rearranged to 2-methyl-5-hydroxyindole (**6b**). Therefore, the electrolyzed sample was allowed to stand at room temperature under nitrogen for 5 h, then the analyte was extracted with four 50-mL portions of ethyl acetate, and the combined extracts were washed with an equal volume of saturated NaCl and dried over Na_2SO_4 for 12 h. Evaporation of the solvent left a maroon residue which showed three components on TLC. The major constituent was isolated by preparative TLC ($CH_3OH/CHCl_3$, 1:9) and was identified as 2-methyl-5-hydroxyindole (**6b**) by the NMR spectra which were completely analyzed and were identical with those of an authentic sample:[24] ^{1}H NMR (Me_2CO-d_6) δ 2.36 (d, J = 1 Hz, 3 H), 5.96 (m, J = 1 Hz, 1 H), 6.59 (dd, J = 2.44 Hz and 8.6 Hz, 1 H), 6.85 (d, J = 2.4 Hz, 1 H), 7.11 (d, J = 8.6 Hz, 1 H), 9.98 (br s, 1 H); ^{13}C NMR (Me_2CO-d_6) δ 13.4, 99.4, 104.1, 110.4, 111.3, 130.6, 131.5, 136.5, 151.1.

Electrolysis of 2,5-Dihydroxyphenylalanine (1c). Similar electrolysis of 2,5-dopa (**1c**) was carried out at +0.2 V for 3 h at pH 7.02 to yield a crude red-brown residue which showed only one main component by TLC. Pressure filtration (N_2) of a methanol/$CHCl_3$ solution through a bed of silica gel yielded a colorless solid having IR and NMR spectra identical with those of authentic 5-hydroxyindole (**6a**). The R_f, mp, and mmp were also identical with those of **6a**.

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Registry No. **1a**, 21581-41-9; **1a**·HBr, 61429-49-0; **1b**, 30891-22-6; **1b**·HBr, 92818-35-4; **1c**, 26122-90-7; **5a**·HCl, 92818-38-7; **6b**, 13314-85-7; **9**, 92818-36-5; **9**·HCl, 92818-37-6; 1-(2,5-dimethylphenyl)-2-aminopropane hydrochloride, 24973-25-9; 5-(benzyloxy)-1*H*-indole, 1215-59-4.

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Is π Delocalization Synonymous with Stabilization? A Theoretical Study of CH_2CN^+ and CH_2CN^-

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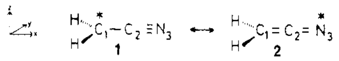
The relationship between π delocalization and stability in CH_2CN^+ and CH_2CN^- has been investigated by using SCF + CI computations. The results have been analyzed with a VB (valence-bond) technique and PMO arguments. The valence-bond analysis of the above species has shown that the π charge delocalization cannot be deduced from the geometrical parameters. The comparison of CH_2CN^+ and CH_2CN^- with CH_2CCH^+ and CH_2CCH^- has indicated that there is no obvious correlation between π charge delocalization and the electronegativity of the atoms. The σ effects have been shown to be the most important in determining the stability of such charged species.

The cyano group directly linked to a radical, a cationic or an anionic center, can lead to two main mesomeric structures.



* = ·, + or −

These three species have already been studied theoretically:[1-7] for each only one minimum is found on the potential energy surface. The problem is thus to determine which mesomeric form 1 or 2 they resemble more.

One way to analyze the electronic distribution of such species is to evaluate the weight of their various valence-bond (VB) structures. This has been done for the $CH_2CN\cdot$ radical[3] and the same method will be employed here for the cation and the anion.

It must be noted that many experimental studies indicate that the electron-withdrawing group CN is not as destabilizing as expected for a cation.[8-9] This result is explained by an important π donation of the CN group into the vacant orbital. Therefore it would seem logical, in order to give a better description of this delocalization, to introduce a configuration interaction (CI) which has not been used in the previous calculations. Furthermore the CN group with two π systems requires often an extensive CI for a proper description.[10]

It is usually believed that there is a relationship between delocalization geometric features, π electronic structure, and stability of a given species. The purpose of this paper is to investigate these relationships in CH_2CN^+ and CH_2CN^- by performing SCF + CI calculations and analyzing the wave function in term of its VB components.

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Table I. Optimized Geometries and Energies of CH_2CN^+ and CH_2CN^-

	CH_2CN^+			CH_2CN^-	
	STO-3G[a]	4-31G SCF	4-31G SCF + CI[c]	4-31G SCF	4-31G SCF + CI[c]
C-C, Å	1.389	1.359	1.376	1.366	1.366
C-N, Å	1.193	1.158	1.193	1.174	1.197
C-H, Å	1.117			1.073	
<HCC, deg	120.5			120.85	
E, au[b]		−130.74845	−130.85258	−131.08756	−131.15076

[a] From 4. [b] 1 au = 627.5 kcal/mol. [c] CI including only single and double excitations between the most important orbitals (see computational methods for details).

Computational Methods

The ab initio calculations have been performed with the MONSTERGAUSS program.[11] Geometry optimizations have been done either without CI, with a gradient procedure, or with CI by parabolic interpolation. In the latter case the CI used is that of the MONSTERGAUSS program and includes only single and double excitations between the most important orbitals (determined in a first stage by CIPSI—see below). To obtain more reliable stabilization energies, we have used an extended CI based on the CIPSI algorithm:[12] the most important determinants of the CI are treated variationally, the others being treated by a second-order Moller–Plesset perturbation. Excitations up to the sixth order are introduced. The core orbitals have been frozen and the determinants having a coefficient greater than 0.02 have been taken into account in the variational part of the CI.

The description of the electronic structures by a valence-bond (VB) analysis has been performed with a program written by P. Hiberty and C. Leforestier.[13] An approximate VB wave function is obtained by projecting a SCF + CI wave function on a complete basis of VB structures. Then, each structure can be given a weight by using a rigorous valence-bond population analysis taking the overlaps between structures into account. In this VB study, only the π_z system has been considered and the determinants introduced are those with a coefficient greater than 0.01 in the correlated wave function (obtained by using the CIPSI algorithm).

A population analysis of Mulliken type has been done after CI with the help of a program adapted on CIPSI$^+$. For this analysis all orbitals have been introduced in the CI. (+ Program adapted on CIPSI by J. P. Flament, Laboratoire de Synthèse Organique, Ecole Polytechnique, Palaiseau, France.)

The split-valence 4-31G basis set has been used both for the cation and the anion as in ref 1, 2, and 6. This basis set is known to reproduce anion geometries satisfactorily.[1,14] Furthermore, it gives a negative energy to the HOMO of CH_2CN^- which is thus nearly correctly described (bound orbital). It is known however that diffuse functions are often necessary to have a good description of the properties of anions, for example their proton affinities.[15] But such basis sets cannot be used for the VB analysis because the diffuse functions cannot be attributed to one center since they are delocalized over the whole molecule. For the same reason the Mulliken analysis is also not reliable. Therefore most of our calculations have been performed with the 4-31G basis set even for the anion. Diffuse functions have been introduced only in the last section for the comparison of delocalization and stabilization energies. (4-31+G basis set: the exponent is 0.04 for C and 0.054 for N. See ref 15.)

Finally in the last section, a Perturbativ Molecular Orbital (PMO) analysis has been performed.[16] The molecules are formally decomposed into two fragments, i and j. The two-orbital two-electron interaction energies are then calculated:

$$E^2 = \frac{2(hij - \epsilon_i Sij)^2}{\epsilon_i - \epsilon_j} \quad \text{or} \quad \frac{2(K - \epsilon_i)^2 Sij^2}{\epsilon_i - \epsilon_j} \tag{1}$$

hij and Sij are respectively the interaction matrix element and the overlap integral between the fragment orbitals ϕ_i and ϕ_j, and ϵ_i and ϵ_j are their energies. The fragments are kept in the same positions as in the initial molecules. In the same manner the two-orbital four-electron interaction is given by eq 2:

$$E^4 = \frac{4Sij^2}{1 - Sij^2}(\epsilon - K) \tag{2}$$

where ϵ is the mean energy of the orbitals i and j.

Results

(1) Geometry. The results of the geometry optimization are given in Table I. At the SCF level all the parameters have been optimized but at the SCF + CI level only the CC and CN bonds have been recalculated. The variations of geometry are greater for the cation than for the anion (especially the CN bond). This would indicate that the CI plays a more important role for the cation. Both bonds are lengthened but CN more than CC. This can arise for two reasons. A CI always lengthens bonds by filling the antibonding orbitals and emptying the bonding orbitals. This concerns both the σ and the π systems. The cyano group having two π systems is more sensitive to CI. The second reason could be the change with CI of the balance between the mesomeric structures **1** and **2**, if the π effects are preponderant in the geometry determination. This will be explained in more detail in the next section.

(2) Valence-Bond Analysis and Electronic Structure. The main VB structures are given in Table II. For comparison a VB calculation has also been made on the SCF wave function.

The structures with a charge separation play an important role which decreases with CI: it is well-known that ionic structures are overestimated at the SCF level. However, a striking feature is the importance of the last two structures. The CH_2CN^+ cation and the CH_2CN^-

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Table II. Weights of the Different Structures of CH_2CN^+ (A) and CH_2CN^- (B) Given by a Valence-Bond Analysis with the 4-31G Basis Set and a CI on the π_z System (CIPSI)

structure	no.	SCF[a]		SCF + CI[b]	
		A			
$H_2C^+-C\equiv N$	**1a**	0.345	0.433	0.438	0.457
$H_2C^+-C^+=N^-$	**1′a**	0.088		0.019	
$H_2C=C=N^+$	**2a**	0.142	0.157	0.158	0.159
$H_2C^--C^+=N^+$	**2′a**	0.015		0.001	
$H_2C-C^+=N$	**3a**	0.073		0.155	
$H_2C^+-C^-=N^+$	**4a**	0.337		0.229	
C^+/N^+		65/35		65/35	
		B			
$H_2C^--C\equiv N$	**1b**	0.318	0.390	0.407	0.424
$H_2C^--C^-=N^+$	**1′b**	0.072		0.027	
$H_2C=C=N^-$	**2b**	0.172	0.197	0.199	0.200
$H_2C^+-C^-=N^-$	**2′b**	0.025		0.001	
$H_2C-C^-=N$	**3b**	0.085		0.134	
$H_2C^--C^+=N^-$	**4b**	0.327		0.233	
C^-/N^-		61/39		62/38	

[a] SCF optimized geometry. [b] SCF + CI optimized geometry.

anion have respectively 16% and 14% of diradical character with the charge on the central atom (structures **3**). They both have 23–24% of "ambident" character with the charge simultaneously on C_1 and N (structures **4**).

Considering these various valence-bond structures, it is difficult to assign a character of triple or double bond to CN and of single or double bond to CC and thus to say that CH_2CN^+ or CH_2CN^- resembles more **1** than **2** since these two structures represent only 62% (64%, respectively) of the total. The π_z charge distribution between C_1 and N is determined by adding the weights of the structures **1**, **1′**, and **4** where C_1 or N bear the positive charge (respectively the negative charge) and substracting the weights of the structure **2′** where C_1 or N bear the negative charge (respectively the positive charge). This gives a π_z charge ratio $C^+/N^+ = 65/35$ for the cation and $C^-/N^- = 62/38$ for the anion. These values can be compared with those obtained by the Mulliken population analysis (Table III).

One can notice first that the electronegativity of N is apparently not directly related to the π_z charge distribution: in fact, the nitrogen bears almost the same π charge whether positive (35%) or negative (38%) and the various VB structures have roughly the same weights in the cation and in the anion. On the contrary, the effect of its electronegativity appears clearly in the total charge since in the CH_2CN^- anion N is more negative than C_1 and in the CH_2CN^+ cation N keeps a negative charge (Table III). The effect of the heteroatom on the π charge distribution will be discussed in a subsequent section.

Secondly the remaining orbitals, particularly the second π_{CN} system, have little influence on the π_z charge distribution: the use of a CI limited to the π_z system modifies only slightly the C/N π_z charge ratio (compare Tables II and III).

Finally, the π_z charge distribution does not vary much either between the SCF and the SCF + CI calculations (Tables II and III). Furthermore CH_2CN^+ shows a slight increase of the C/N charge ratio with CI, indicating a slight decrease of the delocalization. In fact the change arising from CI is in the distribution of the various valence-bond structures especially the diradical **3** and the "ambident" **4** ones. In section 1 we have seen that the effect of CI on the geometry is to lenghten CN much more than CC. Which conclusion can be drawn from the VB analysis? In the structures **3** and **4**, the CC bond has a partial character of double bond and the CN bond a partial character of triple bond. These two structures thus tend to shorten both the CC and the CN bonds. As their total weight diminishes with CI, the CC and CN bonds will be longer. But the weight of structures **1** increases with CI, lengthening CC and shortening CN. The foregoing arguments suggest that CN should not change much but CC should, in contradiction with the actual geometrical results.

It appears from this study that the geometry variation with CI can be correlated neither with the π_z charge distribution nor with the valence bond description of CH_2CN^+ and CH_2CN^- but arises at least in part from the electron density transfer induced by CI from the bonding to the antibonding orbitals (including both π and σ systems).

Therefore we can conclude from this valence-bond study of charged species that the charge delocalization and particularly the relative importance of the most expected structures as **1** and **2** cannot be deduced from the geometrical parameters. A VB analysis is then necessary to give a firmer conclusion about the structure of these species.

(3) Stabilization. In this section we will examine the effect of CI on the stabilization of such delocalized species. The CI used here is based on the CIPSI algorithm (see computational methods for details). Although it is known that diffuse functions will improve the energy values, the calculations are done with the 4-31G basis set in order to have a reasonable size of CI. Thus we shall have only trends and not quantitative values comparable to the experimental values as in the next section.

The energies ΔE_i of the following isodesmic reactions have been considered by numerous authors as the stabilization energies of CH_2CN^+ and CH_2CN^- with respect to the species where the cyano group is replaced by a hydrogen.[1,4-6] Leroy recently pointed out that the ΔE energy

$$CH_2CN^+ + CH_4 \rightarrow CH_3^+ + CH_3CN \qquad \Delta E_1$$

$$CH_2CN^- + CH_4 \rightarrow CH_3^- + CH_3CN \qquad \Delta E_2$$

of the isodesmic reaction and the "intrinsic" stabilization energy are identical if the substituted species is the only stabilized or destabilized species and if the reaction is strictly isodesmic (i.e., $\Delta(\sum E_{AB} = 0)$ where E_{AB} are the

Table III. Population Analysis of CH_2CN^+ and CH_2CN^- with the 4-31G Basis Set

	total charge				π_z charge			
	CH_2CN^+		CH_2CN^-		CH_2CN^+		CH_2CN^-	
	SCF	SCF + CI[b]	SCF	SCF + CI[b]	SCF	SCF + CI[b]	SCF	SCF + CI[b]
C_1	0.153	0.123	−0.572	−0.531	0.744	0.699	−0.678	−0.633
C_2	0.172	0.240	0.127	0.042	−0.165	−0.018	0.135	0.048
N	−0.081	−0.101	−0.675	−0.633	0.421	0.314	−0.457	−0.415
H	0.378	0.369	0.060	0.061				
C/N[a]			46/54	46/54	64/36	69/31	60/40	60/40

[a] C/N gives the π_z ratio C^+/N^+ or C^-/N^-. [b] All orbitals are introduced in the CI (CIPSI).

Table IV. Charges and Stabilization Energies Given by the ΔE of the Isodesmic Reaction

$$^{(\pm)}CH_2X + CH_4 \rightarrow CH_3{}^{(\pm)} + CH_3X \quad X = CN \text{ or } C{\equiv}CH$$

		CH_2CN^+	CH_2CN^-	CH_2CCH^+	CH_2CCH^-
total charge	1	0.153	−0.572	0.061	−0.543
	2	0.172	0.127	−0.231	−0.015
	3	−0.081	−0.675	0.043	−0.676
	$H(C_1)$	0.378	0.060	0.336	0.033
	$H(C_3)$			0.454	0.168
π_z charge	1	0.744	−0.678	0.595	−0.679
	2	−0.165	0.135	−0.179	0.143
	3	0.421	−0.457	0.584	−0.464
π_z charge ratio[a]		64/36	60/40	51/49	59/41
ΔE, kcal/mol (4-31G)		−9.9	61.1	34.7	39.8
ΔE, kcal/mol (4-31+G)		−11.4	50.3	32.3	33.2

[a] Ratio between the charges of atoms 1 and 3.

standard bond energies).[17] These two conditions are generally not fulfilled together. By this method, we cannot have the "intrinsic" stabilization energies but the stabilization energies relative to the unsubstituted species, i.e., the effect of substituting a H by another group. The total energy values obtained after CI are in au (1 au = 627.5 kcal/mol): −131.02080 for CH_2CN^+, −39.24748 for CH_3^+, −131.37447 for CH_2CN^-, −39.50107 for CH_3^-, −40.24350 for CH_4, and −132.01767 for CH_3CN (for the geometries see ref 1 and 18).

The following is deduced:

$$\Delta E_1 = -0.29 \text{ kcal/mol}$$

$$\Delta E_2 = 62.5 \text{ kcal/mol}$$

Let us consider first CH_2CN^+. The ΔE value obtained with the same basis but without CI was −9.9 kcal/mol[6] indicating a destabilizing effect of CN on the cation. Our result would show that, in fact, the cyano group is only slightly destabilizing. Furthermore the ΔE of the reaction has also been calculated with the same extended CI but with the geometry optimized at the SCF level; we have found −2.7 kcal/mol.

These results show the role of the CI for two stages of the calculation, first for the geometry optimization and then for the estimation of the stabilization energy.

The same trend is observed for CH_2CN^- but to a lesser extent. The CI enhances also the stabilizing effect of the CN group from 61.1 kcal/mol[1] to our value of 62.5 kcal/mol. We find here again that the CI plays a more important role for the cation.

(4) Effect of the Heteroatom on the π Charge Distribution. We have noticed before (see the VB analysis) that the same VB components with the same weights exist in CH_2CN^+ and CH_2CN^- and that consequently the nitrogen atom bears almost the same charge whether positive or negative. In order to see the role of the heteroatom on the π charge distribution, we have compared the results obtained above with those obtained with the propargyl cation $C_3H_3^+$ and the propargyl anion $C_3H_3^-$ where all heavy atoms have the same electronegativity. The comparison has been made at the SCF level. We have indeed shown that CI does not significantly influence the π_z charge distribution. Also the relative order of the stabilization energies is not changed by introducing CI.[1]

The geometries of $C_3H_3^+$ and $C_3H_3^-$ reoptimized by gradient from structures described in ref 19 are given in ref 20. In order to simplify the determination of the π_z charge and the comparison with the other compounds, we have constrained the anion $C_3H_3^-$ to be planar (separation of σ and π effects). In fact, this structure is the transition state for the inversion at the carbanion center.[2,19]

The results are given in Table IV. First of all the use of diffuse functions (4-31+G) was necessary: they improve the ΔE values of the anions in better agreement with the experimental values[1] without changing much those of the cations. The rather large difference in the ΔE values for $C_3H_3^+$ and $C_3H_3^-$ came from a bad description of the anion. It is reduced with diffuse functions but always favors the anion.

The comparison between the π_z charge ratio of CH_2CN^- and CH_2CCH^- again shows that the π_z charge distribution is not simply correlated with the electronegativity of the atoms. In fact the charge transfer between the π orbital and the empty p orbital of the cation or between the filled p orbital of the anion and the π^* orbital depends on the energies of these orbitals and on their overlaps. The amount of charge transfer can be qualitatively evaluated by the two-orbital two-electron interaction energies E_i^2 between these various orbitals according to eq 1 (see computational methods for details). The fragmentation has been made between the C_1 and C_2 carbons in each molecule.

$$CH_2CN^- \quad E^2{}_{(p-\pi_z{}^*)} = -58.5 \text{ kcal/mol}$$

$$CH_2CCH^- \quad E^2{}_{(p-\pi_z{}^*)} = -54.3 \text{ kcal/mol}$$

$$CH_2CN^+ \quad E^2{}_{(\pi_z-p)} = -54.9 \text{ kcal/mol}$$

$$CH_2CCH^+ \quad E^2{}_{(\pi_z-p)} = -103.9 \text{ kcal/mol}$$

The relative order of these energies agrees well with that of the π_z charge ratios (Table IV). Consider first the anions. The analysis of the fragment orbitals explains why the CH_2CN^- anion is not more delocalized that the CH_2CCH^- anion, as it is intuitively expected since the effect of N is to lower the π^* orbital and to increase its coefficient on the interacting carbon (C_2). The orbital interactions are shown in Figure 1. The π^* orbitals placed in the electrostatic field of CH_2^- are both raised relative to their position in the reference compounds HCN and $HC{\equiv}CH$, π^*CN remaining lower in energy than π^*CC. The important feature is that the CN bond is polarized due to the electronegativity of N, and the fragment CH_2 placed in the electrostatic field of this dipole has the energy of its p orbital lowered, relative to the reference compound, so that the energy gap between p and π^* becomes more unfa-

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(18) The optimized geometry of CH_3^+ is the following: R_{CC} = 1.076 Å.

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(20) The optimized geometries of $C_3H_3^+$ and $C_3H_3^-$ are the following: for each variable, two values are given, the first corresponding to $C_3H_3^+$, the second to $C_3H_3^-$. C_1C_2: 1.336 Å; 1.375 Å. C_2C_3: 1.216 Å; 1.224 Å. C_3H: 1.062 Å; 1.049 Å. C_1H: 1.076 Å; 1.007 Å. $<HC_1C_2$: 120.85°; 121.36°.

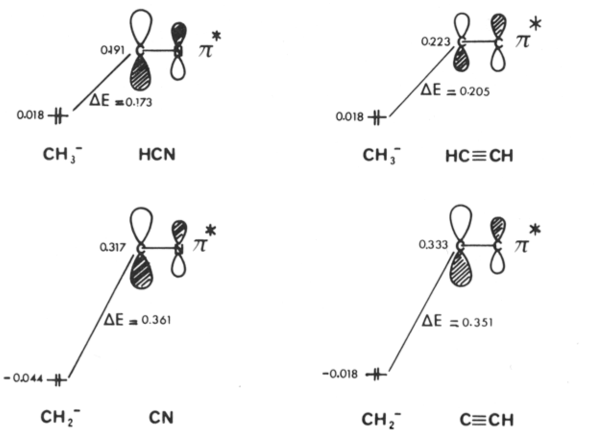

Figure 1. Fragment orbital interactions in CH_2CN^- and CH_2CCH^-. The reference orbitals are those of CH_3^-, HCN, and HCCH (energies are in au).

vorable in CH_2CN^- than in CH_2CCH^-. In addition, the negative charge of the CH_2 fragment induces a polarization of the C≡CH bond, so that the π^*CC orbital also has its larger coefficient on the interacting carbon (C_2) giving the same situation as in CH_2CN^-. The foregoing arguments explain that the two-orbital two-electron interaction energies of CH_2CN^- and $C_3H_3^-$ and therefore their π_z charge delocalization are very close together.

Therefore it is interesting to notice that the field effect of the CN groups prevents by a first-order perturbation (lowering of pCH_2) its favorable delocalizing effect. These two effects being opposed, it is not possible to establish a simple correlation between the delocalization of an anion and the electronegativity of the β atom. This is similar to the "avaricious" behavior of the methyl group.[21] The same feature has been observed for the α-effect:[22] the first-order effect (i.e., electronegativity) of the adjacent heteroatom must be taken into account before doing the second-order perturbational treatment.

Concerning the cations, the explanation is more simple since all factors are going in the same direction (Figure 2). The energy lowering of the orbital from HC≡CH (−0.403 au) to HCN (−0.494 au) is much larger than the lowering of the corresponding π^* orbital (0.091 vs. 0.032 au) and the difference is conserved when the interaction with the CH_2^+ fragment is taken into account (0.10 au). As for the anions the energy difference between the empty p orbitals of the CH_2^+ fragment in CH_2CN^+ and CH_2CN^- is small (0.024 au) and cannot, in the case of the cation, cancel the lowering of the π_{CN} orbital. In addition, the positive charge of the CH_2 fragment induces a polarization of both π_{CN} and π_{CC} but larger for the latter than for the former (a C≡C bond is more polarizable than a C≡N bond). It results in a larger coefficient on the interacting carbon (C_2) for π_{CC} than for π_{CN}.

Therefore the two-orbital two-electron interaction is more favorable in CH_2CCH^+ than in CH_2CN^+ explaining a better delocalization in the former.

(5) π Delocalization and Stabilization. Let us return to Table IV. It is noteworthy that very similar π_z charge ratios (CH_2CN^+, CH_2CN^-, and CH_2CCH^-) correspond to very different stabilization energies. On the contrary, similar energies (CH_2CCH^+ and CH_2CCH^-) correspond to different π_z charge ratios (1 vs. 1.5). It is admitted in the resonance theory that, if two mesomeric structures have similar weights, the species is more stabilized.[23] But it is also well-known that the stabilization of one compound does not depend only on the π interactions but also on the σ interactions especially when it is charged and bears heteroatoms. Previous papers studying the effect of substitution on cations and anions have already emphasized this σ–π interplay.[24–25] The π effect is often considered to be the most important. We will show now that, in the case of the delocalized species studied here, this is not true.

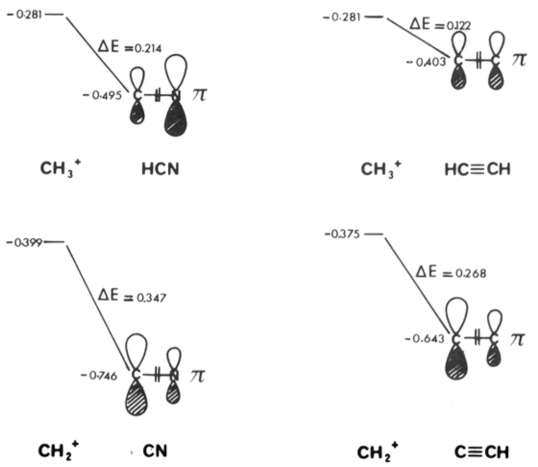

Figure 2. Fragment orbital interactions in CH_2CN^+ and CH_2CCH^+. The reference orbitals are those of CH_3^+, HCN, and HCCH (energies are in au).

In an anion having an α unsaturated substituent, the π effect is not limited to the stabilizing interaction between the p and the π^* orbitals. There is also a destabilizing interaction between the p and the π orbitals (four-electron interaction) which can be calculated according to eq 2 (see computational methods). Thus the effect of an unsaturated substituent on an anion is to stabilize it by the two-electron two-orbital interaction and to destabilize it by the four-electron interaction. The π stabilization energy can be qualitatively represented by the sum $E^2 + E^4$. It can be stabilizing or destabilizing depending on the balance between E^2 and E^4 and hence on the substituent.

The two-orbital four-electron interaction energies E_i^4 calculated for CH_2CN^- and CH_2CCH^- have the following values:

$$CH_2CN^- \quad E^4_{(p-\pi_z)} = 46.8 \text{ kcal/mol}$$

$$CH_2CCH^- \quad E^4_{(p-\pi_z)} = 51.9 \text{ kcal/mol}$$

The sum $E^2 + E^4$ has a slightly negative value for CH_2CCH^- (−2.4 kcal/mol) and a little larger for CH_2CN^- (−11.7 kcal/mol). This result signifies that the two studied anions are far less π-stabilized than the corresponding cations (E^2 = −103.9 and −54.9 kcal/mol, respectively) in spite of their close π-delocalization.

To summarize, one could say that for an anion there is no relationship between the π delocalization (represented qualitatively by the E^2 term) and the π stabilization (represented qualitatively by the sum $E^2 + E^4$). But on the contrary this relationship does exist for a cation.

These examples show that a large π delocalization is not always synonymous with large π stabilization. The only way to explain the large total stabilization of CH_2CN^- and

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$C_3H_3^-$ and the slight total destabilization of CH_2CN^+ is to take into account the σ framework. Both groups C≡CH and CN are electron withdrawing (the later far more than the former) and thus stabilize anions and destabilize cations by inductive effect.

Therefore the σ effect seems to be more important than the π effect in determining the stability of the four species studied in this paper. In a general manner both π and σ interactions are more important for charged species compared to neutral species. Considering only one of these terms would lead to wrong conclusions especially if the contributions are in opposite directions as in CH_2CN^+.

Conclusion

This work shows the following trends: The geometrical parameters do not give sufficient information to describe a delocalized species: in particular they do not give the balance between the most important mesomeric structures. A valence-bond analysis is thus necessary.

There is no evident relation between the π charge distribution of delocalized charged species and the electronegativity of the β atoms. In fact, in anions, the first-order perturbation due to electronegativity (inductive effect) is opposed to the second-order effect, the repartition of the π charge (mesomeric effect). The prevalence of one effect over the other depends on the considered atom and the result is not simply foreseeable.

The most important feature is that there is no relationship between the π delocalization and the stability of the studied species. Firstly because the π delocalization does not represent the π stabilization for the anions and secondly because the σ effects can play a decisive role especially when a heteroatom substituent is present in the system. At this stage the conclusions are limited to these systems. Their generalization would need the study of some more species, which will be undertaken in the future.

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Registry No. CH_2CN^+, 34430-18-7; CH_2CN^-, 21438-99-3; CH_2CCH^+, 21540-27-2; CH_2CCH^-, 31139-07-8.

Redox Behavior of Some New Bipyran and Bithiopyran Derivatives. One- vs. Two-Electron Oxidations

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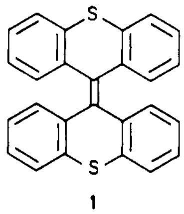
Three classes of $\Delta^{4,4'}$-4*H*-bipyran and -bithiopyran derivatives undergo either two unresolved one-electron oxidations, where $E_2°'$ may be more or less than $E_1°'$, or a single reversible two-electron oxidation, depending on molecular structure. The first class of compounds has one benzene ring fused to the pyran ring, and the second class consists of compounds with at least eight methylidene groups separating the heterocyclic rings. The third class contains compounds with the pyran or thiopyran rings separated by an ethanediylidene group that is substituted by at least one methyl or phenyl substituent. A rationale is proposed for the observed redox behavior.

Introduction

Electron donors exhibiting two reversible one-electron oxidation potentials are quite common.[1] In contrast, electron-donor molecules that exhibit the electrochemical behavior of a single two-electron reversible oxidation are rare.[2,3] This paper describes the synthesis and electrochemical behavior of a class of compounds whose redox behavior is controlled by steric interactions, the distance between the electroactive groups, and the nature of the heteroatom in some simple bipyran and thiopyran derivatives. $\Delta^{4,4'}$-4*H*-Bipyran and -bithiopyran derivatives normally exhibit two reversible one-electron oxidations.[1a,1h,3a-d] We set out to investigate the effect of structural changes on the separation between the first and second oxidation waves of these compounds. We found three distinct classes of pyrans and thiopyrans that exhibit a single reversible two-electron oxidation wave where $\Delta E°'$, i.e., $\Delta E°' = E_2°' - E_1°'$, may be positive, negative, or zero, depending on molecular structure.

Results and Discussion

The first class contains compounds with at least one benzene ring fused to the pyran nucleus. It has been reported that bithioxanthene (1) exhibits a single but irreversible two-electron oxidation at $E_p = +1.34$ V (vs. SCE, CH_2Cl_2).[4] The irreversibility is due to considerable structural and solvent reorganization between the charged and uncharged species.[4] We have shown that the related



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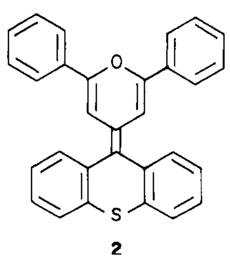

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