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SYNTHESIS AND PULSE RADIOLYTIC STUDIES OF MONO- AND
POLYFLUORINATED BIPHENYLS

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SUMMARY

The polyfluorinated biphenyls investigated were synthesized by reaction of fluorinated anilines with excess benzene and characterized by spectroscopic methods. Upon pulse radiolysis of the polyfluorinated biphenyls in dichloroethane radical cations are formed. By comparison with unsubstituted biphenyl the fluoro-substitution does not exert a strong effect on the optical absorption spectra or the first half-lives of the biphenyl radical cations.

INTRODUCTION

Polyhalogenated biphenyls are widespread pollutants due to their industrial use, e. g. as flame-retardants. Recently the results on pulse radiolytic studies of polychlorinated biphenyls (PCBs) were reported [1]. The optical absorption spectra of their radical cations are strongly dependent on steric factors. In order to compare the oxidation of PCBs and biphenyl itself to that of polyfluorinated biphenyls (PFBs) we now report on

the synthesis and the behaviour under pulse radiolytic conditions of several PFBs in dichloroethane (DCE).

RESULTS AND DISCUSSION

All investigated PFBs were synthesized from fluorinated anilines and excess benzene (Cadogan reaction [2]), except 2-, 4- and 4,4'-fluorobiphenyl (2), (4) and (13), which are commercially available. The crude products were purified by chromatography and recrystallized from methanol or distilled. They were characterized by $^1\text{H-NMR}$ and mass spectrometry, elemental analysis and by their retention data in GC and HPLC analysis[3]. The spectroscopic data are given in Table 1. Pulse radiolytic studies were undertaken in DCE. The more commonly used oxidation by OH-radicals in aqueous solutions is not possible due to the limited water-solubility of the PFBs. Radiolysis of DCE by high energy electrons leads to DCE-radical cations and electrons [1,9,10].



The latter are removed by reaction with a further DCE molecule.



Upon pulse radiolysis of nitrogen-saturated solutions (10^{-3} M) of 1 - 13 in DCE with 1.5 μs pulses, characteristic transient absorption spectra were observed. Those for 1, 4 and 8 are shown in Fig. 1.

As seen in Table 1 there are no significant differences in the absorption maxima and first half-lives of the generated species. All compounds show three absorption maxima, two in the 360-400 nm region, and one weaker visible band around 700 nm. Only for 5, 8, 11 and 12 the second, lower energy band in the UV

TABLE 1

Yield and spectroscopic data of **1** - **13**

| Comp. | F-Subst. | Yield | mp (°C) ^a | MS(M ⁺) ^b | Ret. times (min) | | ¹ H-NMR (δ, ppm) ^e |
|-----------|----------|-------|----------------------|----------------------------------|------------------|-------------------|--|
| | | | | | GC ^c | HPLC ^d | |
| 1 | [5] | - | - | 154 | 5.65 | 4.18 | [4] |
| 2 | [5] | - | - | 172 | 5.67 | 4.06 | 7.11-7.58 (9H) |
| 3 | [6] | 64 | oil | 172 | 6.08 | 4.04 | 7.05 (m; 1H), 7.27, 4.9 (6H), 7.56-7.62 (2H) |
| 4 | [5] | - | - | 172 | 6.05 | 4.02 | 7.13 (m; 2H), 7.32-7.47 (3H), 7.52-7.60 (4H) |
| 5 | [6] | 47 | 46 | 190 | 6.42 | 3.98 | 7.11-7.23 (3H), 7.37-7.58 (5H) |
| 6 | [7] | 46 | 63 | 190 | 5.38 | 3.85 | 6.87-7.00 (2H), 7.34-7.54 (6H) |
| 7 | [6] | 48 | 31 | 190 | 5.82 | 3.83 | 7.00 (m; 1H), 7.08-7.19 (2H), 7.37-7.57 (5H) |
| 8 | [6] | 43 | 93 | 190 | 5.62 | 3.68 | 6.99 (m; 2H), 7.22-7.42 (6H) |
| 9 | [6] | 45 | 41 | 190 | 5.43 | 3.95 | 7.17-7.58 (8H) |
| 10 | [6] | 48 | oil | 190 | 5.57 | 4.04 | 6.79 (t; 1H), 7.07-7.17 (2H), 7.37-7.58 (5H) |
| 11 | [6] | 42 | 97 | 208 | 4.75 | 3.69 | 6.77 (d; 2H), 7.38-7.52 (5H) |
| 12 | [8] | 42 | 103 | 226 | 5.88 | 3.66 | 7.07 (t; 1H), 7.43-7.53 (5H) |
| 13 | [5] | - | - | 190 | 6.62 | 3.68 | AA'XX': 7.08-7.17 (4H), 7.45-7.53 (4H) |

^a Melting points were obtained by a Mettler melting point apparatus.^b Mass spectra were recorded by a Finnigan Mat 44 mass spectrometer.^c GC analysis was performed on a Varian 3700 gas chromatograph using a DB-210-CB capillary column.^d HPLC analysis was carried out on a Varian 500 liquid chromatograph using a Waters RAD PAK A column.^e NMR spectra were recorded by a Bruker WM 270 MHz spectrometer in CDCl₃.

appears as a shoulder. These results are summarized in Table 2. In all cases the absorption bands decay by the same kinetics suggesting that they arise from a single type of species, respectively.

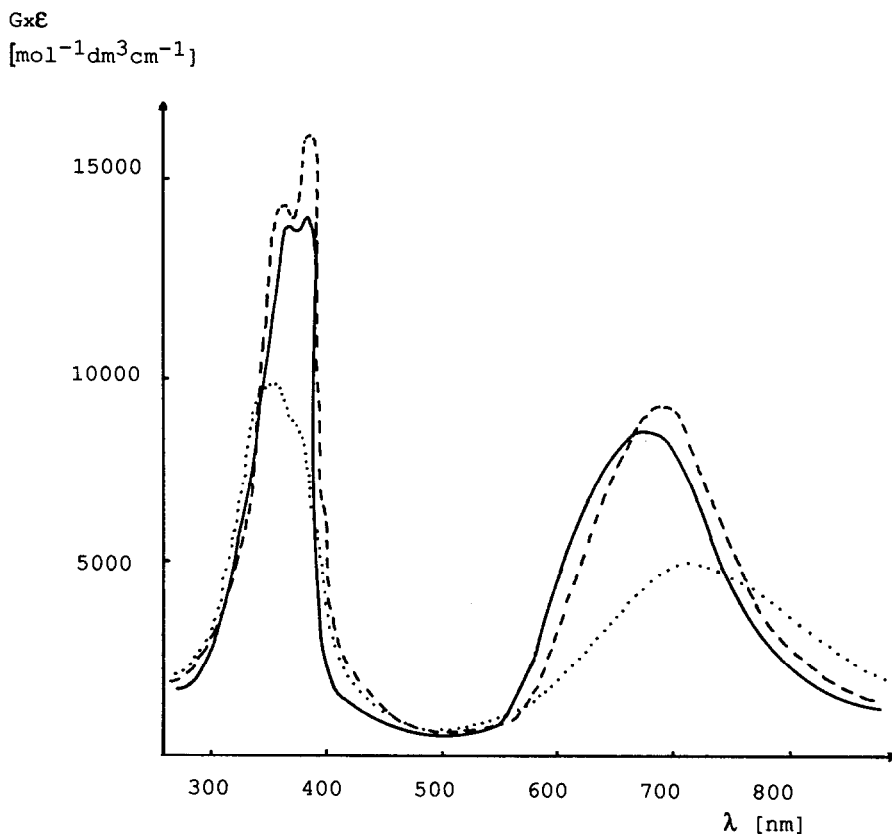


Fig. 1. Optical absorption spectra obtained by pulse radiolysis of **1**, **4** and **8** in DCE (10^{-3} M) and recorded $5\mu\text{s}$ after a $1.5\mu\text{s}$ pulse (— : biphenyl (**1**), --- : **4**, ... : **8**).

TABLE 2

Spectroscopic data of the radical cations of 1 - 13

| Comp. | λ_{max} [nm] | lg (Gx \mathcal{E}) ^a | $\tau_{1/2}$ [μ s] ^b |
|-----------|-----------------------------|--------------------------------------|--------------------------------------|
| <u>1</u> | 370, 392, 690 | 4.19, 4.22, 3.98 | 14 |
| <u>2</u> | 368, 390, 705 | 4.18, 4.18, 3.93 | 12 |
| <u>3</u> | 370, 391, 700 | 4.16, 4.15, 3.89 | 10 |
| <u>4</u> | 370, 396, 685 | 4.21, 4.22, 4.00 | 14 |
| <u>5</u> | 364, 388, 710 | 4.04, 3.96, 3.74 | 9 |
| <u>6</u> | 366, 384, 680 | 4.11, 4.07, 3.85 | 11 |
| <u>7</u> | 364, 384, 705 | 4.00, 3.92, 3.62 | 8 |
| <u>8</u> | 364, 386 ^c , 730 | 3.90, 3.78, 3.60 | 8 |
| <u>9</u> | 370, 394, 690 | 4.05, 4.04, 3.85 | 10 |
| <u>10</u> | 368, 388, 720 | 4.00, 4.00, 3.86 | 10 |
| <u>11</u> | 366, 384 ^c , 725 | 3.95, 3.87, 3.69 | 7 |
| <u>12</u> | 364, 382 ^c , 730 | 4.00, 3.90, 3.71 | 8 |
| <u>13</u> | 370, 392, 680 | 4.25, 4.27, 3.98 | 13 |

- ^a Gx \mathcal{E} -values based on an aqueous thiocyanate dosimeter [11]
^b First half-lives at an absorbed dose of approximate 3.7 Gy
^c Shoulder

Ortho-substituted compounds show a bathochromic shift of the absorption band in the near IR and a small hypsochromic shift of both bands in the UV (cf. 2, 5, 8 and 11). This hypsochromic shift is similar to that reported for several spectra of ortho substituted PCBs and PBBs (polybrominated biphenyls), which is due to the displacement from coplanarity by steric influence of the bulky chlorine and bromine substituents [12,13]. Similar effects have also been observed for 2-fluoro-benzidines [14]. The radical anions and the neutral radicals of

polyhalogenated and non-substituted biphenyls are known to be quenched by oxygen [1,15,16]. Our observed spectra do not change in the presence of oxygen and therefore we conclude that the observed optical absorption bands correspond to the radical cations of PFBs formed by oxidation by DCE-radical cations.



The yield of this reaction may differ since it has to compete with neutralization of the radical cation e.g. by the Cl^- , which is the main negative species formed in reaction (2).



From plots of the half-lives vs inversed dose a mixed order decay results for the radical cations of 2 - 13. Similar behaviour has already been reported for biphenyl itself (1) [15]. The half-lives are all similar or slightly lower than that of the biphenyl radical cation. Apparently the fluoro-substitution does not exert a strongly stabilizing or destabilizing effect on the biphenyl radical cation.

EXPERIMENTAL

All solvents were of reagent grade (DCE: J.T.Baker Co., hexane: Merck, benzene: Merck). The fluorinated anilines were purchased from Aldrich Co.

Synthesis

Synthesis was carried out as described [2]. After evaporation of the benzene the crude product was mixed (1 : 1) with Florisil (Macherey- Nagel). The obtained solid mixture was chromatographed on Alumina (Merck) and eluted with hexane. After recrystallisation from methanol or distillation under reduced pressure the products were obtained in > 99 % purity.

Pulse radiolysis

The pulse radiolysis set-up and procedure for optical detection are described in the literature [17]. The compounds were dissolved in DCE (10^{-3} M). The solvents were deaerated by bubbling with nitrogen (Linde). All experiments were carried out at room temperature. Due to the lack of a specific dosimeter system in DCE the radiation chemical yields are given in terms of Gx and calculated on the basis of an aqueous thiocyanate dosimeter [11]. The actual concentration of the formed species is unknown, so Gx has to be viewed as an approximation.

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