

ions as calculated from the pH. The pH of the reaction solutions, measured with a Radiometer PHM-26 pH meter and Type G202B electrode, was taken as $-\log a_{H^+}$. The added 0.52 M acetone was assumed to change pK_w by the same amount that the same mole fraction of dioxane would. This amount, calculated by interpolation,³⁷ increases pK_w at 35° from 13.681 to 13.805. The values of k_B calculated from amine concentrations obtained in this way, which are listed in Table III, differ by an average of 10% from values that were obtained from amine concentrations calculated from the pH of the reaction solution, pK_w , the pK of the protonated amine, and the total concentration of added amine. Values of k_B obtained in the latter way fit the observed k_6 values more poorly than do the k_B values for monoamines listed in Table III. However, the former method of calculation of concentrations cannot be used for diamines and so the latter was. For both methods of

(37) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York, N. Y., 1958, pp 662, 754, 756.

calculation activity coefficients were calculated from the Davies equation.³⁸

pK Determinations. Potentiometric measurements of pK values were carried out as described previously.¹⁹ All the measurements were carried out at ionic strengths of 0.2 or below except for those on the ω -dimethylaminoalkylamines, which were reported previously,¹⁷ and those on the compounds $Me_3N^+(CH_2)_nNMe_2$ where n is 2 and 3, which were carried out in the ranges of 0.02–0.30 and 0.09–0.30, respectively.

Acknowledgments. We thank Dr. Wu-Shyong Li for making a kinetic run, a pK determination, and a number of calculations, Mrs. Nancy W. Flachskam for preparing some of the DAMCA's, the OSU Instruction and Research Computer Center for the grant of computer time, and the Dow Chemical Company for the polyethylenimines.

(38) C. W. Davies, *J. Chem. Soc.*, 2093 (1938).

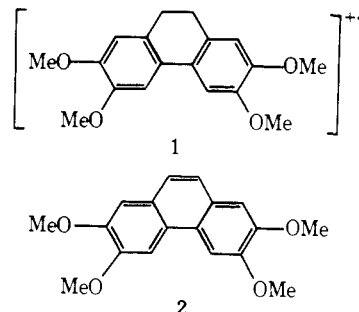
Anodic Oxidation of Methoxybiphenyls. The Effect of the Biphenyl Linkage on Aromatic Cation Radical and Dication Stability

Alvin Ronlán,^{1a} Jim Coleman,^{1a} Ole Hammerich,^{1b} and Vernon D. Parker*^{1b}

Contribution from the Lund Institute of Technology, Chemical Center, Lund 7, Sweden, and the Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark. Received February 6, 1973

Abstract: The biphenyl linkage was shown to have a remarkable stabilizing effect on both cation radicals and dications derived from methoxy-substituted aromatic compounds. In the series of para-substituted compounds $[MeO(C_6H_4)_nOMe]$, maximum stability of ions was observed with $n = 2$ and 3, while the compound with $n = 4$ gave ions more difficultly formed and much less stable. A variety of dimethoxybiphenyls substituted in varying degree and manner with methyl groups have been investigated by voltammetry in acetonitrile, dichloromethane, and trifluoroacetic acid. Steric hindrance to planarity of the two phenyl rings was found to be an important factor in determining ion stability. Slow deprotonation of methoxy-substituted 9,10-dihydrophenanthrene cation radicals and dications was observed although the latter are formally the second conjugate acids of the corresponding phenanthrenes.

In a preliminary communication, we described the intramolecular coupling reaction of 3,3',4,4'-tetramethoxybiphenyl in acetonitrile to the dihydrophenanthrene and pointed out the unusual stability of the cation radical of the product.² The ultimate fate of the cation radical (**1**) was the formation of the phen-



(1) (a) Lund Institute of Technology; (b) University of Copenhagen.
(2) A. Ronlán and V. D. Parker, *Chem. Commun.*, 1567 (1970).

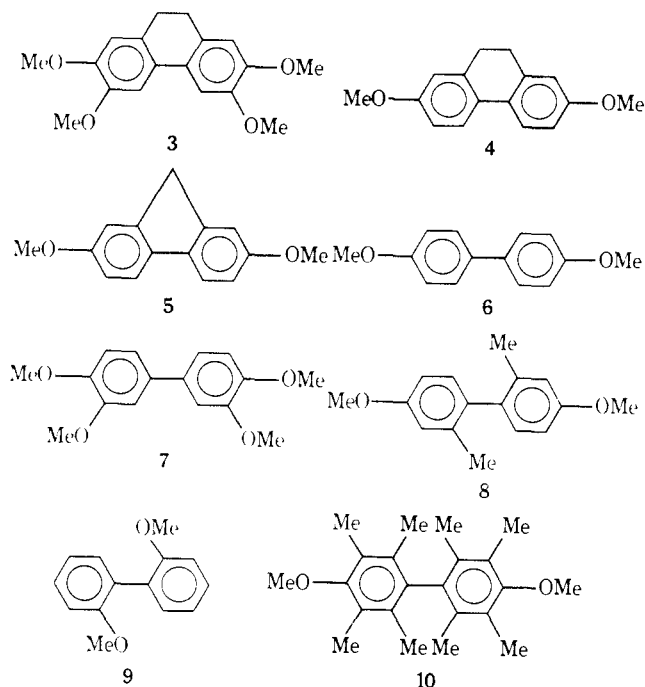
anthrene (**2**). Thus, the long lifetime of **1** could only be due to a slow deprotonation. The latter provided the first clear evidence for the existence of the ECE mechanism of side chain anodic substitution, a reaction on which differing views had been presented.^{3,4} Furthermore, it was pointed out that **1** is formed considerably more easily than **2** is oxidized and that the cation radical of **2** is very short lived. These observations led us to the study of the effect of the biphenyl linkage on the stability and reactions of aromatic cation radicals and dications.

Results

The structures of the methoxybiphenyls which were studied are listed below.

(3) A. E. Coleman, H. H. Richtol, and D. A. Aikens, *J. Electroanal. Chem.*, **18**, 165 (1968).

(4) (a) V. D. Parker, *J. Electroanal. Chem.*, **21**, App. 1 (1969); (b) V. D. Parker and R. N. Adams, *Tetrahedron Lett.*, 1743 (1969).



Voltammetry in Acetonitrile. Cyclic voltammetric analysis of compounds 3–7 indicated that all compounds undergo reversible or quasireversible one-electron oxidation at a voltage sweep rate of 86 mV/sec. The peak separation for the anodic and cathodic processes ($E_{p_{an}} - E_{p_{cath}}$) approached 60 mV and the ratio of peak currents ($i_{p_{cath}}/i_{p_{an}}$) was very close to 1.0 in all cases. On the other hand, compound 8 showed appreciable reversibility only at sweep rates of 10 V/sec or greater while reversibility was not observed even at the latter sweep rate with compounds 9 and 10. The technique used for the voltammetric measurements was to treat the acetonitrile solution with neutral alumina just before making the measurements in the manner recently described.⁵ The results of the voltammetric oxidation of the methoxybiphenyls are summarized in Table I.

Table I. Voltammetry of Methoxybiphenyls in Acetonitrile

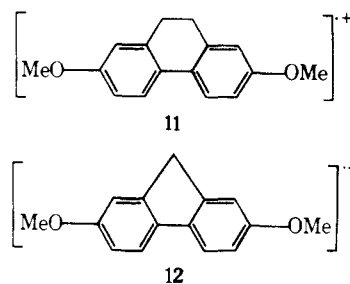
Compd ^a	$E_{p_{an1}}^b$	$E_{p_{cath1}}^b$	$E_{p_{an2}}^b$	$E_{p_{cath2}}^b$	$\Delta E, mV^c$
3	0.94	0.88	1.25 ^d		310
4	1.14	1.07	1.50	1.38	360
5	1.08	1.02	1.46	1.40	380
6	1.28	1.22	1.55	1.48	270
7	1.12	1.05	1.35 ^d		230
8	1.46 ^d				
9	1.45 ^d				
10	1.63 ^d				

^a 1.0 mM in MeCN containing *n*-Bu₄NBF₄ (0.2 M); voltammetry carried out over solid neutral alumina. ^b V vs. the aqueous saturated calomel electrode measured at a sweep rate of 86 mV/sec. ^c $\Delta E = E_{p_{an2}} - E_{p_{an1}}$. ^d Irreversible peak. ^e The reported potentials are reliable to ± 5 mV.

Of the compounds listed in Table I, 4 and 5 gave the most stable cation radicals upon oxidation in acetonitrile. Coulometric oxidation (1.0 F mol⁻¹) of 4 (1.0 mM) in acetonitrile containing lithium perchlorate (0.1 M) gave an emerald green solution showing a strong esr signal which was due to the cation radical, 11.

(5) O. Hammerich and V. D. Parker, *Electrochim. Acta*, 537 (1973).

The visible spectrum of 11, λ_{max} (MeCN) 420 and 765



nm, matched that obtained by treatment of a nitromethane solution of 4 with anhydrous aluminum chloride, a standard method of preparing cation radicals for esr investigations.⁶ The half-life of 11 in acetonitrile at room temperature was determined to be of the order of 1–2 min. Oxidation of 5 under the same conditions gave a deep blue solution, λ_{max} (MeCN) 405 and 742 nm. A deep blue colored solid precipitated from solution, which on dissolution in nitrobenzene gave a solution showing a well resolved esr spectrum of about 70 lines. The room temperature half-life of 12 in nitrobenzene was estimated to be about 6 hr in contrast to a half-life of about 1–2 min in acetonitrile. None of the other compounds gave cation radicals sufficiently stable in MeCN for spectral measurements.

Voltammetry of Methoxybiphenyls in Media Containing Trifluoroacetic Acid (TFA). Reversible or quasireversible one-electron oxidation was observed for all the methoxybiphenyls with the exception of 9 in TFA or in TFA-CH₂Cl₂ (1:5). The use of the latter two solvent systems for the anodic generation of cation radicals has recently been described.^{7,8} A more suitable solvent for the study of the voltammetry of the methoxybiphenyls was found to be CH₂Cl₂-trifluoroacetic acid anhydride (TFAn)-TFA (45:5:1) which has been shown to be suitable for the observation of both aromatic cation radicals and dications.⁵ Results of voltammetric measurements in the latter solvent system are summarized in Table II.

Table II. Voltammetry of Methoxybiphenyls in CH₂Cl₂-TFAn-TFA (45:5:1)

Compd ^a	$E_{p_{an1}}^b$	$E_{p_{cath1}}^b$	$E_{p_{an2}}^b$	$E_{p_{cath2}}^b$	$\Delta E, mV^c$
3	1.04	0.97	1.50 ^d		460
4	1.21	1.14	1.67	1.59	460
5	1.17	1.10	1.67	1.60	500
6	1.37	1.29	1.78	1.70	410
7	1.24	1.17	1.52 ^d		380
8	1.53	1.42	1.78 ^d		250
9	1.65 ^d				
10	1.73	1.63	2.11 ^d		380

^a 1.0 mM in CH₂Cl₂-TFAn-TFA (45:5:1); containing *n*-Bu₄NBF₄ (0.2 M). ^b V vs. sce; sweep rate, 86 mV/sec. ^c $\Delta E = E_{p_{an2}} - E_{p_{an1}}$. ^d Irreversible peak.

Comparison of the Voltammetry of *p,p'*-Dimethoxy-polyphenyls. Voltammetric data for 13, 6, 14, and 15 in CH₂Cl₂-TFAn-TFA (45:5:1) are summarized in

(6) W. F. Forbes and P. D. Sullivan, *J. Amer. Chem. Soc.*, **88**, 2862 (1966); W. F. Forbes, P. D. Sullivan, and H. M. Wang, *ibid.*, **89**, 2705 (1967).

(7) O. Hammerich, N. S. Moe, and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 156 (1972).

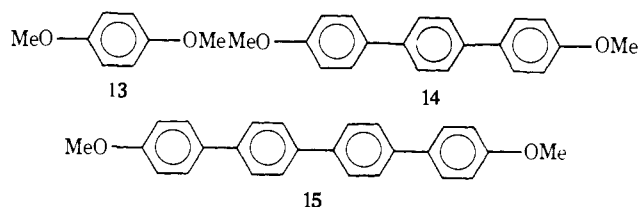
(8) U. Svanholm and V. D. Parker, *Tetrahedron Lett.*, 431 (1972).

Table III. Effect on the Voltammetric Behavior of the Number of Para,para'-Linked Phenyl Groups Separating Two Methoxy Groups

Compd ^a	No. rings	$E_{p_{an1}}^b$	$E_{p_{cath1}}^b$	$E_{p_{an2}}^b$	$E_{p_{cath2}}^b$	ΔE , mV ^c
13	1	1.42	1.35	2.13 ^d		710
6	2	1.37	1.29	1.78	1.70	410
14	3	1.36	1.29	1.65	1.58	290
15	4	1.50	1.42	1.72	1.64	220

^a 1.0 mM in CH₂Cl₂-TFA-TFA (45:5:1); containing *n*-Bu₄NBF₄ (0.2 M). ^b V vs. sce; sweep rate, 86 mV/sec. ^c $\Delta E = E_{p_{an2}} - E_{p_{an1}}$. ^d Irreversible peak.

Table III. The first charge transfer for all four compounds appears to be a quasireversible one-electron step with the peak separation being slightly greater than 60 mV and the ratio of anodic to cathodic peak current being equal to 1.0. The second oxidation



step, cation radical to dication, was reversible for all compounds but 13. Coulometric oxidation (1.0 F mol⁻¹) of all four compounds resulted in nearly quantitative conversion to the corresponding cation radicals. This was verified by the magnitude of the reduction peak currents for the cation radicals as compared with the oxidation peak currents of the substrates before electrolysis. The cation radicals of 6 and 14 appear to be stable indefinitely in the reaction medium while the radical ions of 13 and 15 have very limited lifetimes at room temperature.

Visible Absorption Spectra of Methoxy-Substituted Cation Radicals. The visible absorption spectra of several methoxy-substituted cation radicals are summarized in Table IV. The extinction coefficient of

Table IV. Visible (350–700 nm) Absorption Spectra of Methoxy-Substituted Cation Radicals in CH₂Cl₂-TFA (5:1)

Cation radical of	λ_{max} , nm	Log ϵ	λ_{max} , nm	Log ϵ	λ_{max} , nm	Log ϵ
13	435		462			
6	399	4.18	417	4.47	426	4.52
14	460	4.07	503	3.99		
15	455		470			
4	386	4.31	402	4.51	412	4.62
5	399	4.21	426	4.40		

the cation radicals from 13 and 15 are not tabulated since decomposition of the solutions caused the values to be uncertain.

Esr spectra of all the cation radicals in Table IV were recorded. Resolved spectra of the radical ions from 4 and 6 were obtained.

Discussion

It is a well-known phenomenon that the cation radicals of aromatic hydrocarbons increase in stability as

the number of fused rings increase.⁹ Molecular orbital calculations for linear polyphenyls such as terphenyl and quaterphenyl predict that the spin density of the corresponding cation radicals should be spread over all the rings and thus give rise to enhanced stability.¹⁰ It has not been possible to test the effect of the number of connected rings on ion radical stability since there has been no indication of stability of any cation radicals in this series. The biphenyl linkage has a unique feature in that groups other than hydrogen situated in the ortho,ortho' positions can cause restricted rotation and force the molecule to exist in a conformation in which the rings are nonplanar as in structure 16.¹¹ If cation

radical stabilization is dependent on the degree of conjugation between the rings, contribution of structures such as 16 should diminish the radical ion stability.

The postulated effects of the biphenyl linkage on cation radical and dication stability are clearly borne out by the data (Tables I–III). A substantial increase in stability of both the cation radical and dication are observed in going from 1,4-dimethoxybenzene (13) to 4,4'-dimethoxybiphenyl (6). Also, a decrease in the oxidation potential of about 50 mV was observed in going from 13 to 6 (Table III). The effect of insertion of still another ring was much less dramatic since both the stability and ease of formation of the radical ion of 14 was very similar to that of 6. However, on going to the quaterphenyl (15), the oxidation potential rose significantly (140 mV going from 14 to 15) and the resulting cation radical was much less stable. The formation of the dications becomes progressively easier relative to the first charge transfer as the number of rings increase as reflected by the magnitude of ΔE (Table III) with only 13 showing an irreversible oxidation peak for the second charge transfer. The latter can probably be attributed to increased separation of the like charges as the number of conjugated rings increase. In fact, for 15 the magnitude of both the first and second charge transfers are approaching the expected value for an isolated anisole group which suggests that incorporation of still more rings separating the methoxy groups would eventually result in the observation of a single two electron oxidation peak to give a dication diradical.

It is of interest to compare the ease of formation of the cation radicals of 6, 4, and 5. In the case of the biphenyl (6) there is free rotation around the bond connecting the two rings. The preferred conformation of the 9,10-dihydrophenanthrene (4) is one in which the two rings are twisted out of plane; however, the barrier to passing through a planar conformation is probably quite small. On the other hand, models indicate that the two rings are forced to remain in nearly the same

(9) For a review, see R. N. Adams, *Accounts Chem. Res.*, **2**, 175 (1969).

(10) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969, p 314.

(11) For a review, see J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968).

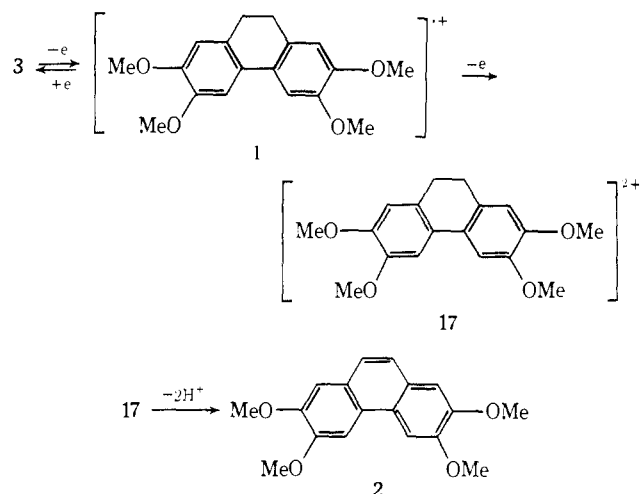
plane in the fluorene (**5**). If the transition state for the formation of the corresponding cation radicals requires the assumption of a planar conformation, the activation energy would be expected to be less for **5** than for **4** and which in turn should be lower than that for **6**. From this analysis, one would expect the ease of oxidation to increase in going from **5** to **4** to **6**. Such a relationship indeed does exist since the potentials increase from 1.08 to 1.14 to 1.28 V in going through the series for the oxidation of the substrates in acetonitrile. Similar differences were observed in the mixed solvent system (Tables I and II). Since the reversible electrode potentials are thermodynamic quantities, it may be more appropriate to consider the relative energies of the cation radicals and corresponding substrates in this series with **5**, and its radical ion is predicted to have the lowest energy difference since the planar conformation is imposed on both the radical ion and the substrate. Although the differences in oxidation potentials are rationalizable in the above manner, specific solvation effects could also bring about the observed differences.

The effect of steric inhibition to coplanarity of the two rings is more clearly brought out by considering the series of biphenyls, **6**, **8**, **9**, and **10**. In the mixed solvent (Table II), **8** with two methyl groups occupying the ortho,ortho' positions is oxidized at a potential 160 mV more positive than the unhindered compound, **6**. With methoxy groups in the ortho,ortho' positions, **9** is oxidized 280 mV more positive than **6**. With all four ortho,ortho' positions occupied by methyl groups, **10** is oxidized at a potential 370 mV more anodic than is **6**. If these differences can be ascribed only to differences in energy of radical ion and substrate brought about by the increased steric inhibition to coplanarity, an assumption which seems reasonable since solvation energies would not be expected to change greatly in this closely related series, we can estimate the strain energies to be 3.7 kcal/mol for the cation radical of **8** and 8.5 kcal/mol for the cation radical of **10**. That is, the energy difference between **10** and its cation radical is 8.5 kcal/mol greater than the corresponding difference between **6** and its radical ion.

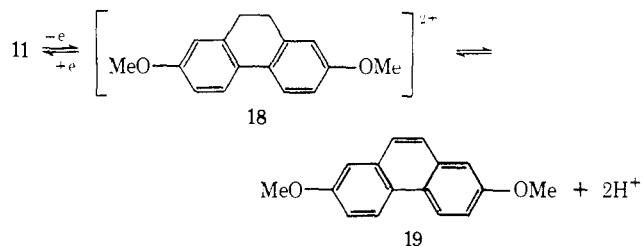
The effect on the ease of oxidation of an additional methoxy group in both rings is evident from comparing **3** with **4** and **7** with **6**. In acetonitrile (Table I) the additional methoxy group has the effect of lowering the oxidation potential by 200 and 160 mV, respectively, while in the mixed solvent the lowering of oxidation potential was found to be 170 and 130 mV, respectively. This, of course, is in accord with the known effect of electron donating groups on the ease of oxidation of aromatic compounds.¹²

It is of interest to compare the voltammetric behavior of the tetramethoxydihydrophenanthrene (**3**) with the dimethoxy compound (**4**). In the former case, reversible behavior is observed for the first charge transfer in both acetonitrile (Table I) and the mixed solvent (Table II) implying the stability of the resulting cation radical. However, the second charge transfer is irreversible in both solvent systems showing that the dication (**17**) undergoes a rapid reaction, probably forming the phenanthrene in analogy to the reaction

(12) For a review, see N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968).



observed in case of the cation radical (**1**).² Since the latter reaction is simply a deprotonation of a diprotonated aromatic compound, it would be expected to be very rapid. However, an anomaly to the above reasoning is evident when we consider the related case, that of **4**. Both charge transfers are reversible in both solvent systems (Tables I and II) indicating stability of both the cation radical (**11**) and the dication (**18**). Obviously, the phenanthrene (**19**) cannot be so basic that it be completely diprotonated in the presence of only 2 equiv of protons in a solvent as basic as acetonitrile. Thus, we must conclude that although **18** is



formally the second conjugate acid of **19**, a favorable kinetic pathway does not exist for the formation of **18** from **19** and that the stability of **18** is a consequence of an unusually slow deprotonation. In fact, attempts to generate **18** by protonation of **19** with $HFSO_3$ in dichloromethane at low temperature failed. Protonation indeed did occur; however, voltammetry failed to show the presence of **18**. A considerably large body of work has been published¹³ dealing with the protonation of aryl ethers and in view of existing data, it is not clear whether carbon¹⁴ or oxygen¹⁵ protonation is to be expected since both types have been reported. However, the voltammetric experiments with **19** show that **18** is not a significant protonation product under the conditions employed.

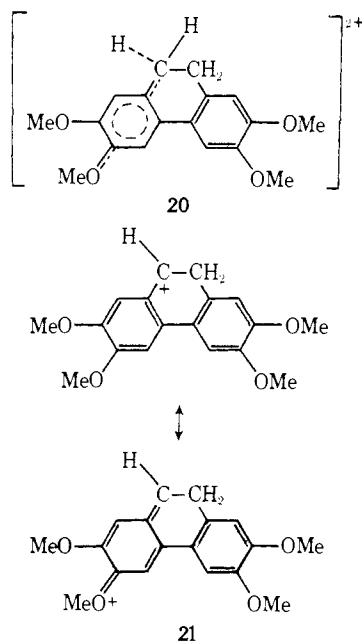
The question then arises, why is **17** deprotonated rapidly under conditions where **18** is relatively stable? Some insight into this question can be gained from the consideration of the transition state (**20**) for deprotonation of **17** to give the methoxy stabilized benzyl cation

(13) For a recent review, see G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, **70**, 561 (1970).

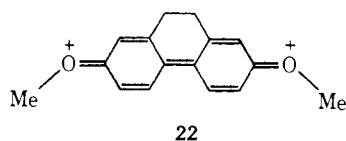
(14) T. Birchall, A. N. Bourns, R. J. Gillespie, and P. J. Smith, *Can. J. Chem.*, **42**, 1433 (1964); T. Birchall and R. J. Gillespie, *ibid.*, **42**, 502 (1964).

(15) D. M. Brouwer, E. L. Mackor, and C. Maclean, *Recl. Trav. Chim. Pays-Bas*, **85**, 109 (1966).

(21). Thus, as depicted by structure 20, the develop-



ment of positive charge in the benzyl position in the transition state for deprotonation is facilitated by resonance stabilization involving the methoxy group para to the generated cationic center. Stabilization in the transition state of the latter type is not possible for 18 which does not have methoxy groups properly situated for that type of interaction. Structures of type 22 in which positive charge is localized on oxygen



would be expected to stabilize the dication and thus bring about an increase in activation energy for deprotonation which would have to pass through a transition state similar to 20, but which is less favorable due to the absence of the stabilizing para methoxy group.

During comparison of the data found in Tables I and II it becomes evident that the first charge transfer for all the compounds occurs more readily (about 100 mV) in acetonitrile than in the less polar mixed solvent. The difference between the potentials of the first and second charge transfers, ΔE , is consistently greater in the mixed solvent. A plausible explanation for the latter facts is that the solvation energies of the monocations are slightly greater while that of the dications are significantly greater in the much more polar solvent, acetonitrile.¹⁶

In conclusion, the work reported here has shown that the biphenyl linkage gives considerable enhance-

(16) Work is in progress on the correlation of reversible electrode potentials for formation of mono- and dications in a variety of solvent systems with the mass spectrometric appearance potentials of the mono- and dicationic ions in order to gain quantitative data for the solvation energies of a variety of aromatic cation radicals and dications.¹⁷

(17) V. D. Parker, *et al.*, unpublished work.

ment of stability to cation radicals and dications as long as coplanarity of the two rings is possible. In polyphenyls, the ability of the methoxy groups on the terminal rings to stabilize the positive ions quickly falls off with increasing number of rings. A comparison which points out the magnitude of the stabilizing influence is that of 4,4'-dimethoxybiphenyl (6) with 9,10-dimethoxyanthracene. As reported here, the former gives a stable cation radical and a relatively stable dication. The latter gives a short-lived cation radical and the corresponding dication cannot be observed by slow sweep cyclic voltammetry. Thus, the biphenyl linkage appears to exert a greater stabilizing influence than the well-known¹⁸⁻²⁰ effect of the anthracene nucleus.

Experimental Section

Reagent grade acetonitrile and dichloromethane were purified by passing through neutral alumina (Woelm W-200) immediately before use. Trifluoroacetic acid and trifluoroacetic acid anhydride were reagent grade and used without further purification. Equipment and techniques used for voltammetry and coulometry have been described previously.^{21,22}

2,3,6,7-Tetramethoxy-9,10-dihydrophenanthrene (3), 2,7-dimethoxy-9,10-dihydrophenanthrene (4), and 2,7-dimethoxyfluorene (5) were prepared by anodic intramolecular coupling of the corresponding bibenzyls and diarylmethane.²³ 4,4'-Dimethoxy-2,2',3,3'-5,5',6,6'-octamethylbiphenyl (10) and 4,4''-dimethoxyquaterphenyl (15) were prepared previously by anodic coupling of the corresponding anisole or biphenyl, respectively.²⁴

3,3',4,4'-Tetramethylmethoxybiphenyl (7)²⁵ and 2,2'-dimethyl-4,4'-dimethoxybiphenyl (8)²⁶ were prepared by Ullman coupling of the corresponding iodo compounds.

4,4''-Dimethoxyterphenyl (14). To a solution of *p*-anisylmagnesium bromide (0.05 mol) in THF (100 ml) was added dropwise cyclohexa-1,4-dione (0.025 mol) dissolved in THF (25 ml). The addition was complete in 20 min. Stirring was continued for another 2 hr. The resulting solution was poured into a 10% solution of NH_4Cl in water (200 ml). The organic layer was washed with water and dried over sodium sulfate, and the solvent was evaporated to yield an oil (8 g). The crude oil was dissolved in toluene (200 ml) containing *p*-toluenesulfonic acid (0.5 g) and allowed to reflux for 6 hr. Upon cooling, the compound (2.1 g) crystallized as brown plates, mp 272-273°. Further purification was accomplished by sublimation in high vacuum, mp 274° (lit.²⁷ 273-275°).

2,2'-Dimethoxybiphenyl (9) was prepared from 2,2'-dihydroxybiphenyl by a standard procedure.²⁸

2,7-Dimethoxyphenylanthracene (19) was prepared according to a literature procedure, mp 166-167° (lit.²⁹ bp 167-168°).

1,4-Dimethoxybenzene (13) and 4,4'-dimethoxybiphenyl (6) were reagent grade and used without further purification.

(18) M. E. Peover and B. S. White, *J. Electroanal. Chem.*, **13**, 93 (1967).

(19) (a) J. Phelps, K. S. V. Santhanam, and A. J. Bard, *J. Amer. Chem. Soc.*, **89**, 1752 (1967); (b) L. S. Marcoux, J. M. Fritsch, and R. N. Adams, *ibid.*, **89**, 5766 (1967).

(20) R. E. Sioda, *J. Phys. Chem.*, **72**, 2322 (1968).

(21) O. Hammerich and V. D. Parker, *J. Chem. Soc., Perkin Trans. 1*, 1718 (1972).

(22) V. D. Parker, *Acta Chem. Scand.*, **24**, 2768 (1970).

(23) A. Ronlan, O. Hammerich, and V. D. Parker, *J. Amer. Chem. Soc.*, **95**, 7132 (1973).

(24) A. Ronlan, K. Bechgaard, and V. D. Parker, *Acta Chem. Scand.*, **27**, 2375 (1973).

(25) E. Späth and K. Gibian, *Monatsh.*, **55**, 342 (1930).

(26) H. Brockmann and A. Dörlars, *Chem. Ber.*, **85**, 1168 (1952).

(27) C. C. Price and G. P. Mueller, *J. Amer. Chem. Soc.*, **66**, 632 (1944).

(28) G. S. Hiers and F. D. Hager, *Org. Syn.*, **1**, 58 (1958).

(29) L. F. Fieser, *J. Amer. Chem. Soc.*, **51**, 2481 (1929).