Matrix Isolation and Photochemistry of Tetrafluoro-*p*-xylylene

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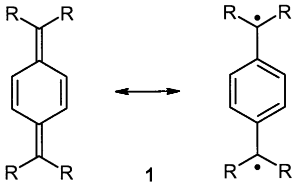
Tetrafluoro-*p*-xylylene **(3)** has been generated by flash vacuum pyrolysis of octafluoro[2.2]paracyclophane **(2)** and subsequent trapping of the products in solid argon at 9 K. Xylylene **3** photochemically rearranges to the ring-expanded heptafulvene **5**. Matrix-isolated species have been identified by comparison of experimental and calculated IR spectra. The temperature-dependence of the thermal fragmentation of paracyclophane **2** has been determined by mass spectrometric analysis of the pyrolysis products.

Introduction

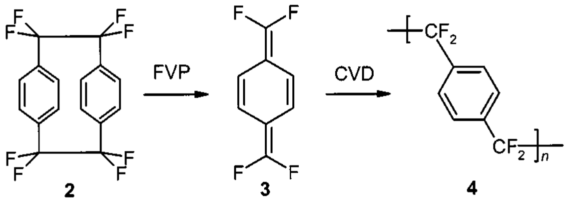
p-Xylylene **1** and its derivatives are highly reactive molecules with both quinoid and biradicaloid character and are of significant theoretical and practical interest.[1][4] In the absence of trapping reagents they dimerize to cyclophanes and oligomerize to produce oligo- and poly(*p*-xylylenes) known as "parylenes". The stability of the *p*-xylylenes depends on the substituents R at the exomethylene groups, and several stable *p*-xylylenes have been synthesized in the past.[2] Among these are tetracyano-*p*-xylylene (R = CN), tetrakis(methoxycarbonyl)-*p*-xylylene (R = $COOCH_3$) and tetrakis(ethylsulfonyl)-*p*-xylylene (R = $SO_2C_2H_5$), and it was shown that these derivatives of **1** are stabilized by mesomeric rather than inductive electron-withdrawing effects.[2]



Scheme 1. Mesomeric stabilization in tetrasubstituted *p*-xylylenes

Thin films of the parylenes are obtained by vapor deposition of reactive *p*-xylylenes on suitable surfaces.[4] These films exhibit low dielectric constants in combination with high thermal (the parylene from the parent *p*-xylylene **1** can be used up to 130 °C)[4] and chemical stability, and are therefore ideally suited as coatings in electronic devices. The thermal stability of the parylenes is even higher when the monomer **1** contains fluorine substituents. Thus, parylene **4**, produced by vapor deposition of tetrafluoro-*p*-xylylene **(3)**, is stable at temperatures as high as 240 °C.[3]

[2.2]Paracyclophanes are easily cleaved thermally to yield *p*-xylylenes, and thus have proven to be suitable precursors of the parylenes.[4][5] Vacuum pyrolysis and subsequent vapor deposition (CVD) produces highly crystalline, polymeric films. Until recently commercial use of parylene **4** was prevented by the lack of practicable synthetic routes to octafluoro[2.2]paracyclophane **(2)**. In 1997 Dolbier et al. published an improved procedure for the synthesis of **2** which now makes this cyclophane available in commercial quantities.[6]



Scheme 2. Flash vacuum pyrolysis (FVP) and subsequent vapor deposition (CVD) of octafluoro[2.2]paracyclophane (**2**)

In view of a more widespread future use of polymer **4** we investigated the flash vacuum pyrolysis (FVP) of cyclophane **2** using the matrix isolation technique and mass spectrometry. Tetrafluoro-*p*-xylylene **(3)** – like the parent hydrocarbon **1** (R = H) – is unstable at ambient temperature but can be trapped and spectroscopically characterized in low temperature matrices.

Results and Discussion

The thermal decomposition of octafluoro[2.2]paracyclophane **(2)** was investigated by flash vacuum pyrolysis (FVP) and detection of the products with a quadrupole mass spectrometer and matrix IR spectroscopy. At temperatures above 250 °C, the M^+ peak (m/z = 352) of **2** decreases and completely disappears above 450 °C. Simultaneously m/z = 176, corresponding to tetrafluoro-*p*-xylylene **(3)**, increases in intensity. Other fragments are not observed, even at 600 °C, which indicates a very clean thermal reaction.

The IR spectrum of cyclophane **2**, matrix isolated in argon at 9 K, exhibits very strong absorptions at 1266 and 1153 cm^{-1} assigned to CF stretching vibrations. In contrast to the parent [2.2]paracyclophane, which on UV irradiation is cleaved to *p*-xylylene,[7] **2** is completely photostable even

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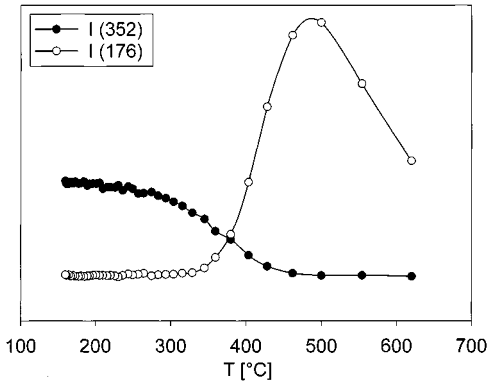


Figure 1. Pyrolysis temperature dependence of the *m*/*z* = 352 and *m*/*z* = 176 mass peaks between 140 and 620°C; since the mass spectrum of cyclophane **2** also displays an *m*/*z* = 176 mass peak the *m*/*z* = 176 curve is corrected for the fraction arising from **2**

towards prolonged irradiation with the 248 nm light of a KrF excimer laser.

Flash vacuum pyrolysis (FVP) of **2** at 600°C, with subsequent trapping of the products in argon at 9 K, results in the quantitative cleavage of **2** and formation of a single new species with a very intense IR absorption at 1693 cm^{-1} and strong absorptions at 1710, 1267, and 1080 cm^{-1} (Figure 2, Table 1). This IR spectrum is in excellent agreement with the IR spectrum of tetrafluoro-*p*-xylylene (**3**) calculated at the B3LYP/6−31++G(d,p)[8] level of theory. The dominant absorption at 1693 cm^{-1} is assigned to the antisymmetrical combination of the $C{=}CF_2$ stretching vibration $\nu_{as}(C{=}CF_2)$. The corresponding symmetrical mode $\nu_s(C{=}CF_2)$ is not IR active. The medium intensity band at 1710 cm^{-1} is assigned to a Fermi resonance, analogous to the 1735 cm^{-1} band of the parent *p*-xylylene **1** (R = H).[9] The weak absorption at 1590 cm^{-1} is the B_{2u} symmetrical stretching vibration of the ring double bonds. In unsubstituted **1** the corresponding band is observed at 1591 cm^{-1},[10] and in *p*-benzoquinone at 1592 cm^{-1}.[11][12] This vibration is obviously highly characteristic of the ring system. All other bands between 600 and 1700 cm^{-1} are in-plane ring deformation modes or in-plane C−H bending modes, or combinations thereof, except for the weak absorption at 800 cm^{-1} which is assigned to an out-of-plane C−H bending vibration.

Table 1. IR spectroscopic data of tetrafluoro-*p*-xylylene (**3**)

Mode	Symm.	$\tilde{\nu}_{exp.}$[a]	$I_{rel.,exp.}$[c]	$\tilde{\nu}_{calcd.}$[b]	$I_{rel.,calcd.}$[c]
18	B_{1u}	678	0.11	674	0.09
21	B_{3u}	800	0.02	809	0.07
22	B_{1u}	956	0.02	971	0.01
26	B_{1u}	1080	0.34	1086	0.43
27	B_{2u}	1118	0.03	1138	0.04
30	B_{2u}	1267	0.26	1272	0.27
32	B_{2u}	1341	0.19	1354	0.13
33	B_{1u}	1423	0.11	1454	0.11
35	B_{2u}	1590	0.01	1630	0.002
37	B_{1u}	1693	1.00	1733	1.00
18+26		1710	0.26	−	−

[a] Argon, 9 K. – [b] Calculated at the B3LYP/6−31++G** level of theory. The assignment is tentative and is based on band positions and intensities. – [c] Relative intensities (based on the strongest absorption).

The UV/Vis spectrum of **3** displays a broad band at 198 nm and two intense bands at 266 and 277 nm. The UV/Vis spectrum of *p*-benzoquinone, with a similar electronic structure, exhibits a strong absorption at 240 nm with a shoulder at 276 nm.[13] An additional weak absorption of the quinone at 445 nm is due to the n → π* transition of the carbonyl groups and thus is not observed in **3**.

Xylylene **3** proved to be labile towards short wavelength UV irradiation, and 248 nm irradiation (KrF Excimer Laser) results in partial conversion into a new compound

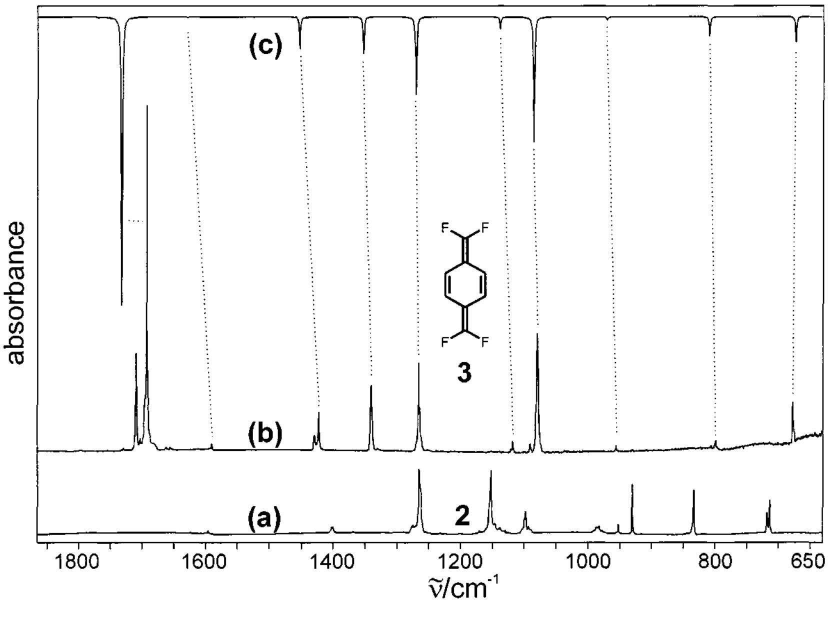


Figure 2. (a) IR spectrum of octafluoro[2.2]paracyclophane (**2**) (Ar, 9 K); (b) IR spectrum of FVP products of **2** (Ar, 9 K); (c) Calculated IR spectrum of tetrafluoro-*p*-xylylene (**3**) [B3LYP/6−31++G(d,p), unscaled]

with strong IR absorptions at 1698, 1608, and 1293 cm^{-1} (Figure 3, Table 2). Since the formation of fragments such as CF_2, FCCF, HCCH, and F_2CCF_2 can be excluded by comparison with the known experimental IR spectra of these species, the new compound apparently is the product of an intramolecular rearrangement of **3**. The IR spectrum shows no evidence for triple bonds, cyclopropane, or cyclopropene moieties, but closely matches the calculated {B3LYP/6−31++G(d,p)} spectrum of tetrafluoroheptafulvene **(5)** (Figure 3, Table 2).

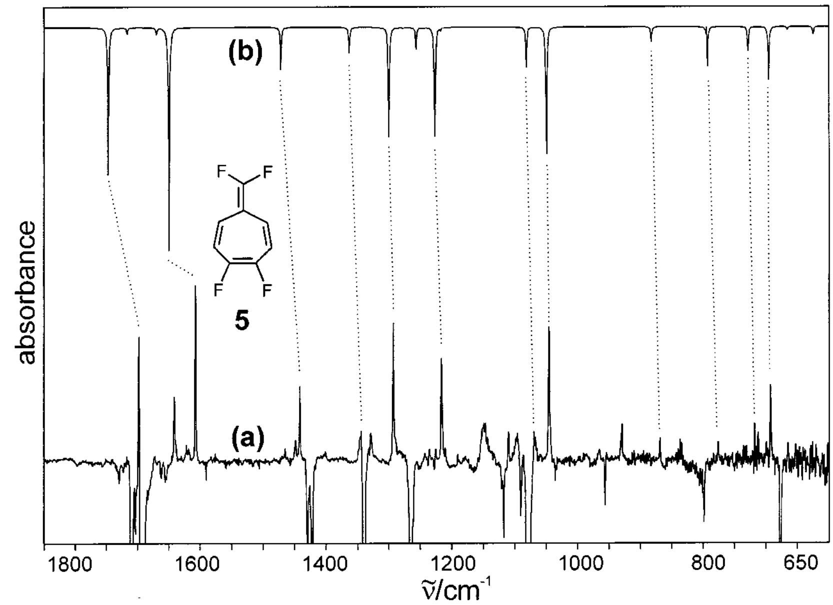


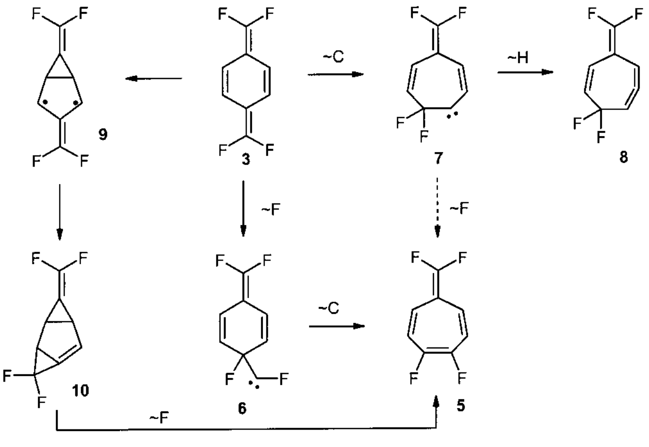
Figure 3. (a) IR difference spectrum showing the photochemistry of tetrafluoro-*p*-xylylene **(3)** (Ar, 9 K); bottom part, bands disappearing; top part, bands appearing on irradiation with 248 nm; (b) Calculated IR spectrum of tetrafluoroheptafulvene **(5)** [B3LYP/6−31++G(d,p), unscaled]

Table 2. IR spectroscopic data of tetrafluoroheptafulvene **5**

Mode	Symm.	$\tilde{\nu}_{exp.}$ [a]	$I_{rel.,exp.}$ [c]	$\tilde{\nu}_{calcd.}$ [b]	$I_{rel.,calcd.}$ [c]
18	A_1	693	0.45	696	0.24
19	B_2	719	0.29	730	0.11
20	B_1	777	0.10	794	0.18
22	A_1	870	0.14	883	0.07
25	A_1	1046	0.77	1050	0.57
26	B_2	1070	0.16	1082	0.18
28	A_1	1217	0.60	1227	0.49
31	B_2	1293	0.77	1300	0.49
32	B_2	1345	0.15	1363	0.12
33	B_2	1442	0.41	1472	0.19
35	A_1	1608	1.00	1651	1.00
38	A_1	1698	0.78	1748	0.66

[a] Argon, 9 K. – [b] Calculated at the B3LYP/6−31++G** level of theory. The assignment is tentative and is based on band positions and intensities. – [c] Relative intensities (based on the strongest absorption).

The rearrangement **3** → **5** requires both a ring expansion and migration of a fluorine atom, and several mechanisms for this rearrangement have to be considered. One mechanism starts with a [1,2]-F shift to fluorocarbene **6**, followed by ring expansion to heptafulvene **5**. Alternatively, a ring expanding [1,2]-C migration to produce the cyclic carbene **7** could be the primary step. Carbene **7** could subsequently rearrange to **5** by [1,2]-F migration. However, a rapid [1,2]-H shift in **7** should compete with the [1,2]-F shift and produce the cyclic allene **8**, with characteristic IR absorptions, which were not found in our experiments. A third mechanism involves the trimethylenemethane **9** and the strained tricycloheptene **10** as short-lived intermediates. None of these species were observed, and the experiments therefore do not allow us to draw a final conclusion on the reaction mechanism leading to **5**.



Scheme 3. Possible mechanisms for the photochemical **3** → **5** rearrangement

Conclusion

FVP of octafluoro[2.2]paracyclophane **(2)** with both mass spectrometric and matrix IR detection demonstrate that at 450−600°C tetrafluoro-*p*-xylylene **(3)** is produced in quantitative yield. Thus, **2** is an excellent thermal precursor of parylene **4**. As expected, **3** is thermally labile and can only be isolated in low temperature matrices. The novel photochemical rearrangement of **3** to heptafulvene **5** must proceed by a multistep mechanism with reorganization of CC and CF bonds. Unfortunately, no other intermediates were observed during the photolysis which could have provided additional mechanistic insights. In contrast, the parent *p*-xylylene **1** (R = H) is stable towards prolonged UV irradiation,[10] and in 1994 Domingo et al. reported the failure of the photochemical rearrangement of perchloro-*p*-xylylene to perchloroheptafulvene.[14] Further experiments with substituted *p*-xylylenes should show whether the **3** → **5** rearrangement is unique to fluorine-substituted derivatives of **1** or a more general novel photochemical rearrangement.

Experimental Section

Octafluoro[2.2]paracyclophane (**2**) was prepared according to a procedure published by Dolbier et al.[15] 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 reactive species on a cold CsI window. To obtain optically clear matrices, the cold window was retained at 30 K during deposition, and the matrix was subsequently cooled to 9 K. Flash vacuum pyrolyses were carried out by slowly subliming a sample of **2** through a 7 cm quartz tube heated electrically by a tantal wire. The pressure was approximately 10^{-5} mbar and no carrier gas was used for the pyrolyses. Infrared spectra were recorded on a Bruker IFS66 FTIR spectrometer with a standard resolution of 0.5 cm^{-1} in the range of 400−4000 cm^{-1}. UV/Vis spectra were recorded with a Hewlett−Packard 8452A diode array spectrophotometer. Irradiations were carried out with a Lambda Physik Compex 100 Excimer Laser (KrF, $\lambda = 248$ nm). Mass spectra were measured with a VG Quadrupoles SXP Elite spectrometer directly coupled to a pyrolysis tube similar to that used in the matrix IR experiments.

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