*J. Am. Chem. Soc.* **1981**, *103*, 903-906

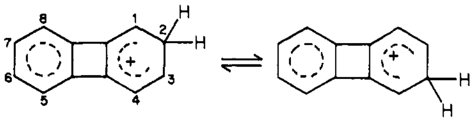
# Special Behavior of Octamethylbiphenylene in Acid. Acid-Catalyzed Electron Transfer

**Harold Hart,* Avraham Teuerstein, and Mary Ann Babin**

*Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824.* *Received August 18, 1980*

**Abstract:** Dilute solutions of octamethylbiphenylene (**2**) in chloroform show $^1$H singlets at δ 2.02 and 2.16 and $^{13}$C peaks at δ 16.14 and 16.96 for the C2,3,6,7 and C1,4,5,8 methyls, respectively. When treated with 0.01–10 equiv of trifluoroacetic acid (TFA), the peaks due to the C2,3,6,7 methyls disappear, but the peaks due to the C1,4,5,8 methyl protons and carbons remain. Such solutions also exhibit an ESR spectrum attributed to the octamethylbiphenylene radical cation $\mathbf{2}^{+\cdot}$. Only 0.02–0.2% of **2** is converted to $\mathbf{2}^{+\cdot}$, and the odd electron density in $\mathbf{2}^{+\cdot}$ is mainly at C2,3,6,7; consequently, only the NMR peak due to those methyls is wiped out by the exchange between **2** and $\mathbf{2}^{+\cdot}$. An acid-catalyzed electron-transfer mechanism is proposed to rationalize the results. A similar effect was noted with trichloroacetic acid, trifluoroacetic anhydride, or iodine in place of TFA but not with acetic acid. Biphenylene (**1**) itself did not show any comparable behavior. 2,3,6,7- and 1,4,5,8-tetramethylbiphenylenes showed intermediate behavior. Cyclic voltammetry indicates an 11.8-kcal/mol difference in oxidation potentials between **1** and **2**, which helps explain their different behavior toward TFA.

Biphenylene is protonated preferentially at the 2-position, as shown by isotopic exchange in trifluoroacetic acid (TFA) containing 3% perchloric acid.[1] At −80 °C in stronger acid ($HSO_3F$–$SbF_5$–$SO_2ClF$) ion **1-H**$^+$, which is involved in such exchanges, can be observed directly by NMR.[2] At higher temperatures in the same solvent, degenerate rearrangement of the C2–C3 protons occurs ($k \simeq 25$ s$^{-1}$ at −32 °C).[2]

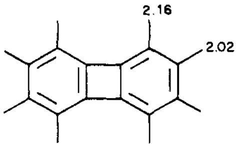


1-H$^+$

We studied the behavior of octamethylbiphenylene (**2**)[3] in acid with the purpose of determining whether similar degenerate methyl migrations occurred and whether they would be confined to positions 2, 3, 6, and 7 or whether they would involve methyls on all positions of the biphenylene framework. We found that the behavior of **2** in TFA differs substantially from that of unsubstituted biphenylene and is quite remarkable in that one can measure NMR and ESR spectra on exchanging species present simultaneously in such solutions. Our observations can be rationalized in terms of an acid-catalyzed electron-transfer process.

## Results and Discussion

In $CDCl_3$, the $^1$H NMR spectrum of **2** consists of two sharp singlets at δ 2.16 and 2.02 for the C1,4,5,8 and C2,3,6,7 methyl protons, respectively.[4] Addition of TFA to such solutions causes the peak at δ 2.02 to *disappear*, but the peak at δ 2.16 remains with varying degrees of sharpness, depending on the molar ratio of TFA/**2** (Figure 1). At a TFA/**2** molar ratio of only 0.1 the peak at δ 2.02 disappears in less than 2 min, whereas the peak at δ 2.16 remains sharp for more than 5 h. At higher TFA/**2** ratios disappearance of the δ 2.02 is instantaneous, and although the peak at δ 2.16 remains, it gradually broadens. On the other hand, at a TFA/**2** molar ratio of only 0.01, it takes several minutes for the δ 2.02 peak to disappear, and the peak reappears after several hours. With a 1:1 solution of TFA/**2** in $CDCl_3$ containing a small amount of added $CHCl_3$ as an internal reference, integration showed that although the peak at δ 2.16 broadened appreciably, its area remained constant over 15 h. When any of these solutions was quenched with water, octamethylbiphenylene was recovered quantitatively.



**2**

Similar results were obtained with the $^{13}$C NMR spectra. The methyl carbons of **2** appear at δ 16.96 and 16.14 in $CDCl_3$; with added TFA (1:1) the peak at δ 16.14 disappeared whereas that at δ 16.96 remained.

The presence or absence of oxygen had no effect on the described NMR behavior. Use of TFA-*d* did not result in any significant deuterium incorporation in the recovered octamethylbiphenylene.

Solutions of **2** in chloroform containing TFA also exhibit an ESR spectrum (Figure 2). The signal is broad at room temperature (3400 G; $\Delta H_{pp} = 10 \pm 1$ G) but resolves to a 13-line spectrum at −60 °C, $a_H = 2$ G. A standard ruby was used to measure the spin concentrations (Table I), which were a function of time and molar ratio of TFA/**2**. About 10 times as many spins are produced when the TFA is present in large excess (10:1) as when the molar ratio of TFA/**2** is 1:1; in each case, the spin concentration increases with time and then tapers off or decreases slightly. At a TFA/**2** molar ratio of 1:1, only about 0.02% of the octamethylbiphenylene is present in a form which gives rise to

Table I. Percent Spin ($\times 10^2$) in $4 \times 10^{-2}$ M Solutions of **2** in $CDCl_3$ Containing Added TFA

| | molar ratio of TFA/2 | |
|---|---|---|
| time, h | 1 | 10 |
| 0.083 | 1.5 | 3.0 |
| 2 | 2.2 | 7.5 |
| 6 | 2.7 | 14.7 |
| 21 | 2.4 | 23.9 |
| 47 | 2.0 | 27.1 |

---

[1] Streitwieser, Jr. A.; Schwager, I. *J. Am. Chem. Soc.* **1963**, *85*, 2285. Blatchly, J. M.; Taylor, R. *J. Chem. Soc.* **1964**, 4641. Streitwieser, Jr., A.; Lewis, A.; Schwager, I.; Fish, R. W.; Labana, S. *J. Am. Chem. Soc.* **1970**, *92*, 6525. Figeys, H. P.; Defay, N.; Martin, R. H.; McOmie, J. F. W.; Ayres, B. E.; Chadwick, J. B. *Tetrahedron* **1976**, *32*, 2571.

[2] Bodoev, N. V.; Mamatyuk, V. I.; Krysin, A. P.; Koptyug, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 1199; *Bull. Akad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1978**, *27*, 1043.

[3] Hart, H.; Teuerstein, A. *Synthesis* **1979**, 693.

[4] The assignment is clear by comparison with reference compounds; for example, the methyl protons in 1,4,5,8-tetramethyl- and 2,3,6,7-tetramethylbiphenylene appear at δ 2.12 and 2.02, respectively, in the same solvent.

[5] We are indebted to Professor James L. Dye for assistance with these measurements.

0002-7863/81/1503-903$01.00/0

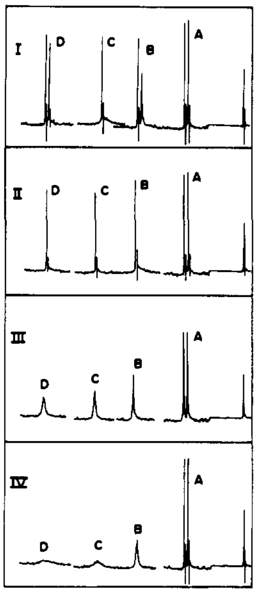


Figure 1. $^1$H NMR spectra of octamethylbiphenylene (2, 4 × $10^{-2}$ M) in TFA and CDCl$_3$. The molar ratio of TFA/2 from top to bottom is 0.01, 0.1, 1, and 10. Spectra A are taken before addition of TFA and show peaks at $\delta$ 2.02 and 2.16. Spectra B–D are shifted in scale and were taken after 2 min, 2 h, and 5 h, respectively; when they show only one peak, it is at $\delta$ 2.16.

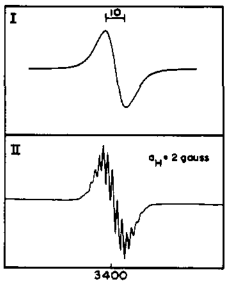


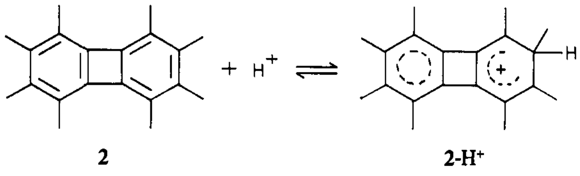
Figure 2. ESR spectra of octamethylbiphenylene (2, 4 × $10^{-2}$ M) in CDCl$_3$ containing TFA (ratio of TFA/2 of 1) at room temperature (top) and at −60 °C (bottom).

the ESR signal. Use of TFA-*d* did not change the shape of the signal, suggesting that the signal does not come from a protonated (deuterated) radical.

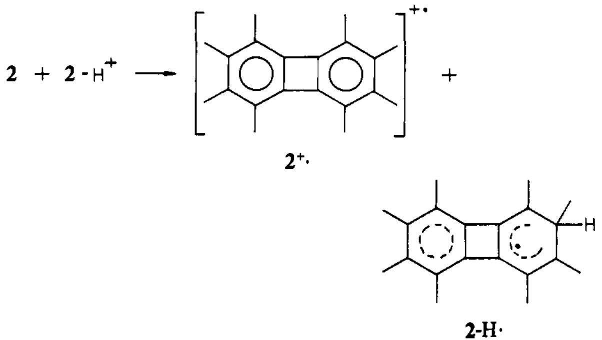
Trichloroacetic acid (TCA), trifluoroacetic anhydride (TFAA), and iodine had the same effects as did TFA on the proton NMR spectrum of octamethybiphenylene. For example, at only 0.1 mol/mol of 2, each caused the $\delta$ 2.02 peak to disappear and the $\delta$ 2.16 peak to remain sharp. Spin concentration measurements showed TFAA to be as effective as TFA at the same concentrations, but TCA produced much lower spin concentrations (only 0.0024% and 0.012% at TCA/2 molar ratios of 1 and 10, respectively). Acetic acid was ineffective at bringing about the described NMR or ESR changes.

Chloroform solutions of 2 to which TFA, TCA, or TFAA is added have a beautiful blue color. Solutions of 2 and TFA (each 3 × $10^{-3}$ M) in chloroform have a $\lambda_{max}$ at 600 nm and a shoulder at 560 nm. Using the spin concentration measurements (Table I) and assuming that the same species which gives the ESR signal also gives the visible absorption, we estimate $\epsilon = 2 \times 10^3$. There is no significant change in the ultraviolet region of the spectrum on addition of TFA.

**Mechanism.** We ascribe all of the above phenomena to the formation in low concentration of the octamethylbiphenylene radical cation, probably according to the scheme shown in eq 1–3. Protonation at C2 (eq 1) is followed by electron transfer from octamethylbiphenylene to the carbocation, giving radical cation $2^{+\cdot}$ and the radical 2-H· (eq 2). Degenerate electron transfer between 2 and $2^{+\cdot}$ (eq 3) should result in a broad ESR signal which



(1)



(2)

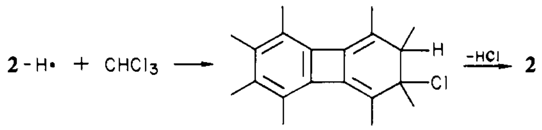
$2 + 2^{+\cdot} \rightleftharpoons 2^{+\cdot} + 2$ (3)

only shows fine structure when the temperature is lowered. The 13-line spectrum observed at −60 °C is consistent with $2^{+\cdot}$, where the odd electron density (and the positive charge) are located predominantly at C2,3,6, 7. In the biphenylene radical cation itself ($1^{+\cdot}$), the ESR spectrum shows a major five line pattern due to splitting by the C2,3,6,7 protons ($a_H$ = 3.69 G), with only minor further splitting by the C1,4,5,8 protons ($a_H$ = 0.21 G).[6,7]

The NMR integration experiments (no measurable decrease in area of the $\delta$ 2.16 peak), the spin counting results (only 0.02% of spins), and the quenching results all show that the predominant species present in these acidic solutions is octamethylbiphenylene itself (approximately 99.98% 2, 0.02% $2^{+\cdot}$). But because of electron exchange (eq 3), the $\delta$ 2.02 signal due to the methyl protons at C2,3,6,7 is wiped out instantly; the much lower odd-electron density in $2^{+\cdot}$ at C1,4,5,8 permits the $\delta$ 2.16 signal to persist.

More needs to be said about the proposed electron transfer in eq 2 and the fate of 2-H·. Biphenylene is somehwat destabilized because of the four-membered ring. Destabilization is partly due to strain and partly to antiaromaticity. The highest occupied molecular orbital is fairly close to being nonbonding. This situation should be worsened in 2 because of electron donation to the ring by the eight methyl groups. Consequently we expect 2 to be a better electron donor than 1, and the reaction in eq 2 might proceed with 2 but not with 1 (see the cyclic voltammetry results below).

Regarding the fate of 2-H·, one likely possibility in solvents such as chloroform is that it is rapidly reconverted to 2 (eq 4) through chlorine atom abstraction and loss of hydrogen chloride.



(4)

2-HCl

When isopropylbenzene was substituted for chloroform in the

---

(6) McDowell, C. A.; Rowlands, J. R. *Can. J. Chem.* **1960**, *38*, 503. Carrington, A.; Dos Santos-Veiga, J. *Mol. Phys.* **1962**, *5*, 285. Hindle, P. R.; Dos Santos-Veiga, J.; Bolton, J. R. *J. Chem. Phys.* **1968**, *48*, 4703.

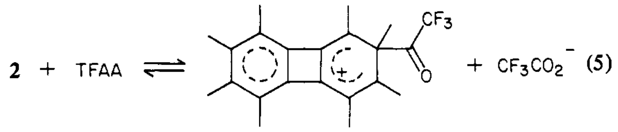
(7) The reason why odd electron density is confined mainly to C2,3,6,7 in radicals such as $2^{+\cdot}$ or 2-H· (and why the positive charge in 2-H$^+$ or $2^{+\cdot}$ is similarly localized, why biphenylenes undergo electrophilic attack mainly at C2, etc.) has often been discussed. In brief, such structures convey less cyclobutadiene-like (hence, antiaromatic) character to the central ring than do structures with odd electron density (or charge) at C1,4,5,8. For discussions, see: Cava, M. P.; Mitchell, M. J. "Cyclobutadiene and Related Compounds"; Academic Press: NY, 1967; Chapters 10 and 11 and pp 400–411.

(8) The Hückel energies for the HOMO's of biphenyl and biphenylene, for example, are 0.705$\beta$ and 0.455$\beta$, respectively: Coulson, C. A.; Streitwieser, Jr., A. "Dictionary of $\pi$-Electron Calculations"; W. H. Freeman and Co.: San Francisco, 1965.

experiments we have described, workup after quenching gave recovered **2** which showed an M + 2 peak in its mass spectrum. Although very weak, the peak was five times more intense than the M + 2 peak obtained with pure **2**, suggesting the possible presence of some dihydro-**2**, possibly resulting from reaction of **2**-H· with isopropylbenzene.[9]

The increased spin concentration with increased acidity (Table I) can be rationalized, since the equilibrium in eq 1 should be shifted to the right with higher acidity. The lower spin concentration with TCA and lack of reaction with acetic acid are similarly explained. The gradual increase in spin concentration with time (Table I) suggests that there is a rate-limiting step, probably eq 2. The final tapering off or eventual decrease in spin concentration suggests that there is some reaction whereby $2^{+\cdot}$ is consumed. This is also seen in the NMR experiment at a TFA/**2** ratio of 0.01, where the peak at δ 2.02 disappears and then reappears after 5 h (Figure 1). The mechanism by which radical cation is consumed cannot at present be specified.

Brief study of the reaction of **2** with trifluoracetic anhydride was prompted by the recent report that TFAA oxidizes tertiary amines.[10] TFAA was equally effective as TFA in producing a radical cation from **2**, as measured by spin counting. Possibly TFAA replaces the acid as an electrophile in the first step of the reaction sequence (eq 5), or, alternatively, an electron is transferred



(5)

directly from **2** to TFAA. This may well be the reaction involved in radical cation formation from **2** and iodine.

**Other Methyl-Substituted Biphenylenes.** Biphenylene itself, treated in chloroform solution ($10^{-2}$ M) with more than a 10-mol excess of TFA, showed no changes in its $^1$H NMR spectrum similar to those observed with **2**, nor did these solutions exhibit a color change or ESR spectrum.

2,3,6,7-Tetramethylbiphenylene (**3**) in $CDCl_3$ ($4 \times 10^{-2}$ M) containing an equivalent amount of TFA lost its methyl signal (δ 2.02) in about 1 h, but the aromatic proton peak at δ 6.23 remained sharp and undiminished in area even after 20 h. With a higher acid ratio (TFA/**3** ratio of 10) the methyl signal was gone in a few minutes whereas the aromatic signal remained but broadened appreciably.

It seemed from these experiments that radical cation was formed, but in lower concentration than with **2**, and this conclusion was verified by the ESR results. A solution with a TFA/**3** ratio of 10 in chloroform at room temperature gave a broad ESR signal at 3400 G ($\Delta H_{pp} = 15 \pm 1$ G); spin counting showed 0.018% of **3** present as the species with spin. This is only about 10% of the number of spins observed under comparable conditions with **2**. At −60 °C, the ESR signal resolved into 17 lines.

Even less conversion to radical cation was observed with 1,4,5,8-tetramethylbiphenylene (**4**). NMR experiments with a TFA/**4** ratio of 1 or 10 showed only a small decrease in the aromatic proton signal (δ 6.26) relative to the methyl signal (δ 2.12) after 20 h. At the higher acid ratio, the aromatic proton signal did show broadening. At the 10:1 ratio, the solution gave a weak ESR signal ($\Delta H_{pp} = 8$ G). Spin counting gave 0.0002% of **4** present as the species with spin. The signal was broad but showed some splitting at −70 °C.

It is clear from these results that radical cation is produced through acid catalysis with the following order of ease: **2** > **3** ≫ **4** > **1**. Methyl substitutents in all positions increase the basicity of the biphenylene (B); methyls at C2,3,6,7 particularly stabilize $BH^+$ and $B^{+\cdot}$ since the positive charge and/or odd-electron densities are greatest at these positions. Thus **2** and **3**, which have methyl substituents in the most strategic positions, show radical cation formation and the accompanying dramatic effect on the NMR spectrum; **4**, with methyls less favorably located, shows an ESR signal, but apparently the radical cation concentration is too low to affect the NMR spectrum, and with biphenylene itself neither result is observed.[11]

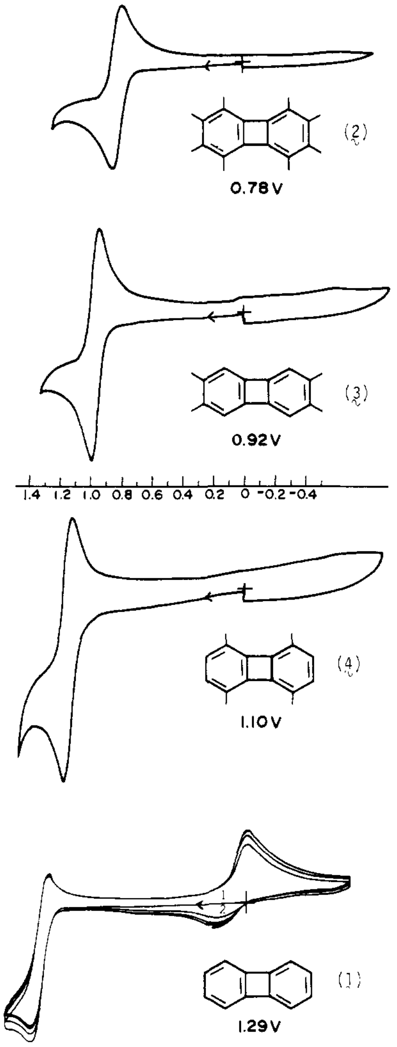


**Figure 3.** Cyclic voltammograms of **1**–**4** in acetonitrile containing tetrabutylammonium perchlorate as supporting electrolyte.

**Cyclic Voltammetry.** In order to place these results on a more quantitative basis, cyclic voltammograms were measured on **1**–**4** in acetonitrile with tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte.[12] The results are given in Figure 3. There is a progression in oxidation potentials which is in agreement with the NMR-ESR experiments and a very substantial 0.51-V (11.8 kcal/mol) difference in oxidation potentials between **1** and **2**.[13] Except for biphenylene itself, only a single oxidation process is seen, i.e., radical cation formation. With biphenylene, oxidation to the radical cation in the first cycle is followed by two reduction processes, the second presumably being reduction of neutral biphenylene to its radical anion; subsequent cycles show both processes, with $E_{1/2}$ for radical anion formation being 0.08 V. There was no evidence for reduction of **2**–**4** to radical anions under these conditions. If higher anodic potentials were applied additional, irreversible peaks were noted, possibly due to dications as has been

---

[9] We searched for but could not find dicumyl; if formed, however, the expected yield would probably be much less than 0.1%. The mass spectrum did show a significant peak corresponding to the *m/e* of $C_6H_5\dot{C}(CH_3)_2$.

[10] Schreiber, S. L. *Tetrahedron Lett.* **1980**, 1027.

[11] Of course with stronger acids and oxidizing agents such as concentrated sulfuric acid, the radical cation of biphenylene can be produced.[6]

[12] We are indebted to Professor C. K. Chang and Mr. Brian Ward for assistance with these measurements.

[13] The value of 1.29 V for **1** is in reasonable agreement with the value 1.35 V reported in $CH_2Cl_2$–TFAA–TFA (45:5:1) by: Ronlan, A.; Parker, V. D. *J. Chem. Soc., Chem. Commun.* **1974**, 33.

observed with biphenylenes under more strenuous oxidizing conditions.[13,14]

**Summary.** Octamethylbiphenylene (**2**, $10^{-2}$ M in chloroform) is converted to its blue radical cation by 0.01–10 equiv of trifluoroacetic acid. The fraction of **2** converted to radical cation is only 0.02–0.2%, allowing one to measure NMR and ESR spectra on the same solutions. The NMR spectrum of **2** under these conditions shows only a singlet for the methyls at C1,4,5,8; the signal for the C2,3,6,7 methyls is wiped out as a consequence of exchange between **2** and its radical cation and the fact that odd electron density in the radical cation is located primarily at C2,3,6,7. These phenomena are not observed with biphenylene itself because of the 11.8-kcal/mol difference in oxidation potential between it and its octamethyl derivative. Methyls at the 2, 3, 6, and 7 positions are shown to be more important than those at positions 1, 4, 5, and 8 in bringing about these phenomena. A mechanism involving acid-catalyzed electron transfer is proposed to account for the results, the key step being electron transfer from a neutral biphenylene to its C2-protonated form.

## Experimental Section

$^1$H NMR spectra were run on a Varian T-60 or A56-60 spectrometer. $^{13}$C NMR spectra were determined on a Varian CFT-20 instrument. All chemical shifts are reported in parts per million ($\delta$) relative to tetramethylsilane as an internal reference. A Varian E-4 spectrometer was used for the ESR measurements, and UV–visible spectra were recorded on a Cary 17 spectrophotometer. Melting points are uncorrected.

**Preparation of the Biphenylenes.** Biphenylene (**1**) was prepared from anthranilic acid.[15] Octamethylbiphenylene (**2**) was prepared from 1,2-dibromo-3,4,5,6-tetramethylbenzene.[3] 1,4,5,8-Tetramethylbiphenylene (**4**) was prepared from 3,6-dimethylanthranilic acid via the diazonium carboxylate:[15,16] mp 228.5–229.0 °C; NMR ($CDCl_3$) $\delta$ 2.12 (12 H, s), 6.26 (4 H, s).[17] 2,3,6,7-Tetramethylbiphenylene (**3**) was prepared from 4-bromo-5-iodo-*o*-xylene[18] by reaction with magnesium in ether:[19] mp 231.0–231.5 °C (lit.[19] mp 224–225 °C); NMR ($CDCl_3$) $\delta$ 2.02 (12 H, s), 6.23 (4 H, s).

**NMR Experiments with Octamethylbiphenylene (2).** Stock solutions of **2** ($4 \times 10^{-2}$ M) and trifluoroacetic acid (2 M) in $CDCl_3$ were mixed in appropriate amounts such that the ratios of TFA/**2** were 0.01, 0.1, 1, and 10, and the spectra were recorded with time. Typical results are shown in Figure 1 and are described in the text. An integration experiment was performed with a TFA/**2** ratio of 1 and 1% $CHCl_3$ added as a reference. The ratio of chloroform to total aromatic methyl signal was initially 0.347 (before addition of TFA). After addition of TFA, the ratios were 0.689 (2 min), 0.686 (30 min), and 0.682 (15 h). At this point water was added to the NMR tube, and the ratio became 0.346. In the initial and final measurements, methyl singlets were present at $\delta$ 2.02 and 2.16, whereas in the intermediate measurements, only the $\delta$ 2.16 signal was present.

With a TFA/**2** ratio of 1 there was no change in the singlet at $\delta$ 2.16 as the temperature was lowered to –70 °C (180-MHz Bruker spectrometer).

The effect of oxygen was studied in the following ways. A degassed ($10^{-4}$ torr) solution of TFA in $CDCl_3$ was distilled into an NMR tube containing a similarly degassed solution of **2** ($4 \times 10^{-2}$ M). The molar ratio of TFA/**2** was 1. After an additional freeze–thaw cycle, the tube was sealed and warmed to room temperature. The blue solution showed only a singlet at $\delta$ 2.16. In another experiment, oxygen was bubbled through a 1:1 solution of TFA/**2**, and the spectrum was determined every hour for 5 h; there was no change in the position or area of the $\delta$ 2.16 signal. A control with oxygen bubbling through **2** (but TFA omitted) also showed no change in the NMR spectrum (equal area peaks at $\delta$ 2.02 and 2.16).

Table II. Cyclic Voltammetry Data

| compd | $10^4 \times$ (concn), M | scan rate, mV/s | range, $\mu$A/V | $E_{p,a} - E_{p,c}$ |
|---|---|---|---|---|
| **1** | 15 | 500 | 100 | 200[a] |
| **2** | 5.3 | 50 | 10 | 80 |
| **3** | 1.44 | 50 | 5 | 60 |
| **4** | 5.3 | 50 | 5 | 80 |

[a] Refers to the left-hand wave in Figure 3.

The $^{13}$C NMR spectrum of **2** in $CDCl_3$ showed signals at $\delta$ 16.14, 16.96 (methyls), 123.66, 134.22, and 146.46 (aromatic). A spectrum with a TFA/**2** ratio of 1 showed only one signal at $\delta$ 16.93 (6-h acquisition time, 26 291 pulses).

Quenching experiments were done as follows. A solution of **2** (100 mg) in $CDCl_3$ (50 mL) was treated with excess (10×) TFA. The blue solution showed a broad singlet at $\delta$ 2.16. After 5 h the solution was quenched with aqueous sodium bicarbonate and worked up to give 98 mg of pure (NMR, melting point, mass spectrum) recovered **2**. In a similar experiment with TFA-*d*, quenched with $D_2O$, the mass spectrum of recovered **2** showed no deuterium incorporation.

Experiments on the NMR spectrum of **2** in the presence of trichloroacetic acid (TCA), trifluoroacetic anhydride (TFAA), and iodine were carried out in the same manner as with TFA. The results are described in the text.

**ESR Experiments with Octamethylbiphenylene (2).** Spectra were measured on $4 \times 10^{-2}$ M $CDCl_3$ solutions of **2** to which TFA was added to give the desired TFA/**2** ratios (1 and 10). Spectra at room temperature and –60 °C are shown in Figure 2 and are described in the text. Intermediate spectra were taken at 10 °C intervals, and the onset of hyperfine splitting was first visible at –10 °C. Similar spectra were obtained with TFAA and TCA.

Spin concentrations were measured against a standard ruby ($Al_2O_3$;$Cr^{3+}$) by using eq 6, where $I$ is the intensity of the ESR signal

$$\frac{I(\Delta H_{pp})^2/ar}{I_0(\Delta H_{pp})_0{}^2/a_0r_0} = \frac{1}{2}\,\frac{Ng}{N_0g_0}\,\frac{1}{U^{\alpha_0\beta_0}} \qquad (6)$$

(height of the signal from peak to peak in arbitrary units), $\Delta H_{pp}$ is the width of the signal from peak to peak, $a$ is the modulation amplitude, $r$ is the receiver gain, $N$ is the number of spins, $g = 2.003$ (average values for most organic radicals), and $U^{\alpha_0\beta_0}$ is the orientation factor for the standard (=1.162). Subscript zeros are defined the same way for the ruby standard, with $N_0 = 11.96 \times 10^{15}$ and $g_0 = 1.9818$. The percent of molecules present as radicals (times $10^2$) at various times for **2** and TFA are given in Table I. For a TFAA/**2** ratio of 1 the percent spin (5 min) was $1.92 \times 10^{-2}$; for a TFAA/**2** ratio of 10 the value was $2.71 \times 10^{-2}$; for TCA/**2** ratios of 1 and 10 the values where $2.44 \times 10^{-3}$ and $1.24 \times 10^{-2}$, respectively.

**Electronic Spectra of 2 and TFA.** A solution of **2** ($3 \times 10^{-3}$ M) in methylene chloride had $\lambda_{max}$ 371 nm ($\epsilon$ 5500), 353 (4300), 335 (2400), 320 (sh), 270 (86 300), and 262 (sh). Addition of 0.01 mL of 0.1 M TFA in $CH_2Cl_2$ (molar ratio of TFA/**2** of 1) did not change the shape of the spectrum but decreased peak intensities by about 3%. Addition of 0.1 mL of TFA solution (molar ratio of TFA/**2** of 10) caused a 9% decrease in peak intensity at 371 nm but increased the peak intensities at 353 and 335 nm by about 3%. The $\lambda_{max}$ of the 353-nm peak shifted to 350 nm. The radical cation appears to have an absorption at about 340 nm. Excess TFA shifted the 270-nm peak to 275 nm. Although **2** shows no visible absorption, addition of TFA produced a maximum at 600 nm with a shoulder at 560 nm. From the optical density at a TFA/**2** ratio of 1 and the ESR spin count, we estimate $\epsilon = 2 \times 10^3$.

**Experiments with 3, 4, and 1.** These were carried out in the same manner as described for **2**, and the significant results are discussed in the text.

**Cyclic Voltammetry.** The apparatus was a Bioanalytical Systems, Inc., Model CV-1A instrument which uses a platinum electrode against a SCE reference with a sodium acetate salt bridge. The data are summarized in Table II. In all cases the concentration of TBAP was 0.1 M. The difference between the anode and cathode potentials indicates that the oxidation to the radical cation is electrochemically reversibly with **2–4**. Values of $E_{1/2}$ are given in Figure 3.

**Acknowledgment.** We are indebted to the National Science Foundation for financial support of this research (Grant CHE-05956).

---

(14) Bodoev, N. V.; Matatyuk, V. I.; Krysin, A. P.; Koptyug, V. A. *Izv. Akad. Nauk, SSSR, Ser. Khim.* **1976**, 2644; *Bull. Akad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1976**, 2464. Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 6045.

(15) Logullo, F. M.; Seitz, A. M.; Friedman, L. *Org. Synth.* **1968**, *48*, 12.

(16) Hart, H.; Jiang, J. B.-C.; Sasaoka, M. *J. Org. Chem.* **1977**, *42*, 3840.

(17) Olah and Liang[14] report chemical shifts of $\delta$ 2.58 and 6.83; we have no explanation for the discrepancy.

(18) Varma, P. S.; Venkat Raman, K. S. *J. Indian Chem. Soc.* **1935**, *12*, 245.

(19) Constantine, P. R.; Hall, G. E.; Harrison, C. R.; McOmie, J. F. W.; Searle, R. J. G. *J. Chem. Soc. C* **1966**, 1767.