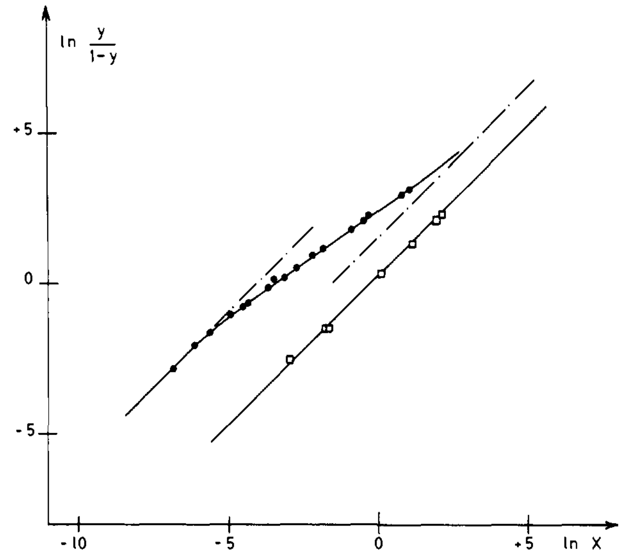

**Figure 1.** Hill plots of ln $Y/(1 - Y)$ vs. ln $[L_A][L_B]$ for $NaClO_4$ ($10^{-2}$ M) in binary mixtures of pyridine/THF (□) and ethylenediamine/THF (●). The theoretical tangents of unit slope are shown for the ethylenediamine/THF system in order to better visualize the curvature of the Hill plot.

of ln $[L_A]/[L_B]$, $Y$ being the fraction of sites on the $Na^+$ cation occupied by an amine ligand, and $L_A$ and $L_B$ being the THF reference solvent. *In a formal sense*, the fixation of a ligand on the sodium cation is indeed equivalent to the determination of the cooperativity in the binding of a ligand to a biomolecule with four subunits, such as the binding of $O_2$ to hemoglobin. For *unidentate* ligands,

$$Y = \sum_{i=1}^{4} \frac{i\alpha_i}{4} = \sum_{i=1}^{4} \frac{i\beta_i X^i}{4D} \qquad (1)$$

with $X = [L_A]/[L_B]$; $\beta_i = K_1.K_2...K_i$; $D = \sum_{i=0}{}^4 \beta_i X^i$. For bidentate ligands, the saturation fraction $Y$ is given by eq 2, where $R_A$ and $R_B$ are the molar volumes of the constituents $L_A$ and $L_B$.

$$Y = \{\beta_1 X + 2\beta_2 X(R_A X + R_B) + 3\beta_3 X^2(R_A X + R_B) + 4\beta_4 X^2(R_A X + R_B)^2\}/\{4[1+ \beta_1 X + \beta_2 X(R_A X + R_B) + \beta_3 X^2(R_A X + R_B) + \beta_4 X^2(R_A X + R_B)^2]\} \qquad (2)$$

A typical linear unit slope Hill plot, as obtained for *each* of the unidentate amines studied,[13] is shown in Figure 1. This finding demonstrates[17] the equality of the intrinsic constants $k_1 = k_2 = k_3 = k_4$, i.e., the absence of cooperativity with such ligands.

Conversely, the Hill plots for bidentate ligands[14] (see Figure 1 for a representative example) *deviate strongly from linearity with a unit slope*. For each of these bidentate ligands, analysis of these Hill plots[14,17] shows that, within an uncertainty of ca. 20%, $k_1 = k_3$ and $k_2 = k_4$ (Table I). The successive binding of the first and second amine *molecules* onto $Na^+$ are independent and equal steps. However, pronounced positive cooperativity occurs in the binding of the first and second nitrogen *atoms* from the same bidentate ligand: measuring this chelate effect by the $\alpha_2/\alpha_1$ ratio, we find values of 4.5 (cadaverin), 8.0 (1,3-diaminopropane), and 12.0 (ethylenediamine).

This new definition of the chelate effect bypasses the traditional snags, which have made it a controversial topic,[18] i.e., the choice of concentration units,[19-21] and of the appropriate standard states,[22,23] when comparing the equilibrium constants for a unidentate and for the corresponding bidentate ligand.

Our approach bypasses both these problems completely. Since all the results are obtained relative to one and the same reference solvent (THF), we isolate the chelate effect with no ambiguity from data obtained solely on the bidentate ligands. Instead of an *inter*molecular comparison between bidentate and unidentate ligands, we make the more appropriate *intra*molecular comparison between unity and the second *intrinsic* binding constants for a bidentate ligand, corrected for the presence of the reference solvent ($K_2R_B$).

Two other features of our results[13,14] deserve mention here. With the *unidentate* amines, we find that intrinsic equilibrium constants $k$ are simply proportional to the $^{23}Na$ chemical shifts measured for $Na^+$ in the pure amine solvents. It may appear surprising that a thermodynamic quantity ($k$) is related to a chemical shift, i.e., to an electronic distribution. However, there is precedence for such an observation: the $^{23}Na$ chemical shifts are also linearly correlated to another thermodynamic quantity, the Gutmann donicity of the solvent, when a salt such as $NaBPh_4$ is dissolved in a series of oxygen- and nitrogen-donor solvents.[24] The strength of the (predominantly electrostatic) chemical bond between $Na^+$ and nitrogen increases with nitrogen basicity, which is measured indirectly by the $^{23}Na$ chemical shift, and obeys the sequence aniline < pyridine < quinoline < pyrrolidine < benzylamine < propylamine < isopropylamine.

Furthermore, four clean straight lines arise when plotting the square root of the line widths reduced to unit viscosity $(\nu_i*)^{1/2}$ against the chemical shift $\delta_i$ for each of the four solvates ($i$ = 1–4).[25] Such a linearity is that predicted from the Deverell approach,[26] in which the quadrupolar coupling constant $\chi = e^2qQ/\hbar$ is proportional to the paramagnetic part of the shielding constant $\sigma_p$, as already observed experimentally for $^{23}Na$ in sodium cryptates.[27] These four $(\nu_i*)^{1/2}$ vs. $\delta_i$ lines converge to a single focal point, corresponding to the *diamagnetic* part of the shielding constant $\sigma_d$. This amounts to a direct experimental determination of $\sigma_d$ for $Na^+$ ions dissolved in mixtures of THF and amines: it differs by ca. −11 ppm from that for the hexaquo ion.

Thus, one may characterize fully, using the Hill procedure, each distinct solvate from its position in the $^{23}Na$ $(\delta,\nu*)$ configuration space. This mapping reduces into a single axis because chemical shifts and (line widths)$^{1/2}$ are proportional to one another. In this manner, an abundant array of hitherto poorly understood facts begins to be put into satisfying order.

**Acknowledgment.** We thank Fonds de la Recherche Fondamentale Collective for grants (2.4504.78 and 21.420 D) which allowed the purchase of the spectrometer used in this study.

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(17) Gill, S. J.; Gaud, H. T.; Wyman, J.; Barisas, B. G. *Biophys. Chem.* **1978**, *8*, 53–59.

(18) Munro, D. *Chem. Br.* **1977**, *13*, 100–105.

(19) Jameson, R. F. *MTP Int. Rev. Sci.: Phys. Chem., Ser. One* **1972**, *10*, 45–56.

(20) Agterdenbos, J. *J. Chem. Educ.* **1968**, *45*, 230.

(21) Prue, J. E. *J. Chem. Educ.* **1960**, *46*, 12–16.

(22) Beech, G. *Q. Rev., Chem. Soc.* **1969**, *23*, 410–429.

(23) Bell, C. F. "Metal Chelation, Principles and Applications", Oxford Chemistry Series, Oxford University Press: London, 1977.

(24) Erlich, R. H.; Popov, A. I. *J. Am. Chem. Soc.* **1971**, *93*, 5620–5623.

(25) Delville, A.; Detellier, C.; Gerstmans, A.; Laszlo, P. *J. Magn. Reson.*, in press.

(26) Deverell, C. *Prog. Nucl. Magn. Reson. Spectrosc.* **1969**, *4*, 235–334; *Mol. Phys.* **1969**, *16*, 491–500.

(27) Kintzinger, J. P.; Lehn, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 3313–3314.

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## Mediated Photochemical Oxidative Dimerization

*Sir:*

Despite the efficiency of electron ejection as a primary photoprocess in carbanion photochemistry,[1] a variety of anions resist

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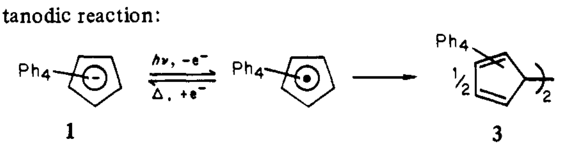
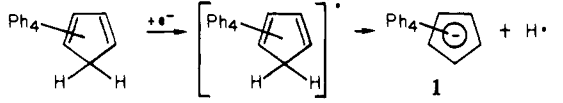
**Scheme I.** Possible Mechanism for Photoinduced Oxidative Dimerization

Photanodic reaction:



1 3

Dark cathodic reaction:



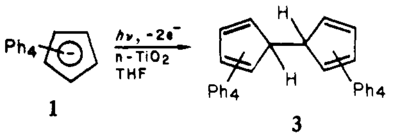
1

photoreaction in homogeneous solution in the absence of reactive electron acceptors. Presumably, this net excited-state deactivation is accomplished by recombination of the ejected electron with the product of the photooxidation. Thus, for a resonance-stabilized anion, $A^-$, photoexcitation may lead to production of a neutral radical paired with an electron (eq 1) while thermal recombination

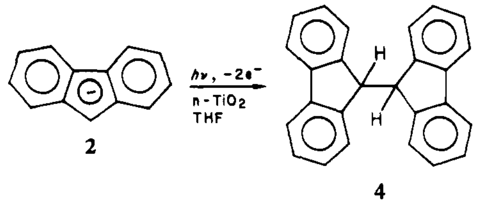
$$A^- \xrightarrow{h\nu} A\cdot + e^- \qquad (1)$$

(the reverse of eq 1) regenerates the ground state. Indeed, the inhibition of electron recapture (back-reaction) in the photooxidation of neutral compounds has been the key goal in recent photoelectrochemical studies.[2] The most successful approach to this problem has involved the underpotentials developed at semiconductor electrodes, either as irradiated surfaces[3] or as metallized powders.[4] We report here a comparison of the photochemistry of the tetraphenylcyclopentadienyl anion (**1**) and the fluorenyl anion (**2**) in aprotic solvents in homogeneous solution and at the surface of a semiconductor electrode. These experiments represent a new route for a visible-light-induced dimerization of their hydrocarbon precursors and an unexplored method for establishing a mechanism in the photolysis of easily oxidized organic compounds.

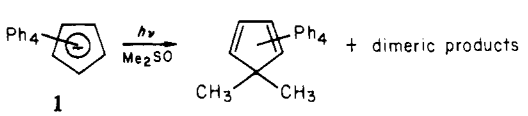
If a tetrahydrofuran (THF) solution of a 1:1 mixture of tetraphenylcyclopentadiene or fluorene with their lithium salts **1** or **2**[5] (~0.1 M) was irradiated in the visible (focused GE 250 sunlamp) or far-ultraviolet (Rayonet 350-nm phosphor-coated low-pressure mercury lamps) wavelength regions under argon for 24 h, no changes in the proton NMR spectrum of the photolysis mixture could be observed, and the neutral hydrocarbons could be recovered virtually quantitatively after an acid quench. In contrast, if these irradiations were similarly conducted at the surface of a doped single-crystal n-type $TiO_2$ electrode (area ~2 $cm^2$) in a photoelectrochemical cell, octaphenyldihydrofulvalene[6] **3** and bifluorenyl **4** could be detected (eq 2 and 3). In homogeneous dimethyl sulfoxide ($Me_2SO$) solution, a 1:1 hydrocarbon:potassium salt mixture of **1** or **2** irradiated under the same conditions led to dimethylated products[7] [28% and 45%, respectively, after overnight irradiation (eq 4 and 5)], a reaction known[8] to involve photoinduced electron transfer to solvent. When this photolysis was conducted at the surface of the potentiostated (0.0 eV vs. Ag) n-$TiO_2$ electrode, both alkylation (eq 4 and 5) and dimerization (eq 2 and 3) products can be detected.



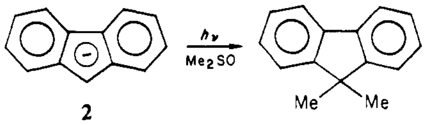
1 3 (2)



2 4 (3)



1 5 (4)



2 6 (5)

A conceivable mechanism for the photoelectrochemical conversion of **1** to **3** consistent with our experimental results is shown in Scheme I. Here the chemistry is assumed to occur in two half-cells. Since oxidative photocurrents are observed, we characterize these as a photoanodic reaction and a dark cathodic reaction. This scheme incorporates several key features: photoinduced electron ejection as the primary photoprocess, rapid bimolecular coupling of the photogenerated radicals, capture of the expelled electron by hydrocarbon, and loss of hydrogen from the anion radical. Each of these steps has reasonable precedent in related reactions.

Photochemical electron ejection is a nearly ubiquitous reaction among carbanions. The very low oxidation potentials of **1** and **2** (see below) make transfer of electrons from anion to acceptors under the influence of long wavelength ultraviolet–visible light (2–3.5 eV) certainly reasonable. Accordingly, the transient formation of the stilbene anion radical can be detected when a $N_2$ laser flash[9] is used to excite THF solutions of **1** or **2** in the presence of *trans*-stilbene. Furthermore, an anodic photocurrent (0.5–10 $\mu A/cm^2$) can be observed if dilute solutions of **1** or **2** are irradiated at the surface of an n-$TiO_2$ semiconductor electrode in a previously described photoelectrochemical cell.[10]

Radical coupling is known to be a very rapid process, and literature preparations of dimers **3**[6] and **4** probably proceed through a radical dimerization. Such radicals could be generated under conditions similar to those encountered at the surface of the semiconductor if a preparative electrolysis were conducted. Cyclic voltammetry[11] of solutions of $\mathbf{1}\cdot K^+$ in $Me_2SO$ or $\mathbf{1}\cdot Li^+$ in THF on platinum reveals irreversible anodic waves at +0.25 eV (vs. Ag). An analogous oxidation of $\mathbf{2}\cdot M^+$ could also be observed; $K^+$ (+0.15 eV, $Me_2SO$/*t*-BuOK); $Li^+$ (+0.30 eV, THF/*n*-BuLi vs. Ag). Although the electrochemical oxidative dimerization of enolate anions has been described,[12] nearly no chemical characterization of products derived by preparative electrochemical oxidation of carbanions has been undertaken.[13] Preparative electrochemical oxidation (1 faraday/mol) of $\mathbf{1}\cdot K^+$ (10 mmol) in $Me_2SO$ at +0.5 eV led to a mixture containing **3** (50%), an

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(1) Fox, M. A. *Chem. Rev.* **1979**, *79*, 253.

(2) Gerischer, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *58*, 263. Archer, M. D. *J. Appl. Electrochem.* **1975**, *5*, 17.

(3) Gerischer, H.; Willig, F. *Top. Curr. Chem.* **1976**, *61*, 31.

(4) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 5985, and references cited therein.

(5) The salts were prepared by treating a solution of the parent hydrocarbon with 1.1 equiv of *n*-butyllithium or potassium *tert*-butoxide.

(6) Pauson, P. L.; Williams, B. J. *J. Chem. Soc.* **1961**, 4158.

(7) **5**: NMR ($CDCl_3$) δ 6.6–7.7 (m, 20 H), 2.08 (s, 6 H); mass spectrum, (*m/e*) 320, 382, *383*, 397, 398 ($P^+$); anal. C, H. **6**: mp 98 °C. Spectral properties were identical with those of authentic material.

(8) Tolbert, L. M. *J. Am. Chem. Soc.* **1978**, *100*, 3952.

(9) The flash experiments were conducted at the Center for Fast Kinetics Research at the University of Texas at Austin with the assistance of Dr. M. A. J. Rodgers. CFKR is supported by the National Institutes of Health and by the University of Texas at Austin.

(10) Fox, M. A.; Kabir-ud-Din *J. Phys. Chem.* **1979**, *83*, 1800.

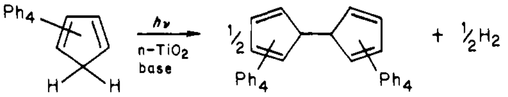
(11) Cyclic voltammetry (cv) was conducted in freshly distilled, degassed solvent containing 1 M $LiClO_4$. Upon addition of neutral hydrocarbon precursor and upon injection of a THF solution of base in sufficient quantity to generate the anion, the potential was scanned in the region from +1.5 to −1.5 eV vs. Ag.

(12) Kern, J. M.; Federlin, P. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *96*, 209.

(13) For an exception to this generalization, see: Schäfer, H.; Azrak, A. A. *Chem. Ber.* **1972**, *105*, 2398. Lochert, P.; Federlin, P. *Tetrahedron Lett.* **1973**, 1109. Also see ref 17.

uncharacterized product of further oxidation[14] (35%, $C_{58}H_{40}$), and recovered **1**. The ratio of **3** to $C_{58}H_{40}$ decreased during the electrolysis, consistent with initial production of **3**. The analogous oxidation of **2** (10 mmol) was cleaner, **4** being produced in ~80% yield after a 1 faraday/mol oxidation. Methylation products were specifically absent from both electrolyses.

If the doped semiconductor surface functions as an electrochemical half-cell,[15] the photoinjected electron must be returned to an easily reducible acceptor. To the extent that the radical functions as an acceptor, the reaction efficiency will be reduced. Alternatively, the solvent or some dissolved reducible species can accept an electron at the dark cathodic half-cell. Possible acceptors include the hydrocarbon precursor of the anion (shown in Scheme I) or the dimeric product. Since the radical anions of cyclopentadiene[16] and fluorene[17] are known to lose a hydrogen atom to generate the aromatic anions, this reduction would ultimately regenerate anionic starting material. The dimeric product can play an analogous role.[18,19] If this scheme is correct, the net conversion is given in eq 6. Estimation[20] of the bond energy change involved in eq 6 predicts this conversion to be endothermic, making eq 6 a photoelectrosynthetic reaction where the thermicity is supplied by the excitation energy of anion **1**. The major factor limiting the utility of this reaction is its very low photoefficiency,[21,22] crudely estimated as $\leq 10^{-4}$ if the anion is selectively excited.



(6)

The contrasting photoreactivity observed in homogeneous solution can also be accommodated by this scheme. If the semiconductor surface is absent, primary electron transfer to solvent will occur upon exciting the anions in $Me_2SO$, and the formation of methylation products would be expected.[8] Such products would not be expected in THF where the thermal back-reaction (eq 1) would occur more readily than any bimolecular radical reaction. The semiconductor surface may function therefore as an electron acceptor to separate the radical and electron for a period long enough to allow dimerization and to reduce electron transfer to solvent. The generation of reactive radicals in the mediated oxidation of acetate[4] on metallized powders provides precedent for this function of the semiconductor. Here, however, in the absence of reducible protons, the radicals generated by photoinduced electron expulsion will accumulate, ultimately giving rise to the dimer. It is significant to note that these products can be formed by irradiation with wavelengths absorbed either by the semiconductor (in analogy with a photovoltaic cell; $\lambda > 300$ nm) or by the anion (in analogy with a sensitized photogalvanic cell; $\lambda > 420$ nm).

New routes for carbon–carbon bond formation initiated by photolysis at semiconductor surfaces are under active investigation in our laboratory, as are further mechanistic details of these reactions.

**Acknowledgment.** We are grateful to the U.S. Department of Energy, Office of Basic Energy Sciences, and to the Robert A. Welch Foundation for partial support of this research. We thank Dr. Ronald Wilson of General Electric Research for the gift of the single-crystal n-$TiO_2$ electrodes used in this study.

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(14) $C_{58}H_{40}$: NMR ($CDCl_3$) $\delta$ 6.5–8.0 (m); mass spectrum, *m/e* 368, 370, 736 ($P^+$); anal. C, H.

(15) Bard, A. J. *J. Photochem.* **1979**, *10*, 59.

(16) Bitman, G. L.; Perevolova, E. C.; Skorokhodov, I. I.; Myaskovskii, I. F. *Zh. Fiz. Khim.* **1969**, *43*, 1290; *Teor. Eksp. Khim.* **1970**, *6*, 418.

(17) Borhani, K. J.; Hawley, M. D. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *101*, 407.

(18) If bifluorenyl is reduced cathodically, some C–C cleavage to regenerate monomeric anion may be anticipated.[17] Since the $pK_a$ of 9-methylfluorene is lower than that of fluorene,[19] however, deprotonation of the dimer by **2** might be expected to protect the dimer from this cleavage, at least at low conversions of **2**.

(19) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.

(20) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

(21) Photoefficiency here is defined as a product of the quantum yield for dimer formation and the fraction of light effective in exciting molecules at the surface of the electrode. Direct determination of light absorbance at the electrode is difficult, but since the order of magnitude of the photocurrents observed here corresponds to those reported for charge injection by dye sensitization[22] (rhodamine B on ZnO), we assume here comparable overall efficiency.

(22) Spitler, M.; Calvin, M. *J. Chem. Phys.* **1977**, *66*, 4294; *Ibid.* **1977**, *67*, 5193.

(23) Alfred P. Sloan Research Fellow, 1980–1982.

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*Received May 5, 1980*

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## The Possibility of π-Electron Donation by the Electron-Withdrawing Substituents CN, CHO, $CF_3$, and $^+NH_3$

*Sir:*

Solvolysis studies[1] and PRDDO calculations[2] both show that cyano groups destabilize an $\alpha$ cation less than a $\beta$ cation. This effect was attributed to $\pi$ donation by the cyano group, a result contrasted to the effects of carbonyl[3] and trifluoromethyl groups[4] on cationic centers. The importance of $\pi$ donation by cyano, carbonyl, and other groups which possess relatively high-lying filled $\pi$ orbitals was postulated earlier to account for the regioselectivity of cycloadditions of highly electrophilic addends to electron-deficient alkenes.[5] Such $\pi$ donation by strong inductive electron withdrawers has even been proposed for the trimethylammonio substituent to explain the very different values of the Hammett and Brown substituent constants of $\sigma_p = 0.88$ and $\sigma_p{}^+ = 0.41$, respectively.[6]

In order to assess the relative $\sigma$-inductive withdrawal and $\pi$-donor effects of these substituents for cations, and to compare these ambivalent substituents to the trifluoromethyl group, which is generally thought to be a relatively pure electron withdrawer, ab initio (STO-3G and 4-31G) calculations have been carried out on a variety of primary, secondary, and tertiary cations containing these substituents in $\alpha$, $\beta$, $\gamma$, and $\delta$ positions.

The frontier molecular orbital theory predictions that the unsubstituted olefinic carbon of acrylonitrile should be more nucleophilic than the substituted one[5] are verified by calculations. At various theoretical levels, protonation of the double bond of acrylonitrile is predicted to give the cation $\alpha$, rather than $\beta$, to the cyano group.[7-9] The proton affinity for $\alpha$ protonation is 147

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(1) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 1214.

(2) Dixon, D. A.; Charlier, P. A.; Gassman, P. G. *J. Am. Chem. Soc.* **1980**, *102*, 3957. We thank Professor Gassman for communicating these results to us prior to publication. (b) These results contrast with the recent conclusion that CN is only a $\sigma$ and $\pi$ acceptor: Dill, J. D.; Greenbury, A.; Liebman, J. F. *Ibid.* **1979**, *101*, 6814.

(3) Creary, X. *J. Org. Chem.* **1979**, *44*, 3938.

(4) Koshy, K. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1980**, *102*, 1216.

(5) (a) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361, and references therein. (b) Houk, K. N.; Domelsmith, L. N.; Strozier, R. W.; Patterson, R. T. *J. Am. Chem. Soc.* **1978**, *100*, 6531.

(6) (a) English, P. J. Q.; Katritzky, A. R.; Tidwell, T. T.; Topsom, R. D. *J. Am. Chem. Soc.* **1968**, *90*, 1767, and references therein. (b) Leffler, J. E.; Grunwald, E. "Rates and Equilibrium of Organic Reactions", Wiley: New York, 1963; p 204.

(7) Computational levels are specified as follows: level at which energy calculation was performed//level at which geometry optimization was performed. The ab initio calculations were carried out with the GAUSSIAN 70 program (*QCPE* 236, by Hehre, W. G.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A.) with the STO-3G or 4-31G basis sets.

(8) On the basis of experimental gas-phase proton affinities (PA) of ethylene (160 kcal/mol)[9a] and of alkylnitriles (188–193 kcal/mol, where N is protonated),[9b] acrylonitrile (PA = 188.8 kcal/mol)[9b] will protonate on nitrogen.