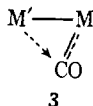


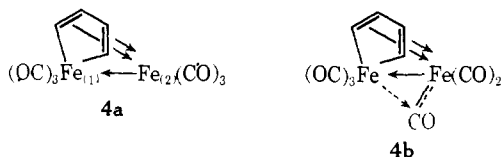
The final step to pass from **2** to the actual structure is to have one of the CO groups on Fe₍₂₎ lean toward Fe₍₁₎ to form the *semibridging CO group*,¹¹ SBCO, first observed^{11a} in 1961.

One of the uniquely important things about this molecule is that it gives a clue to the nature of the bonding in SBCO's and, hence, a prediction of *one* set of circumstances in which they may be expected to occur. We think that in this molecule it is obvious that the relatively electron-rich Fe₍₁₎ atom in **2** is forming a weak $d \rightarrow \pi^*$ dative bond to the C(1)-O(1) group. In short, *the semibridging CO group provides a mechanism for a metal atom otherwise tending to be excessively negative to transfer electron density to a CO group on a less negatively charged metal atom.* A convenient diagrammatic representation, useful in drawing structures, is **3**, imply-



ing that one π^* orbital continues to back-accept $d\pi$ electrons from M, while the other π^* orbital is at least partially used to accept electron density from M'. As this process occurs, the M-C-O chain bends and the acceptor orbital for M' will acquire carbon s character, thus making it a better acceptor.

This interpretation of the SBCO group serves to explain its occurrence in some other cases. In molecules of type **4**,^{11a,c} the hypothetical structure **4a**, without an SBCO, has Fe₍₁₎ and Fe₍₂₎ formally negative and positive, respectively. Introduction of the SBCO, **4b**,



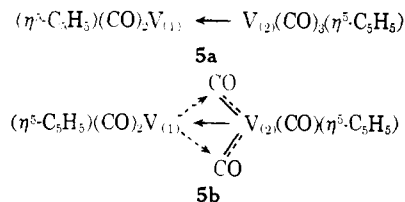
alleviates this by directly removing electron density from Fe₍₁₎ and causing the CO which acts as the SBCO to π -accept less from Fe₍₂₎. Again, in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_2(\text{CO})_8$,^{11b} the Rh atoms tend to bear greater charges than the iron atoms since their ligands are $\eta^5\text{-C}_5\text{H}_5$ groups which donate more than they back-accept, whereas one of the iron atoms, which bears four CO groups, tends to be less electron-rich than the other, which has three. Hence, two appropriately positioned CO groups on the Fe(CO)₄ group become SBCO's and lessen the density on the Rh atoms.

In $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}_2(\text{CO})_8$ (**5**) a hypothetical structure omitting SBCO formation would be **5a**. Here each V atom has a 16-electron configuration (an acceptable situation in group IV and V compounds), but V₍₁₎ is negative relative to V₍₂₎. The use of two CO groups on V₍₂₎ as SBCO's, **5b** (the actual structure), helps to spread charge more evenly.¹²

In $\alpha\text{-H}_2\text{Ru}_4(\text{CO})_{13}$ ^{11e} the metal atom with the greatest number of CO groups uses two of them as SBCO's to remove electron density from two others.

(11) (a) A. A. Hock and O. S. Mills, *Acta Crystallogr.*, **14**, 139 (1961); (b) R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, **88**, 4847 (1966); (c) H. B. Chin and R. Bau, *J. Amer. Chem. Soc.*, **95**, 5069 (1973); (d) M. R. Churchill and M. V. Veidis, *J. Chem. Soc. A*, 2170 (1971); (e) D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, **11**, 838 (1972).

(12) The V-V bond order may exceed unity because of additional electroneutral V-V bonding. As observed before,⁸ "the order of this bond is uncertain."



In a case such as the Fe₄(CO)₁₃⁻ ion^{11b} three SBCO's are so correlated that the associated three metal atoms are charge equivalent in the actual structure but would be also in a structure without the SBCO's (similar to Ir₄(CO)₁₂) as well as one with regular symmetrical bridges (similar to Co₄(CO)₁₂ and Rh₄(CO)₁₂). Charge equalization cannot explain the occurrence of the SBCO's in this or any similar case, e.g., Fe₃(CO)₁₂. Instead, there may simply be a very small variation in the free energy as a function of structure through the entire range covered by concerted shifts of two (in Fe₃(CO)₁₂) or three (in Fe₄(CO)₁₃⁻) CO ligands from essentially terminal toward symmetrically bridging positions.

Finally, we note that a need for charge equalization is not a sufficient condition for formation of SBCO's since none exists in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Mo}(\mu\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_4$ where it would seem likely that there is a Mo→Mn bond, thus making Mn appreciably negative relative to Mo.^{13,14} However, there are several features of this molecule, namely, only one CO on the Mo atom, the presence of four CO's on the Mn atom to help disperse its formal charge, and a very long Mo-Mn bond which might militate against the stability of an SBCO.¹⁵

Supplementary Material Available. A table of crystal data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-1233.

(13) R. Hoxmeier, B. Deubzer, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **93**, 536 (1971).

(14) The authors would welcome correspondence concerning any other apparent exceptions.

(15) We are grateful to the National Science Foundation (Grant No. GP33142X) for support and to The Robert A. Welch Foundation for funds to purchase the diffractometer.

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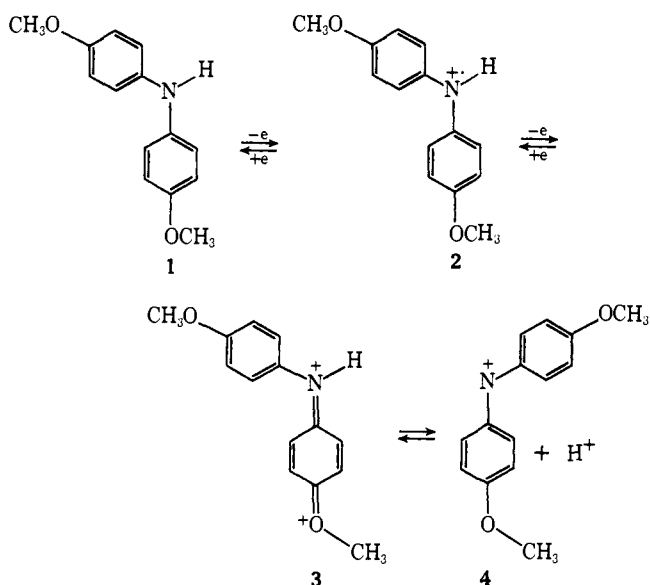
The Chemistry of the Dianisylnitrenium Ion. The Observation of Stable Protonated Nitrenium Ions.

Sir:

We report the direct observation of the dianisyl-nitrenium ion and its conjugate acid, the protonated nitrenium ion. Cyclic voltammetry of di-*p*-anisylamine (**1**) in dichloromethane in the presence of suspended alumina¹ (Figure 1) results in the observation of two reversible one-electron redox couples with oxida-

(1) Aprotic solvents can be rendered "nucleophile free" by suspension of neutral alumina particles which allows for the observation of otherwise very short-lived intermediates such as aromatic dication: O. Hammerich and V. D. Parker, *Electrochim. Acta*, **18**, 537 (1973).

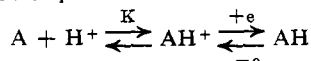
tion peak potentials of $+0.81$ and $+1.56$ V.³ The product of the first electron transfer is the stable cation radical **2** and further one-electron oxidation produced the protonated nitrenium ion **3** which is in equilibrium with the deprotonated form **4**. Similar behavior was ob-



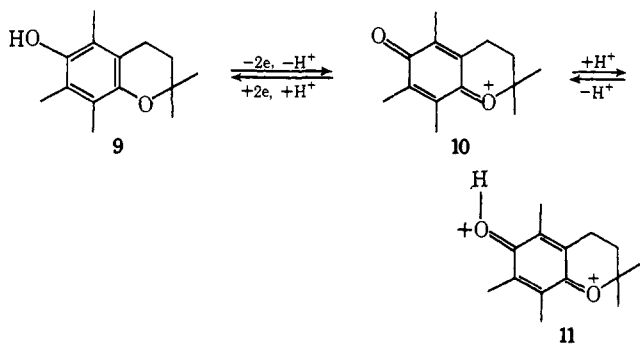
served when the voltammetric experiment was conducted in acetonitrile over neutral alumina. It is clear that in a solvent as basic as acetonitrile that the deprotonated form **4** would be favored by the equilibrium.³ Voltammetry indicates that the lifetime of **4** in neutral acetonitrile is about 1 sec. Coulometry^{4,5} on a solution of **1** (1.0 mM) in dichloromethane gave first **2** (λ_{max} 364 nm, ϵ 2.24×10^4 and $\lambda_{\text{max}} \sim 770$, ϵ_{750} 3.26×10^4) accompanied by the consumption of 1.0 faraday/

(2) All potentials refer to oxidation or reduction at a platinum electrode vs. the saturated aqueous calomel electrode.

(3) The observation of a reversible cyclic voltammogram for the oxidation of **2** does not distinguish between the products **3** and **4**. In fact, calculations (R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964)) indicate for the equilibrium



that a reversible voltammogram for the reduction of AH^+ will be observed if K for the protonation is as low as about 10^{-6} . An analogous case has recently been observed. In either neutral or acidic acetonitrile, **9** is oxidized reversibly to **10** which is stable in acidic acetonitrile, but much stronger acid conditions are necessary to observe the protonated form, **11** (U. Svanholm, K. Bechgaard, and V. D. Parker, submitted to *J. Amer. Chem. Soc.*)



(4) The apparatus and techniques used for coulometry and voltammetry have previously been described.⁶ Reagent grade solvents were passed over neutral alumina before use, and the supporting electrolyte was $n\text{-Bu}_4\text{NBF}_4$ (0.2 M).

(5) (a) V. D. Parker, *Acta Chem. Scand.*, **24**, 2768 (1970); (b) O. Hammerich and V. D. Parker, *J. Chem. Soc., Perkin Trans. 1*, 1718 (1972).

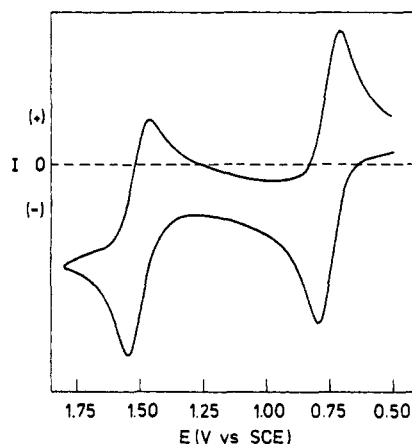
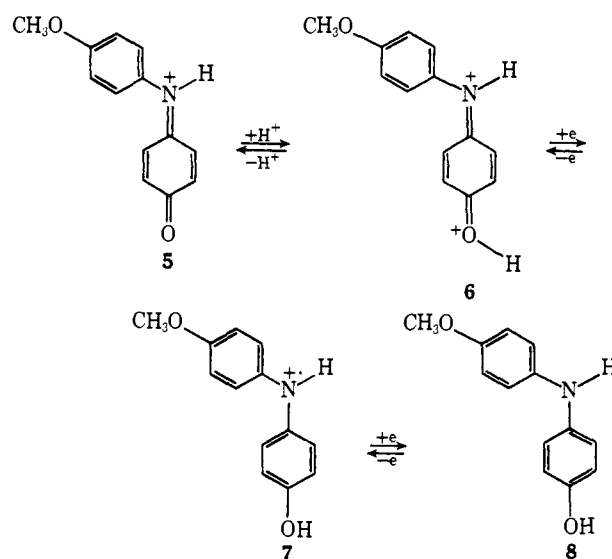
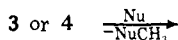


Figure 1. Cyclic voltammogram of di-*p*-anisylamine (1.0 mM) in dichloromethane ($n\text{-Bu}_4\text{NBF}_4 = 0.2$ M) over neutral alumina. Voltage sweep rate = 30 mV/sec at a Beckmann platinum button electrode.

mol. Cathodic reduction of the solution of **2** resulted in quantitative regeneration of **1** as demonstrated by identical voltammograms before and after the oxidation reduction cycle. Acidification of a similar dichloromethane solution of **2** with HFSO_3 (1% by volume), followed by one-electron coulometric oxidation, resulted in a solution of **3** which could be quantitatively reduced to **2**. The visible spectrum of **3** (λ_{max} 670 nm, ϵ 9.70×10^4) generated by antimony pentachloride oxidation of **1** in dichloromethane was identical with that of the electrochemically generated ion. The bis(hexachloroantimonate) salt of **3** was insufficiently soluble in dichloromethane to obtain an nmr spectrum. However, the salt was isolated after oxidation of **1** in the presence of excess SbCl_5 in dichloromethane and gave satisfactory Cl analysis.

One-electron oxidation of **2** in dichloromethane containing TFA (1%) resulted in the formation of **5** which was also prepared by the oxidation of **8** in the same



medium. Acidification of the dichloromethane-TFA solution of **5** with HFSO_3 (1% by volume) gave a solution of **6** (λ_{max} 638 nm, ϵ 8.50×10^4) which was reduced

cathodically to the cation radical (7) which has a visible spectrum identical with that of 2. A stable solution of 6 could also be prepared by the antimony pentachloride oxidation of 8 in dichloromethane.

The formation of 5 during oxidation of 1 most likely occurs by nucleophilic attack on either 3 or 4 by water or other trace impurities in the solvent-electrolyte system. In neutral media, the deprotonation of 3 would be expected to be rapid compared to nucleophilic attack, and thus the most likely species to undergo demethylation under those conditions is the nitrenium ion 4. On the other hand, in more acidic media 3 is the favored species and would be expected to be more reactive toward nucleophiles than 4. The question then arises, why is 3 stable in strongly acidic media? The function of strong acid in stabilizing 3 must be the deactivation of nucleophilic impurities by protonation. Evidence for the latter effect is that 2 is oxidized irreversibly in acetonitrile containing TFA (1%) but upon addition of TFA anhydride (a very effective nucleophile scavenger) a reversible cyclic voltammogram for oxidation of 2 was observed and the solution still contained 3 (25% yield) after oxidation which required 6.5 min for total conversion of 2.

The present state of knowledge of the chemistry of nitrenium ions is largely due to the investigations of Gassman and coworkers.⁶ The reactions of aryl-nitrenium ions reflect the relative electronegativities of nitrogen and carbon providing a new means of nucleophilic aromatic substitution of anilines.⁷ While it is clear from Gassman's work that nitrenium ions are indeed intermediates in a variety of reactions involving organic nitrogen compounds, the voltammetric observation of 4 in neutral acetonitrile and the isolation of a salt of 3 along with the spectroscopic observation of 3 in strongly acidic media appears to be the first indication of stability of such species.

Protonated aryl-nitrenium ions have been observed during oxidation of several other aromatic amines, for example, di-*p*-tolylamine. The stability of the ions is greatly affected by the substitution on the aryl groups, methoxy groups being very effective stabilizing groups. Details of the anodic and antimony pentachloride oxidation of anilines to aryl-nitrenium ions will appear later.

(6) For a recent review see P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

(7) P. G. Gassman, G. A. Campbell, and R. C. Frederick, *J. Amer. Chem. Soc.*, **94**, 3884 (1972).

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Concerning the Separation of Polar and Resonance Effects in the Ionization of 4-Substituted Pyridinium Ions¹

Sir:

According to the field model,² the protonation of 4-substituted pyridines (I) and 4-substituted quinuclidines

(1) This work supported in part by the National Science Foundation.

(2) (a) F. H. Westheimer and J. G. Kirkwood, *J. Phys. Chem.*, **6**, 513 (1938); (b) L. M. Stock, *J. Chem. Educ.*, **49**, 400 (1972).

(II) to good quantitative approximation should be accompanied by (large) equal polar effects of X.



Both experimental and theoretical evidence have been obtained in support of this conclusion in analog systems. The ionization of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and the ionization of the para-substituted benzoic acids have been interpreted as having equal polar effects,³ providing the basis for definition of σ_R parameters.⁴ The calculation of F atom σ electron densities by CNDO/2 theory has shown equal polar effects of corresponding 4 substituents in fluorobenzenes and bicyclo[2.2.2]octyl 1-fluorides.⁵

A critical test of the behavior anticipated for I and II is made possible by recent developments. Although the ionization of 4-substituted pyridinium ions in water at 25° is rather poorly fitted by either σ_p or σ_p^+ ($SD > 0.30$), the data are well fitted by the dual substituent parameter (DSP) eq 1⁶ ($n = 13$; $SD = 0.14$).

$$\log (K/K_0)_I = 5.15\sigma_I + 2.69\sigma_{R^+} \quad (1)$$

The σ_{R^+} parameters, which are structurally appropriate for this reaction, are from Ehrenson, *et al.*,⁷ and are based upon independent basis sets.

The ionization constants of 4-substituted quinuclidinium ions in water at 25° have been reported for an extensive series of substituents by Grob and associates.⁸ According to the field model and eq 1, these data should follow eq 2. Figure 1 illustrates that eq 2 is indeed

$$\log (K/K_0)_{II} = 5.15\sigma_I \quad (2)$$

followed. The values of $\log (K/K_0)_{II}$ are shown plotted *vs.* σ_I with a regression slope of 5.15 indicated. The least-squares regression for this correlation is: $\log (K/K_0)_{II} = 4.81\sigma_I + 0.20$; $n = 21$, $SD = 0.15$, $r = 0.990$. A DSP equation analysis gives: $\log (K/K_0)_{II} = 5.21\sigma_I - 0.24\sigma_{R^+}$; $n = 13$, $SD = 0.13$. No significance is attached to the second term. The essential identity of corresponding polar effects in the ionization of I and II appears to provide further support^{3b,c} for the field over the internal inductive model. The different bond transmission modes for I and II probably would not be expected to be equal.⁹

Since polar effects in series I and II are essentially

(3) (a) J. D. Roberts and W. T. Moreland, *J. Amer. Chem. Soc.*, **75**, 2167 (1953); (b) H. D. Holtz and L. M. Stock, *ibid.*, **86**, 5188 (1964); (c) C. F. Wilcox and J. S. McIntyre, *J. Org. Chem.*, **30**, 777 (1965).

(4) (a) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13; (b) R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, **90**, 6537 (1968).

(5) R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, **92**, 7007 (1970).

(6) P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, **6**, 147 (1968).

(7) (a) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Progr. Phys. Org. Chem.*, **10**, 1 (1973); *cf.* also S. Dayal, S. Ehrenson, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 9113 (1972).

(8) (a) E. Ceppi, W. Eckhardt, and C. A. Grob, *Tetrahedron Lett.*, 3627 (1973); (b) J. Paleček and J. Hlavatý, *Collect. Czech. Chem. Commun.*, **38**, 1985 (1973). These authors have reported pK_A values for a somewhat more limited series of II bases in three aqueous-organic solvents. They are the first to report satisfactory correlation of $\log (K/K_0)_{II}$ values with σ_I parameters.

(9) This point is by no means certain, however. Recent evidence has indicated that the polarizability of phenyl and cyclohexyl groups are very similar; *cf.* R. W. Taft, M. Taagepera, K. D. Summerhays, and J. Mitsky, *J. Amer. Chem. Soc.*, **95**, 3811 (1973).