Electrochemistry of Biphenylenes. Observation of Biphenylene Cation Radicals and Dications

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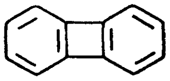
Summary The biphenylene ring system imparts greatly enhanced stability to cation radicals and dications as compared to other simple ring systems such as the biphenyl system.

The Hückel "$4n + 2$" rule predicts enhanced stability of dications of compounds having the biphenylene ring structure since they can formally be regarded as dibenzocyclobutadienes.[1] It has been reported that **(1)** forms a stable cation radical on dissolving in concentrated sulphuric acid,[2] providing evidence that the biphenylene ring structure exerts a stabilizing influence on the cation which implies interaction between the two rings. In order to investigate the possibility of observing Hückel aromatic biphenylene dications, the voltammetric oxidation of **(1)** and the tetramethoxy-derivative, **(2)**, was examined.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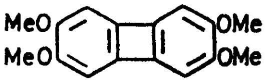
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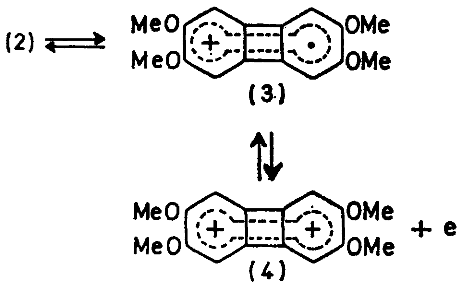

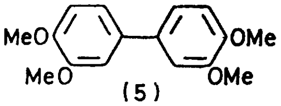
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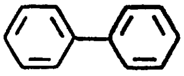
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In dichloromethane–trifluoroacetic acid anhydride–trifluoroacetic acid (CH_2Cl_2–TFAn–TFA = 45 : 5 : 1),[3] **(1)** was found to undergo reversible one-electron oxidation to give the stable cation radical at a potential of +1·35 V† and a further irreversible oxidation peak was observed at +2·23 V. No indication of reversibility of the second charge transfer could be observed even on cooling the solution to −60°. More intriguing results were obtained for the oxidation of **(2)**. In acetonitrile containing H_2O (*ca.* 10 mM) at a voltage sweep rate of 31 mV/s, an irreversible oxidation peak is observed at +0·54 V (O_1) and a small reversible couple (O_2–R_2) is seen at +0·98 V. Increasing the voltage sweep rate to 120 mV/s brought about an enhancement of O_2–R_2. This trend continued with O_2–R_2 growing relative to O_1 as the sweep rate increased. At still higher sweep rates (15,600 mV/s) a reduction peak, R_1, appeared and both couples O_1–R_1 and O_2–R_2 were completely reversible and the peak currents for the two couples were of equal magnitude. These results indicate that at slow voltage sweep rates irreversible reaction of the cation radical is the predominant reaction occurring. On the other hand, at higher sweep rates further reactions of the cation radical are "outrun" and both electron transfers appear to be reversible. Thus, the cation radical formed at O_1 is far less stable in acetonitrile than is the dication formed at O_2. It is remarkable that there is this stability reversal of the cation and dication in going from structure **(1)** to structure **(2)**. In very dry acetonitrile or in CH_2Cl_2–TFAn–TFA (45 : 1 : 1) both couples, involving formation of the monocation (O_1–R_1) and the dication (O_2–R_2), are reversible even at slow voltage sweep rates implying that electrophilic reaction with H_2O is the fate of **(3)** in wet acetonitrile.

Coulometric oxidation of **(2)** (1·0 mM) in dry acetonitrile resulted in the consumption of 1·0 Faradays per mole and the precipitation of a dark blue solid. In carefully degassed solvent mixture consisting of CH_2Cl_2–TFAn–TFA (45 : 5 : 1), **(2)** underwent two consecutive one-electron oxidations giving first a deep blue (λ_{max} 414, 680; ϵ 28,000, 19,300) and then a yellow (λ_{max} 459, ϵ 55,500) solution. The substrate, **(2)**, was regenerated by two-electron cathodic reduction. The one-electron oxidation product could also be obtained by air oxidation of **(2)** in TFA and further oxidation to the two-electron product could be achieved by the addition of small amounts of perchloric acid to the TFA solution. In concentrated sulphuric acid, **(2)** was immediately transformed to the two-electron oxidation product as shown by the visible spectrum (λ_{max} 459). The one-electron oxidation product gave an e.s.r. spectrum in TFA of about 23 resolved lines. Only a weak, broad e.s.r. signal, most likely due to residual one-electron oxidation product, could be detected for the two-electron oxidation product.

The combination of voltammetric, coulometric, and spectral results can only be explained by the occurrence of two consecutive one-electron transfers to give first the cation radical **(3)** and then the dication **(4)**. Due to insolubility in acetonitrile it was possible to isolate the cation radical perchlorate in high yield. The trifluoroacetate salt was obtained by evaporation of the solvent after air oxidation of **(2)** in TFA. Both salts gave satisfactory elemental analysis. Attempts to obtain pure salts of the dication **(4)** by evaporation of the solvent from the perchloric acid oxidation of **(2)** in TFA have so far failed. Salts are obtained giving the dication spectrum. However, unidentified decomposition products are always present.

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† All potentials are referred to the aqueous saturated calomel electrode.

In order to assess the effect of the biphenylene structure on the ease of formation and stability of positive ions, we can compare the results for (**2**) with those for the corresponding biphenyl, (**5**). While the two one-electron transfers occur at +0·53 and 1·06 V in the mixed solvent for (**2**), the two consecutive one-electron transfers occur at +1·24 and +1·62 V for (**5**) in the same solvent system. The cation radical derived from (**5**) shows limited stability and the dication has not been observed. Thus, the positive ions possessing the biphenylene ring system are both more easily formed and also more stable than the corresponding biphenyl. The difference between the parent compound and biphenyl (**6**) is even more pronounced. As pointed out earlier, (**1**) gives a relatively stable cation radical while it has not been possible to observe the cation radical of (**6**).

It has been reported that (**2**) reacts with bromine to give a σ-complex initially which reacts further.[4] We find that the first product of the reaction of (**2**) with bromine or iodine exhibits visible and e.s.r. spectra identical to the radical ion produced both electrochemically and by air oxidation in TFA.

(*Received*, 4*th October* 1973; *Com.* 1379.)

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