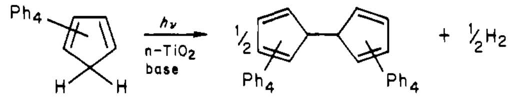
uncharacterized product of further oxidation[14] (35%, $C_{58}H_{40}$), and recovered **1**. The ratio of **3** to $C_{58}H_{40}$ decreased during the electrolysis, consistent with initial production of **3**. The analogous oxidation of **2** (10 mmol) was cleaner, **4** being produced in ~80% yield 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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[23] Alfred P. Sloan Research Fellow, 1980–1982.

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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 α cation less than a β cation. This effect was attributed to π donation by the cyano group, a result contrasted to the effects of carbonyl[3] and trifluoromethyl groups[4] on cationic centers. The importance of π donation by cyano, carbonyl, and other groups which possess relatively high-lying filled π orbitals was postulated earlier to account for the regioselectivity of cycloadditions of highly electrophilic addends to electron-deficient alkenes.[5] Such π 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 σ-inductive withdrawal and π-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 α, β, γ, and δ 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 α, rather than β, to the cyano group.[7-9] The proton affinity for α protonation is 147

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[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.

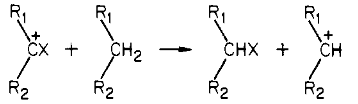
Table I. Stabilization Energies ($\Delta E > 0$) or Destabilization Energies ($\Delta E < 0$) of Cyano-, Formyl-, Trifluoromethyl-, and Ammonio-Substituted Cations

			ΔE		
entry	cation	eq[a]	STO-3G//stnd	STO-3G//STO-3G	4-31G//STO-3G
1	$H_2{}^+CCN$ (Figure 1)	1(2)	−4.9	+0.1	−9.9
2	$CH_3{}^+CHCN$	1	−9.3	−5.0	−14.7
3	$(CH_3)_2{}^+C$	1		−8.4	−17.3
4	$^+CH_2CH_2CN$ (eclipsed)	2	−19.0[d]	−18.3	−22.5
5	$^+CH_2CH_2CH_2CN$	2	−13.7[d]		
6	$^+CH_2CH_2CH_2CH_2CN$	2	−9.1[d]		
7	$^+CH_2CHO$ (pl) (Figure 1)	1	+15.2	+15.5	−6.1
8	$^+CH_2CHO$ (perp)[b]	1		+3.5	−10.8
9	$CH_3{}^+CHCHO$ (pl)	1		+10.5	−9.3
10	$CH_3{}^+CHCHO$ (perp)[b]	1		+2.0	
11	$(CH_3)_2{}^+CCHO$	1		+6.9	−9.9
12	$^+CH_2CHO\cdots H_2O$[c]	1	+9.5	+9.8	
13	$^+CH_2CH_2CHO$	2	−7.2	+1.2	−11.8
14	$^+CH_2CH_2CH_2CHO$	2	−1.2	−0.7	−5.1
15	$^+CH_2CF_3$ (Figure 1)	1	−3.0	−4.4	−37.3
16	$^+CH_2CH_2CF_3$	2	−10.9		
17	$^+CH_2CH_2CH_2CF_3$	2	−6.7		
18	$^+CH_2{}^+NH_3$ (Figure 1)	1	−171.6	−163.5	−156.9
19	$^+CH_2CH_2{}^+NH_3$	2	−135.4		
20	$^+CH_2CH_2CH_2{}^+NH_3$	2	−105.2		

[a] See text for equations. [b] HCCO dihedral angle = 90°. [c] Including a water molecule hydrogen bonded to the carbonyl group at an H–O distance = 2.95 Å. [d] From ref 12.

kcal/mol, while that for β protonation is 154 kcal/mol at the 4-31G//STO-3G[7] level. Protonation of either terminus is more difficult than protonation of ethylene, which has a proton affinity of 171 kcal/mol at this level.[8] At least one experimental result is available to suggest that electrophiles (NOCl) attack the unsubstituted carbon of acrylonitrile,[10] and the more electrophilic termini of dienes and 1,3-dipoles often do so as well.[5]

A more general assessment of the influence of electron-withdrawing groups on cationic centers was made by carrying out complete geometrical optimizations of a variety of cyano-, formyl-, trifluoromethyl-, and ammonio-substituted cations and neutral hydrocarbons at the STO-3G level, followed in most cases by single-point 4-31G calculations on these geometries. The effects of these groups on the energies of various cations have been assessed by the following isodesmic reactions (eq 1 and 2).[11] In



$$\overset{R_1}{\underset{R_2}{\overset{+}{C}X}} + \overset{R_1}{\underset{R_2}{C}H_2} \rightarrow \overset{R_1}{\underset{R_2}{C}HX} + \overset{R_1}{\underset{R_2}{\overset{+}{C}H}} \quad (1)$$

$$X(CH_2)_n\overset{+}{C}H_2 + H(CH_2)_nCH_3 \rightarrow X(CH_2)_nCH_3 + H(CH_2)_n\overset{+}{C}H_2 \quad (2)$$

these equations, R_1 and R_2 = H or alkyl and X = CN, CHO, CF_3, or $^+NH_3$. A positive reaction energy indicates that X stabilizes the cation relative to the alkane. Table I summarizes the results. Previous calculations on nonconjugated cyano-substituted cations indicated destabilization which is only weakly attenuated by intervening methylene units.[12] Our STO-3G calculations on the cyanomethyl cation (entry 1) imply small *stabilization* (0.1 kcal/mol) of the carbonium ion with respect to H. The importance of π donation (resonance) in the cyanomethyl cation is supported by the geometry of the species (Figure 1) and by the π overlap populations and atomic charge densities in these species.[2] However, STO-3G calculations overestimate π donation by the cyano group. The *cyano* group is correctly predicted to destabilize the cyclohexadienyl cation regardless of the site of substitution, but ortho- and para-protonated benzonitriles are incorrectly predicted to be less destabilized (−14.2 and −14.4 kcal/mol, respectively) than meta-protonated benzonitrile (−14.8 kcal/mol). Similar results were found for metal and para protonation of benzonitrile by McElvey et al.[13] Calculations on $^+CH_2CN$ with the more reliable 4-31G basis set indicate that the cyano group destabilizes the carbonium ion by 10 kcal/mol with respect to hydrogen. The overestimation of π donation is a general problem in STO-3G calculations, since the vacant p orbital adjacent to a potential π-donor in effect expands the basis set available for stabilization of the substituent π electrons.[14] However, the STO-3G results

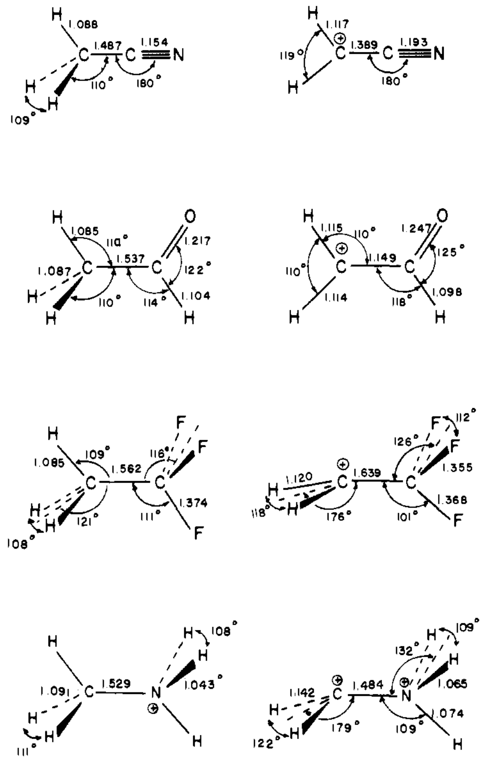


Figure 1. STO-3G optimized geometries of substituted methanes and methyl cations.

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should be qualitatively reliable for the nonconjugated cations (entries 4–6, 13, 14, 16, 17, 19, and 20).

The π-donor effect of the cyano group is rapidly attenuated with successive introduction of methyl groups (entries 1–3). That is, the most stable cations are destabilized most by the cyano group. This occurs since the inductive effect drops off only slowly as the cation is stabilized whereas the π-donor effect is rapidly diminished as the cation LUMO is destabilized by donor alkyl groups.

Each methyl group attenuates the stabilization due to π donation of the cyano group by 4–5 kcal/mol. Reduced π donation is reflected in a shortening of the CN bond length by ~0.013 Å, and a lengthening of the C–C$^+$ bond by 0.025 Å per methyl group. For $^+CH_2CN$, π donation is stabilizing by 15–20 kcal/mol, assuming that the inductive destabilization of $^+CH_2CN$ is about 5 kcal/mol greater than that for the β-cyanomethyl cation.

With the formyl substituent, calculations at the STO-3G level predict an unrealistic stabilization of 16 kcal/mol (entry 7) in the formylmethyl cation whereas the 4-31G calculation predicts destabilization, but to a lesser extent than is observed with cyano. When the formyl group is rotated 90° out of planarity, an additional 5 kcal/mol destabilization results (entry 8). This is to be expected since π-conjugated effects are now absent. Introduction of methyl groups again attenuates the π donation of the formyl group by ca. 3 kcal/mol (entries 7, 9, and 11; 4-31G results) per methyl group. Although the geometry of the $^+CH_2CHO$ species reflects substantial π donation by the formyl group, the C=O bond length of $^+(CH_3)_2CCHO$ is lengthened by only 0.009 Å with respect to that in 2-methylpropanal, which indicates little or no π delocalization in this cation. These data, together wth those of entries 13 and 14, indicate that the inductive effect of the formyl group destabilizes the methyl cation by ≥19 kcal/mol, and π donation stabilizes the same group by ≥13 kcal/mol.

Thus, the smaller destabilization of an α cation by formyl than by cyano is a result of the larger σ-electron withdrawal by cyano, which is only partially counteracted by the greater π donation by cyano. Geometric changes, charge densities, and overlap populations as well as energetic estimates made earlier for the cations confirm the greater π donation by cyano. For example, the $^+C_\alpha$–C bond length contracts by 0.098 Å in the cyanomethyl cation but only by 0.047 Å in the formylmethyl cation (Figure 1). The π charge at the cationic center is +0.71 in the cyanomethyl cation and +0.83 in formylmethyl although the total charges on the CH_2 groups are in the opposite direction, +0.71 and +0.67, respectively.

A substituent usually thought to be purely inductively electron withdrawing, CF_3, has a larger destabilizing influence on cations than CN or CHO, but calculations performed at the STO-3G level imply that even CF_3 shows abnormally low destabilization of an α cation as compared to a more remote cation. Our results indicate that CF_3 is intermediate between CN and CHO in σ-withdrawing ability (as reflected in σ^* values)[15] but provides much less resonance stabilization when α to a cationic center. The 2,2,2-trifluoromethyl cation is distorted in exactly the same fashion as the ethyl cation.[16] However, very little π density (0.04 electron density) resides in the cation p orbital compared with the cyano and formyl cations (0.21 and 0.24 electrons, respectively). At the 4-31G level, the 2,2,2-trifluoroethyl cation is destabilized by 37 kcal/mol. This result indicates that there is no hyperconjugative stabilization by the trifluoromethyl group.

The potential π-donor[6] effect of the ammonio substituent is suggested at the STO-3G level by the typical hyperconjugatively distorted geometry of the dication, especially the shortened CN bond as compared to that in the methylammonium cation. However, this effect is small energetically: pure coulombic interactions between two plus charges located at the distance separating N and C$^+$ in the γ, β, and α ammonio cations would destabilize these species by 87, 135, and 209 kcal/mol; calculations with the STO-3G basis set indicate destabilizations of 105, 135, and 172 kcal/mol, respectively.

In summary, we emphasize again that the π-donor effect of CN and carbonyl substituents is only manifested when these substituents are attached to very unstable cations. For this reason, the π-donor effect of groups is not easily detected in "classical" systems designed to prove substituent effects. For example, σ_p and σ_p^+ constants for CN, CO_2Et, and CF_3 are quite similar (σ_p = 0.66, 0.45, and 0.54; σ_p^+ = 0.66, 0.48, and 0.61, respectively).[6b] Since the cyclohexadienyl cation is highly stabilized, the π-donor effects of these substituents are largely suppressed.

Hydrogen bonding of hydroxylic solvents to the heteroatoms of groups such as cyano, formyl, or trifluoromethyl should exacerbate the destabilization of cations. For example, the $CH_3CHO\cdots HOH$ hydrogen bond has an energy of 6 kcal/mol, whereas no stable hydrogen-bonding minimum is found for the corresponding cation. On the other hand, polar solvents will stabilize cations through direct (electrostatic or overlap) effects on the cationic center, and this will level differences in stabilization of cations. Schleyer et al. found that approximately 40–50% of the stabilization of the allyl cation caused by methyl groups appears in the transition state of solvolysis reactions.[11]

The strong acceleration of S_N2 reactions by α-cyano and carbonyl substituents[17] may also be related to the phenomena described here. That is, in a transition state where little or no plus charge is built up on the center undergoing substitution, but considerable p-orbital character develops, then cyano and carbonyl groups can provide large conjugative stabilization of the transition state, just as a vinyl substituent does, without the necessity of secondary orbital interactions.

In the full account of this work, the optimized structures of many of these species will be reported, along with a more complete survey of electron-withdrawing group effects on cations.

Acknowledgment. We are grateful to the National Science Foundation for support of this research and to Professor R. A. More O'Ferrall for stimulating discussions.

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Dynamics and Energetics of the Singlet–Triplet Interconversion of Diphenylcarbene

Sir:

Numerous calculations of the energy spacing separating the lowest singlet and triplet states of carbenes have been reported.[1] In contrast, almost no quantitative experimental information is available concerning the dynamics of interconversion or the energetic separation of the triplet and singlet states of carbenes, although many investigations of the products arising selectively from one of the two spin states have appeared. From competition experiments and kinetic analysis of the reactions of diphenylcarbene (DPC), it has been suggested that singlet diphenylcarbene

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