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ELECTROCHEMICAL OXIDATION OF 5,13-DIMETHOXY[2.2]METACYCLOPHANE TO THE CORRESPONDING RADICAL CATION AND DICATION

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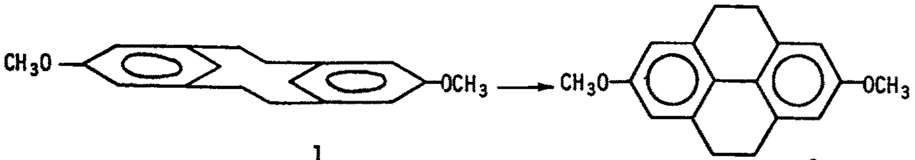
The anodic cyclization of bibenzyls has recently received attention both from a synthetic and mechanistic viewpoint.[1-4] In the present study (2,2)-metacyclophanes, which can be considered special bibenzyls, were anodically oxidized. It was expected that coupling of the aromatic rings would result as shown below, but that because of the unusual electronic interactions between the rings[5,6] and special steric effects that the details of the coupling mechanism might prove interesting. It has been found that the cation radical and dication have unusual stability.



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Compound 1 was chosen for study. Cyclic voltammetry (CV) studies using either acetonitrile $(C_2H_5)_4N^+$, BF_4^- or trifluoroacetic acid:methylene chloride/$(\underline{n}\text{-}C_4H_9)_4N^+$,$BF_4^-$ as electrolytes were undertaken as well as preparative oxidations in the former solvent. In each case a platinum working electrode and Ag/0.1 M $AgNO_3$ in CH_3CN reference electrode were employed. As shown in Table I, the CV of 1 shows two quasi reversible oxidation processes[8] which should correspond to formation of the cation ($1^{+\cdot}$) and dication (1^{++}). The peak separations (ΔE_p) are generally near to the 59 mV demanded for reversible one-electron processes and the ratio of peak currents (i_p) is one at fast sweep rates. The E_p values are independent of sweep rate and the i_p vary linearly with the square root of sweep rates over the range 0.1-1.0 V/sec.

Table I. Cyclic Voltammetry Data for Compounds **1** and **2**.[a]

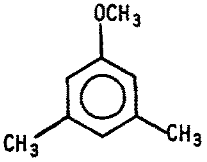
Cpd	Solvent	Supporting electrolyte (.15 M)	E^{I}_{ox}(V)	E^{I}_{red}(V)	ΔE^{I}(mV)	E^{II}_{ox}(V)	E^{II}_{red}(V)	ΔE^{II}(mV)
1	CH_3CN	Et_4NBF_4	0.64	0.54	100	1.05	0.98	70
	CH_3CN	$LiClO_4$	0.65	0.58	70	1.04	0.95	90
	$CH_2Cl_2CF_3COOH$ (2:1)	Bu_4NBF_4	0.72	0.65	70	1.26	1.20	60
2	CH_3CN	$LiClO_4$	0.80	0.70	100			
	$CH_2Cl_2CF_3COOH$ (2:1)	Bu_4NBF_4	0.94	0.86	80			

[a] Scan rate 0.5 V/sec. Ref. electrode Ag/0.1 M $AgNO_3$ conc. 1.2×10^{-3} M.

Cyclization from the dication can be deduced from a CV run in 2 CH_2Cl_2:CF_3CO_2H containing 4% H_2O. Here the cathodic peak at 0.98 V is diminished and a new couple has appeared which corresponds precisely to that for $\mathbf{2}^{+\cdot} \rightleftarrows \mathbf{2}$ obtained independently. As expected, preparative oxidation of **1** in acetonitrile produced **2** in >90% yield.

The CV data indicates that $\mathbf{1}^{+\cdot}$ and $\mathbf{1}^{++}$ are stable on the time scale of the CV experiment (~1 sec). In comparison the cation radicals of **3**, **4** cannot be detected by fast sweep CV. The dication stability is especially impressive since direct evidence for dications has generally been obtained only when specially dried[9] solvents or low temperature[10] were employed.

This stability is even more surprising when one considers that in the stable anti conformation these ions are geometrically organized in a precisely proper position for coupling of the rings. Thus, one could incorrectly expect a low activation energy for coupling due to the entropy factor. This anomalously low reactivity is explained in part by the fact that $\mathbf{1}^{+\cdot}$ and $\mathbf{1}^{++}$ can be stabilized by delocalization between the aromatic rings.[6]



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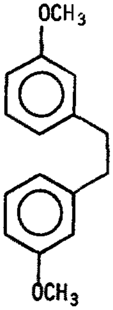

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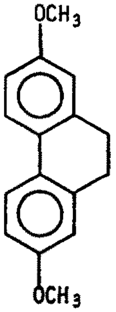

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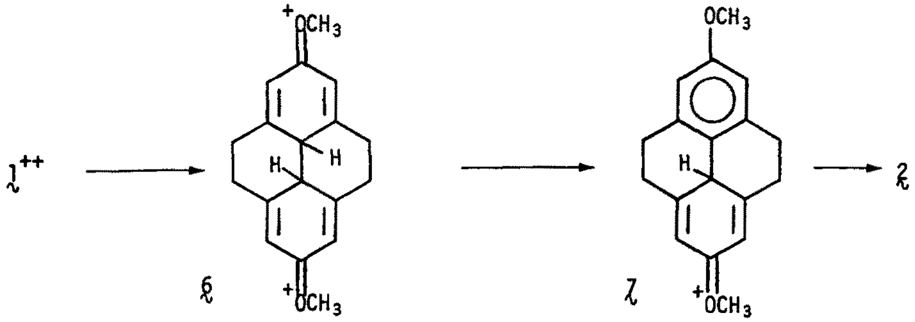
The ease of formation of $\mathbf{1}^{+\cdot}$ is consistent with such stabilization and with its low reactivity. $\mathbf{1}^{+\cdot}$ is formed at potentials some 0.5 V below **3**, **4**. Even more impressively, however, **1** oxidizes at potentials slightly lower than **2** or **5** ($E_{½}$ = 0.81 V[9]) where there is strong π-type delocalization between the rings. The low reactivity of $\mathbf{1}^{+\cdot}$ and $\mathbf{1}^{++}$ can be understood in that their special stabilization (compared to $\mathbf{4}^{+\cdot}$ or $\mathbf{4}^{++}$) is lost when coupling takes place.

Compare, specifically, the coupling of $\mathbf{1}^{++}$ with that of $\mathbf{4}^{++}$ using a detailed exemplary mechanism:



We have shown above that $\mathbf{1}^{++}$ is more stable than $\mathbf{4}^{++}$. This special stabilization is, however, lost when the undelocalized, but somewhat strained intermediates **6** or **7** are formed. The activation energy for coupling of $\mathbf{1}^{++}$ is, therefore, understandably larger than that for $\mathbf{4}^{++}$. Similar arguments are obvious for $\mathbf{1}^{+\cdot}$.

Further mechanistic aspects of this process are under investigation and a complete discussion of the ion stability will be presented.

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