

planned structure of immobilized OX/RED is not achieved owing to synthetic misadventure during immobilization, substantial variation in  $E^{\circ'}_{\text{surf}}$  could result.<sup>6</sup> Last, if immobilized OX or RED interact strongly (or differently) with the underlying electrode material, as in classical electrode adsorption,<sup>7,8</sup> or coherently with each other to form two-dimensional pseudocrystalline phases,<sup>9</sup> shifts in  $E^{\circ'}_{\text{surf}}$  would result. Absence of large  $E^{\circ'}_{\text{surf}} - E^{\circ'}_{\text{soln}}$  differences does not of course prove these effects absent, merely that in general they are of modest size.

Table I results show that immobilized OX/RED electrochemistry is thermodynamically predictable. The examples of Table I include also new immobilization schemes extrapolated from solution chemistry; this surface synthetic ability indirectly favors chemical reliability of step II. Thus, surface-bound aminosilane is employed as an amide former (e.g., R9, O1, O3) and also as a nucleophilic reagent (e.g., O4), just as one would expect from solution chemistry. Likewise, surface-bound pyridinesilane behaves as a ligand as expected (e.g., R11, O11, and immobilization of the important ruthenium bipyridyl system is achieved). The butyryl chloride silane is a new reagent which formed amides (e.g., O5, O7) with ease. Acid chloride functionalities on carbon bind amines (R1, R7, O6) in the expected manner. Preparation of a family of immobilized metallotetraphenylporphyrins (R2-R6) was possible using reaction conditions similar to solution metalations; R2 is a particularly interesting member of this family.

Unaddressed above is the important but separate question of step I and II kinetics, which must be understood before electrocatalytic design can be truly predictive. One qualitative example of designed electrocatalysis using a chemically modified electrode has appeared.<sup>2</sup>

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## References and Notes

- (1) (a) P. R. Moses and R. W. Murray, *J. Am. Chem. Soc.*, **98**, 7435 (1976); (b) P. R. Moses and R. W. Murray, *J. Electroanal. Chem.*, **77**, 393 (1977); (c) J. R. Lenhard and R. W. Murray, *ibid.*, **78**, 195 (1977); (d) J. C. Lennox and R. W. Murray, *ibid.*, **78**, 395 (1977).
- (2) J. F. Evans, T. Kuwana, M. T. Henne, and G. P. Royer, *J. Electroanal. Chem.*, **80**, 409 (1977).
- (3) Unreferenced  $E^{\circ'}_{\text{surf}}$  values in Table I represent newly synthesized surface systems, preparative and other electrochemical details of which will be reported elsewhere. The  $E^{\circ'}$  are averages of the cathodic and anodic peak potentials. All examples included have symmetrically shaped waves with small (typically <30 mV)  $\Delta E_{\text{peak}}$  and  $i_{p,c}/i_{p,a} = 1.0$  signifying good electrochemical and chemical reversibility.
- (4) A. P. Brown and F. C. Anson, *Anal. Chem.*, **49**, 1589 (1977).
- (5) J. C. Lennox and R. W. Murray, *J. Am. Chem. Soc.*, **100**, 3710 (1978).
- (6) Absence of such variation in itself supports the correctness of the surface structures indicated.
- (7) R. H. Wopschall and I. Shain, *Anal. Chem.*, **39**, 1514 (1967).
- (8) Deliberate use of a solvent in which OX/RED is poorly soluble may provoke otherwise unimportant immobilized OX/RED surface interactions.<sup>5</sup>
- (9) C. M. Elliott and R. W. Murray, *J. Am. Chem. Soc.*, **96**, 3321 (1974).

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## Nonbonded Interactions in Phenylcarbenium Ions

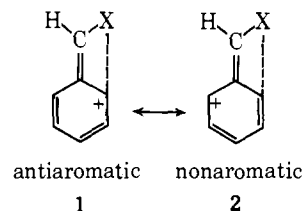
Sir:

The intriguing concept of nonbonded electronic interactions, as developed recently by Epiotis, provides an explanation for several cases of torsional isomerism where a more sterically

crowded geometry is more stable than less crowded geometries.<sup>1-7</sup> In this communication we suggest that nonbonded interaction may also have a substantial influence on the distribution of electrons within a molecule, particularly in charged, conjugated systems.<sup>8</sup> Specifically, attractive and repulsive nonbonded interactions are discussed in relation to the distribution of charge in phenylcarbenium ions (benzyl cations) with the aim of providing an explanation for some unusual <sup>13</sup>C NMR chemical shifts.

The concept of nonbonded electronic interactions is based on orbital symmetry arguments and as such may be expressed in various ways. The simplest approach is to consider whether a possible interaction is aromatic, nonaromatic, or antiaromatic.<sup>3,9</sup> Nonbonded interactions of this type occur when two atoms (not formally bonded) approach closely enough for orbital overlap so that the overlap completes a continuous cycle of overlapping orbitals. With Hückel topology for the cyclic array of orbitals, attractive nonbonded interactions will be present if the cycle is aromatic, i.e., when  $4N + 2$  electrons are in the cycle. Repulsive nonbonded interactions are expected for a cycle of  $4N$  electrons.

In phenylcarbenium ions substituted at the carbenium center, nonbonded  $\pi$ -electron interactions can be considered for a 4-atom cycle of p orbitals that is completed by long-range overlap between the substituent and the syn ortho carbon, in analogy with cis-1,2-disubstituted ethylenes.<sup>1,3-5</sup> Considering only the two resonance structures that place charge in the ortho positions, it can be seen that, with the substituent contributing  $2\pi$  electrons,<sup>10</sup> the 4-atom cycle contains  $4\pi$  electrons and is thus antiaromatic when the charge is at the syn ortho carbon. Resonance structure **1** with repulsive, antiaromatic interactions

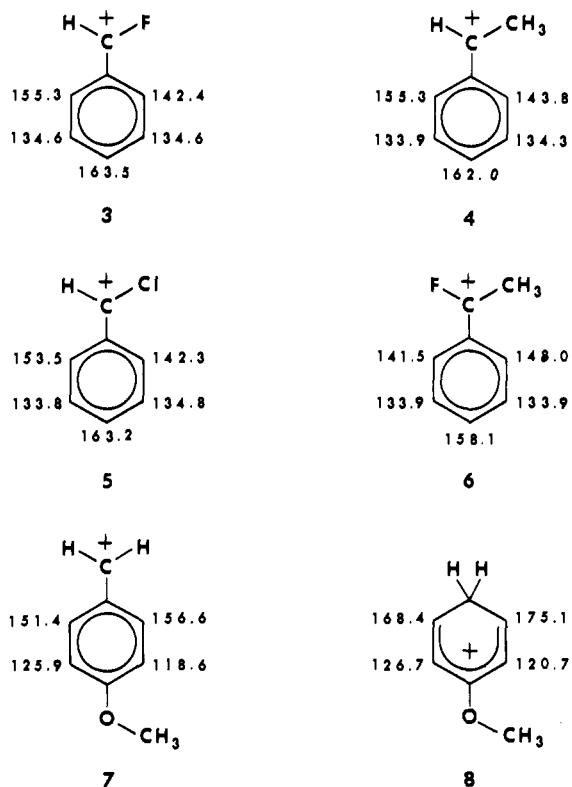


should contribute less to the resonance hybrid than structure **2** where such effects are absent; hence, less positive charge is expected to reside at the syn ortho carbon than the anti ortho carbon.

Chart I presents the <sup>13</sup>C NMR chemical shifts for ring carbons in some stable phenylcarbenium ions.<sup>11</sup> The ortho and para carbons are deshielded owing to positive charge, but there is a large difference between the ortho carbons in ions **3-5**. The difference is 12.9 ppm in **3**, 11.2 ppm in **4**, and 11.5 ppm in **5**. The syn ortho carbon is substantially shielded relative to the anti ortho carbon or the para carbon, consistent with the prediction of less positive charge due to repulsive nonbonded interactions. However, it is difficult to quantitatively assess this postulated effect in terms of  $\pi$ -electron densities, because the well known  $\gamma$ -substituent effect is probably operative also in shielding both ortho carbons. The shielding effect of a  $\gamma$  substituent is usually larger in a syn or gauche alignment relative to anti, but no other cases have been reported where the difference between syn and anti effects approaches the magnitude of 11-13 ppm.<sup>12</sup>

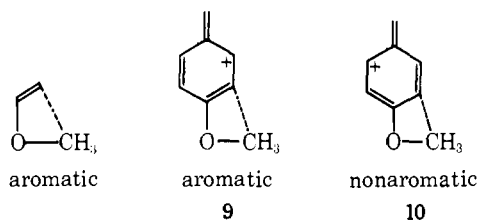
The data for ion **6** indicate that the shielding of the syn ortho carbons is not a constant effect of the nearby carbenium substituent. If the shielding effect were constant and additive, extrapolation from ions **3** and **5** would predict a difference of 1.4 ppm instead of the 6.5-ppm difference observed for the ortho carbons in ion **6**. A reasonable conclusion is that orbital interaction is more effective for fluorine than methyl, so that the repulsive interaction involving the fluorine atom dominates. The methyl repulsive interaction would shift charge from the

**Chart I.**  $^{13}\text{C}$  chemical shifts are in parts per million relative to external (capillary)  $\text{Me}_4\text{Si}$ .



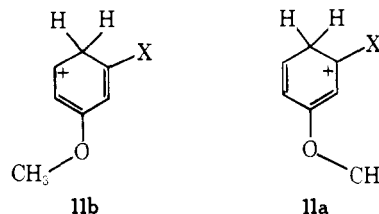
syn ortho carbon partially to the anti ortho carbon, but in 6 such a shift would be unfavorable because of the fluorine interaction.

Even more unusual  $^{13}\text{C}$  chemical shift behavior occurs in the *p*-methoxyphenylcarbenium ion **7** and the *p*-methoxybenzenium ion **8**. The rotation of the methoxy group is "frozen out" in these ions. The carbons ortho to methoxy have non-equivalent chemical shifts as expected, but the carbons meta to methoxy also differ by  $>5$  ppm. Since the meta carbons are not sterically proximate to the methoxy group, it is difficult to ascribe this large difference to any direct substituent influence. However, considering only the two resonance structures which place charge at the relevant positions, it can be seen that an aromatic cycle exists in structure **9** which is analogous to the aromatic cycle responsible for the attractive nonbonded interactions in methyl vinyl ether.<sup>6</sup> Structure **10** has double



bonds cross-conjugated with the possible cycle, so the nonbonded  $\pi$  interaction would be nonaromatic. Thus, a greater contribution of **9** than **10** to the resonance hybrid could account for the chemical-shift difference for the carbons meta to methoxy on the basis of  $\pi$ -electron densities.<sup>13</sup>

The postulated difference in charge densities is verified by protonation of *m*-methylanisole and *m*-fluoroanisole in  $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$  to form benzenium ions (**11**). At  $-70^\circ\text{C}$ , methoxy rotation is slow. The relative amounts of the two conformers (**11a:11b**) are 74:26 when  $\text{X} = \text{F}$ , and 76:24 when  $\text{X} = \text{CH}_3$ . The electron-releasing substituents favor confor-



mation **11a** in which the carbon bearing the substituent is predicted to have greater positive charge than that in **11b**.

Preliminary MO calculations are consistent with the above arguments.<sup>14</sup> Using the CNDO/2 method, a standard calculation<sup>15</sup> of ion **3** was compared to a calculation in which the overlap between the  $p_z$  orbital on F and the  $p_z$  orbital on the syn ortho carbon was artificially set to zero. In changing from zero to normal overlap, the energy increased, thereby demonstrating that the interaction is net antibonding. Also, the positive charge on the syn ortho carbon decreased while it increased on the anti carbon. The reverse was true for **7**. Changing the overlap between the methyl orbitals and the  $p_z$  orbital on the ortho carbon from zero to normal in **7** results in an energy decrease consistent with a bonding interaction, and the charges again were altered in the direction consistent with our qualitative argument. We are now trying to quantitatively evaluate the influence of nonbonded interactions on charge distributions in further detailed MO and experimental studies.

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## References and Notes

- (1) N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 3087 (1973).
- (2) N. D. Epiotis, D. Bjorkquist, L. Bjorkquist, and S. Sarkanen, *J. Am. Chem. Soc.*, **95**, 7558 (1973).
- (3) N. D. Epiotis, S. Sarkanen, D. Bjorkquist, L. Bjorkquist, and R. Yates, *J. Am. Chem. Soc.*, **96**, 4075 (1974).
- (4) N. D. Epiotis, R. L. Yates, and F. Bernardi, *J. Am. Chem. Soc.*, **97**, 5961 (1975).
- (5) N. D. Epiotis and R. L. Yates, *J. Am. Chem. Soc.*, **98**, 461 (1976).
- (6) F. Bernardi, N. D. Epiotis, R. L. Yates, and H. B. Schlegel, *J. Am. Chem. Soc.*, **98**, 2385 (1976).
- (7) N. D. Epiotis, *Top. Curr. Chem.*, **70**, 1 (1978).
- (8) Torsional Isomerism in polyene cations and anions has been discussed in terms related to the approach of Epiotis: R. Hoffmann and R. A. Olofson, *J. Am. Chem. Soc.*, **88**, 943 (1966).
- (9) The aromaticity concept is used in the same manner as when applied to transition states of pericyclic reactions: H. E. Zimmerman, *Acc. Chem. Res.*, **4**, 272 (1971); M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).
- (10) A methyl group can be considered as a pseudo double bond: ref 8.
- (11) Data for **3** and **4** from G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 3419 (1975), and for **5**, **7**, and **8** from G. A. Olah, R. J. Spear, and D. A. Forsyth, *ibid.*, **98**, 6284 (1976). Ion **6** was prepared from 1,1-difluoro-1-phenylethane in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  at  $-80^\circ\text{C}$ .
- (12) E. L. Eiliel, W. F. Bailey, L. D. Kopp, R. L. Willer, D. M. Grant, R. Bertrand, K. A. Christensen, D. K. Dalling, M. W. Duch, E. Wenkert, F. M. Schell, and D. W. Cochran, *J. Am. Chem. Soc.*, **97**, 322 (1975), and references therein.
- (13) The chemical shifts for **7** and **8** assigned on the basis of expected  $\pi$ -electron densities are in agreement with shifts for meta-substituted *p*-methoxybenzenium ions which exist only in the less crowded conformation: G. A. Olah and D. J. Donovan, *J. Org. Chem.*, submitted for publication.
- (14) The calculations were used only to confirm the orbital analysis and were not intended for quantitative calculation of chemical shifts. No attempt was made to optimize geometries or to choose the best MO method for this type of study. As noted earlier,<sup>11</sup> the CNDO/2 calculations do not reflect the apparent charge density differences at the ortho positions in these ions. Eliminating long-range overlap as described results in small changes of  $\sim 0.5$  kcal/mol and 0.001–0.003 charge units.
- (15) Standard bond lengths and angles were used in calculations with the CNDO/2 method: J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N.Y., 1970.

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