>. Removing the solvent and re-crystallization from petroleum ether (bp 60–80 °C) yielded a light yellow solid (2.7 g, 17.8 mmol, 26%). Mp: 93 °C;  $\nu/\text{cm}^{-1}$  3376, 3074, 2866, 1695, 1595, 1464, 1448, 1383, 1299, 1239, 1138, 988, 964, 893, 753, 672, 654;  $\delta_{\text{H}}$ (200 MHz, CDCl<sub>3</sub>) 10.06 (d, *J* 1.76, 2 H), 8.18 (t, *J* 1.38, 1 H), 7.82 (dd, *J* 17.91, 1.38, 2 H);  $\delta_{\text{C}}$ (50.33 MHz, CDCl<sub>3</sub>) 189.54 (CO), 163.43 (d, *J* 252.7, CF), 139.03 (d, *J* 5.83, C<sub>q</sub>), 126.96 (CH), 120.87 (d, *J* 22.35, CH); *m/z* 152.059 (calc. for C<sub>8</sub>H<sub>5</sub>O<sub>2</sub>F: 152.0274).

### 5-Fluoroisophthalaldehyde bis(propane-1,3-diyl dithioacetal) **12a**

1.1 ml (4.2 mmol) of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (45%) were added to a solution of **11a** (2.7 g, 17.8 mmol) in 45 ml of acetic acid (99–100%). Propane-1,3-dithiol (4.5 ml, 44.4 mmol) was added dropwise under stirring at room temperature. After stirring for another 72 h the colorless precipitate was filtered off and dried *in vacuo* (3.45 g, 58.4%). Mp: 137 °C;  $\nu/\text{cm}^{-1}$  3066, 2935, 2828, 1769, 1711, 1616, 1592, 1528, 1514, 1465, 1442, 1433, 1423, 1344, 1308, 1274, 1244, 1200, 1180, 1130, 1116, 1012, 987, 905, 884, 826, 762, 723, 695, 675, 666;  $\delta_{\text{H}}$ (200 MHz,  $\text{CDCl}_3$ ) 7.35 (t,  $J$  1.51, 1 H), 7.14 (dd,  $J$  9.16, 1.63, 2 H), 5.10 (s, 2 H), 3.09–2.82 (m, 8 H), 2.22–2.08 (m, 2 H), 2.01–1.79 (m, 2 H);  $\delta_{\text{C}}$ (50.33 MHz,  $\text{CDCl}_3$ ) 160.24 (d,  $J$  247.8, CF), 141.67 (d,  $J$  8.75,  $\text{C}_q$ ), 123.29 (CH), 115.05 (d,  $J$  23.33, CH), 50.54 (C–H), 31.79 ( $\text{CH}_2$ ), 24.97 ( $\text{CH}_2$ );  $m/z$  332.0197 (calc. for  $\text{C}_{14}\text{H}_{17}\text{FS}_4$ : 332.0197).

### 5-Fluoro[2.2]metaparacyclophane-2,9-dione bis(propane-1,3-diyl dithioacetal) **13a**

10 ml of a solution of *n*-butyllithium in hexane (1.6 M) were added under argon to a cooled (–32 °C) solution of **12a** (1.67 g, 5 mmol) in 250 ml dry THF and stirred for 1.5 h at the same temperature to generate the dianion. The reddish brown solution of the dianion (–32 °C) and a solution of  $\alpha,\alpha'$ -dibromo-*p*-xylene (1.32 g, 5 mmol) in 250 ml THF (room temperature) were simultaneously added under high dilution conditions over a period of 6 h to refluxing THF (1000 ml). After removing the solvent colorless crystals were obtained by using flash column chromatography ( $\text{CH}_2\text{Cl}_2$ ) (0.98 g, 45%). Dp: >225 °C;  $\nu/\text{cm}^{-1}$  2926, 2910, 2340, 1735, 1671, 1598, 1579, 1499, 1432, 1422, 1411, 1345, 1281, 1262, 1239, 1194, 1171, 1117, 1102, 1015, 989, 954, 938, 924, 902, 889, 864, 855, 815, 791, 734, 719, 703, 677, 608;  $\delta_{\text{H}}$ (200 MHz,  $\text{CDCl}_3$ ) 7.47 (dd,  $J$  10.29, 1.76, 2 H), 7.32 (t,  $J$  1.0, 2 H), 6.66 (t, 1.76, 1 H), 5.97 (t,  $J$  1.0, 2 H), 3.46 and 2.75 (AB quartet,  $J$  13.2, 4 H), 2.90–2.29 (m, 8 H), 1.96–1.83 (m, 4 H);  $\delta_{\text{C}}$ (50.33 MHz,  $\text{CDCl}_3$ ) 163.5 (d, 248.8, CF), 143.5 ( $\text{C}_q$ ), 134.4 ( $\text{C}_q$ ), 129.2 (CH), 128.8 (CH), 127.7 (CH), 114.0 (d,  $J$  24.3, CH), 59.7 ( $\text{C}_q$ ), 53.5 ( $\text{CH}_2$ ), 28.3 (d,  $J$  73.86,  $\text{CH}_2$ ), 24.8 ( $\text{CH}_2$ );  $m/z$  434.0664 (calc. for  $\text{C}_{22}\text{H}_{23}\text{FS}_4$ : 434.0667).

### 5-Fluoro[2.2]metaparacyclophane-2,9-dione **4b**

A solution of **13a** (2.4 g, 5.4 mmol) in 100 ml THF was added dropwise to a stirred slurry of 3.5 g (16.2 mmol) mercury(II) oxide and 4.6 ml (8.8 mmol) of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (45%) in 35 ml THF–15% water at room temperature. After 2 h the addition was complete and the mixture was stirred for 12 h at 40 °C. The solution was filtered off (Celite, sand, silica gel) and dried over  $\text{MgSO}_4$ . After removal of the solvent the cyclophane was purified using thin layer chromatography ( $\text{CH}_2\text{Cl}_2$ ) to yield colorless crystals (150 mg, 10.9%). Mp: 88–90 °C;  $\nu/\text{cm}^{-1}$  3591, 3531, 3362, 2961, 2931, 2858, 1687, 1616, 1584, 1502, 1451, 1411, 1293, 1260, 1168, 1100, 1048, 919, 891, 869, 814, 779, 738, 609;  $\delta_{\text{H}}$ (200 MHz,  $\text{CDCl}_3$ ) 7.07 (s, 4 H), 6.83 (dd,  $J$  8.53, 1.5, 2 H), 5.43 (t,  $J$  1.38, 1 H), 3.91 (s, 4 H);  $\delta_{\text{C}}$ (50.33 MHz,  $\text{CDCl}_3$ ) 201.18 (CO), 161.40 (d,  $J$  252.7, CF), 143.36 (d,  $J$  5.84,  $\text{C}_q$ ), 135.54 ( $\text{C}_q$ ), 132.60 (CH), 119.37 (d,  $J$  3.89, CH), 112.52 (d,  $J$  23.32, CH), 52.53 ( $\text{CH}_2$ );  $m/z$  254.0753 (calc. for  $\text{C}_{16}\text{H}_{11}\text{O}_2\text{F}$ : 254.0743).

### 5-Methylisophthalaldehyde bis(propane-1,3-diyl dithioacetal) **12b**

The reaction of 5-methylisophthalaldehyde<sup>26</sup> (3.2 g, 21.3 mmol) with propane-1,3-dithiol was carried out as described for the preparation of **12a** (5.10 g, 73%). Mp: 163–165 °C;  $\nu/\text{cm}^{-1}$  3447, 3022, 2947, 2901, 2824, 1794, 1599, 1451, 1419, 1378, 1290, 1270, 1241, 1201, 1166, 1107, 1083, 998, 973, 905, 878, 822, 757, 726, 703, 675, 657;  $\delta_{\text{H}}$ (200 MHz,  $\text{CDCl}_3$ ) 7.32 (s, 1 H), 7.21 (s, 2 H), 5.09 (s, 2 H), 3.10–2.82 (m, 8 H), 2.22–1.79 (m, 4H);

$\delta_{\text{C}}$ (50.33 MHz,  $\text{CDCl}_3$ ) 139.98 ( $\text{C}_q$ ), 139.11 ( $\text{C}_q$ ), 128.55 (CH), 124.59 (CH), 51.26 (CH), 32.06 ( $\text{CH}_2$ ), 25.12 ( $\text{CH}_2$ ), 21.22 ( $\text{CH}_3$ );  $m/z$  328.0459 (calc. for  $\text{C}_{15}\text{H}_{20}\text{S}_4$ : 328.0448).

### 5-Methyl[2.2]metaparacyclophane-2,9-dione bis(propane-1,3-diyl dithioacetal) **13b**

The procedure for the synthesis of **13b** is analogous to that of **13a** described above. 1.75 g (5 mmol) of **12b** gave 1.32 g (61%) of **13b** as colorless crystals.  $\nu/\text{cm}^{-1}$  3430, 3033, 2948, 1884, 1734, 1592, 1502, 1455, 1431, 1420, 1346, 1274, 1244, 1191, 1168, 1129, 1107, 1022, 980, 951, 937, 915, 902, 888, 852, 811, 789, 759, 733, 716, 709, 680, 653;  $\delta_{\text{H}}$ (200 MHz,  $\text{CDCl}_3$ ) 7.51 (m,  $J$  1.50, 2 H), 7.29 (m,  $J$  1.26, 2 H), 6.63 (1 H), 5.85 (m,  $J$  1.00), 3.44 and 2.74 (AB-quartet,  $J$  13.17, 4 H), 2.94–2.33 (m, 8 H), 2.36 (s, 3 H), 1.95–1.82 (m, 4 H);  $\delta_{\text{C}}$ (50.33 MHz,  $\text{CDCl}_3$ ) 140.68 ( $\text{C}_q$ ), 137.72 ( $\text{C}_q$ ), 134.50 ( $\text{C}_q$ ), 129.13 (CH), 129.03 (CH), 128.57 (CH), 127.54 (CH), 60.27 ( $\text{C}_q$ ), 53.55 ( $\text{CH}_2$ ), 28.99 ( $\text{CH}_2$ ), 27.44 ( $\text{CH}_2$ ), 24.97 ( $\text{CH}_2$ ), 21.84 ( $\text{CH}_3$ );  $m/z$  430.0909 (calc. for  $\text{C}_{23}\text{H}_{26}\text{S}_4$ : 430.0917).

### 5-Methyl[2.2]metaparacyclophane-2,9-dione **4c**

The procedure for the synthesis of **4c** is analogous to that of **4b** described above. 300 mg (0.7 mmol) of **13b** gave 40 mg (23%) of **4c** as colorless crystals.  $\nu/\text{cm}^{-1}$  3379, 2929, 1698, 1587, 1501, 1447, 1407, 1296, 1257, 1169, 1134, 1101, 1073, 1035, 994, 916, 885, 871, 817, 785, 741, 720, 605;  $\delta_{\text{H}}$ (200 MHz,  $\text{CDCl}_3$ ) 7.03 (s, 4 H), 6.92 (m,  $J$  0.52, 2 H), 5.44 (s, 1 H), 3.87 (s, 4 H), 2.29 (s, 3 H);  $\delta_{\text{C}}$ (50.33 MHz,  $\text{CDCl}_3$ ) 203.21 (CO), 141.47 ( $\text{C}_q$ ), 137.85 ( $\text{C}_q$ ), 135.98 (CH), 132.51 (CH), 125.99 ( $\text{C}_q$ ), 120.75 (CH), 52.55 ( $\text{CH}_2$ ), 21.29 ( $\text{CH}_3$ );  $m/z$  250.0992 (calc. for  $\text{C}_{17}\text{H}_{14}\text{O}_2$ : 250.0994).

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