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Theoretical Evaluation of the Effect of Electron-Withdrawing Substituents on Carbocation Stabilities. Delocalization of Charge to the Carbonyl and Cyano Groups

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Abstract: Theoretical studies of carbocations bearing directly attached electron-withdrawing substituents have been completed by using a combination of the approximate PRDDO method and ab initio calculations using different basis sets. All of the theoretical findings agreed quite well with the experimental observations that α-cyano and α-carbonyl groups, which destabilize incipient carbocation centers inductively, provide considerable conjugative stabilization via charge delocalization to the nitrogen of the cyano group or to the oxygen of the carbonyl moiety. A comparison of results obtained by PRDDO and by ab initio calculations with STO-3G, 4-31G, and double-ζ plus polarization (DZP) basis sets is provided.

Trivalent positively charged carbon has been recognized as a reactive intermediate in organic chemistry for over 50 years.[2] Carbocations are involved in a large assortment of rearrangements, elimination reactions, and substitution reactions of organic compounds. While directly attached alkyl and aryl substituents provide considerable stabilization of carbocationic centers, it was generally accepted that electron-withdrawing substituents, such as the carbonyl and cyano groups, would be quite destabilizing when attached directly to such centers of positive charge. Recent experimental work has indicated that the carbonyl group[3] and the cyano group[4,5] destabilize cations less than would have been anticipated solely on the basis of their inductive effects.[6-8] Theoretical studies[9,10] indicate that this attenuated destabilization arises from a resonance effect which involves delocalization of the π-orbitals on the electron-withdrawing substituent to the carbocationic center. This involves conjugation (back-bonding) of the substituent with the vacant orbital of the carbocation. In introductory communications,[9] we presented results based primarily on minimum basis set calculations. In this paper, we present details of these calculations, as well as results of computations using larger basis sets, which substantiate our earlier conclusions

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and provide more detailed insight into the interaction between carbocations and directly attached cyano and carbonyl groups.

Calculations

The calculations at Minnesota were done at both the PRDDO level, an approximate molecular orbital method,[11] and the ab initio level. All of the ab initio calculations were performed by using various versions of the HONDO program.[12] The ab initio calculations at Pittsburgh were done by using the GAUSSIAN 70 program.[13] Calculations were done with the following basis sets. The PRDDO calculations are done with a minimal basis set of Slater-type orbitals. Exponents for C and N were standard values,[14] while the value of $\zeta(1s)$ was set at 1.2. The ab initio calculations were done by using STO-3G,[14] 4-31G,[15] and double-ζ plus polarizatioin (DZP) basis sets. The DZP basis was taken from Dunning and Hay[16] and is of the form (10,5,1/4,1)/[3,2,1/2,1]. Geometry optimizations were carried out in the following fashion. The PRDDO geometry optimizations were done by using serial searches, as were the STO-3G optimizations (GAUSSIAN 70). Methyl groups in the PRDDO optimizations were given pseudo-3-fold symmetry. In some cases, the STO-3G results were checked by using gradient optimization methods[17] with HONDO:4. Geometries for the large basis set calculations were generated in the following fashion. For $^+CH_2CN$, CH_3CN, $^+CH_3$, and CH_4, the geometries were optimized by using gradient techniques at the DZP level. For the larger molecules, $CH_3{}^+CHCN$, $^+CH_2CH_2CN$, CH_3CH_2CN (bridged and unbridged), CH_3CHO, and $^+CH_2CHO$, appropriately scaled geometries were employed. The scaling for the C–H bond lengths employed the optimized values for CH_3 ($r = 1.082$ Å) and CH_4 ($r = 1.085$ Å) obtained with the DZP basis. The geometry for CH_3CH_2CN was taken from the PRDDO optimization with the C–H distances scaled to the value obtained for CH_4 at the DZP level. For $^+CH_2CH_2CN$, the PRDDO geometry was again employed with the C–H bonds on C_α scaled to that found for CH_4 (DZP), and the C–H bonds at C_β (the carbonium ion center) scaled to that found for $^+CH_3$ (DZP). The geometry for the bridged β-cyanoethyl cation was taken from the PRDDO structure optimized in C_{2v} symmetry, and the C–H distances were scaled to that found for CH_4 (DZP). The PRDDO structures were chosen for these compounds due to the good agreement found between the PRDDO optimized and experimentally determined structures of CH_3CN. The structure of $CH_3{}^+CHCN$ was taken from the STO-3G optimized structure with the C_α–H bond scaled to that found for $^+CH_3$ (DZP) and the C–H bonds at C_β scaled to that of CH_4 (DZP). The STO-3G structure was chosen, since better agreement with the DZP optimized structure for $^+CH_2CN$ was found at the STO-3G level than at the PRDDO level. However, the C–N bond in $^+CH_2CN$ is too long at the STO-3G level as compared to the DZP level and, thus, the C–N bond in $CH_3{}^+CHCN$ was scaled by the ratio $R_{DZP}(CN)/R_{STO\text{-}3G}(CN)$ with $R(CN)$ taken from $^+CH_2CN$. The geometries for CH_3CHO and $^+CH_2CHO$ were taken from the STO-3G optimized structures with appropriately scaled hydrogen distances. The bond distances for the CH_3 group were scaled to that of CH_4 (DZP), the bond distances for the $^+CH_2$ group were scaled to that of $^+CH_3$ (DZP), and the bond distance of the C(O)–H bond was scaled to the value found for that bond in the 6-31G* optimization of CH_3CHO.[18]

Table I. Total Energies (au) for Molecules and Ions

molecule/ ion	basis		
	STO-3G	4-31G	DZP
1	−130.271 54	−131.727 10	−131.951 40
2	−129.324 38	−130.742 83	−130.960 94
3	−168.851 99	−170.704 97	−170.994 25
4	−167.945 90	−169.760 65	−170.044 01
5	−167.924 68	−169.748 27	−170.035 91
6	−167.926 32	−169.733 35	−170.020 64
7	−207.432 62	−209.683 65	
8	−206.560 46	−208.771 17	
9	−150.945 92	−152.684 98	−152.951 45
10	−150.023 33	−151.706 76	−151.970 77
10R	−150.001 70	−151.699 38	−151.966 87
11	−189.526 22	−191.664 30	
12	−188.644 90	−190.728 63	
13	−188.613 70	−190.717 02	
14	−228.106 60	−230.641 39	
15	−227.258 77	−229.740 61	
$CH_3{}^+$	−38.779 48	−39.171 27	−39.242 24
CH_4	−39.726 86	−40.139 76	−40.207 53

Results

Geometries—the Cyano Groups. The optimized geometries obtained in this work for a number of the structures (**1–15**) at the minimal basis set level are shown in Figure 1. The total energies for the various species under consideration are given in Table I at various basis set levels. We first consider the STO-3G geometries of the cyano-substituted structures. The structures of the neutral cyano species show structures that follow the predictions of normal chemical models. CH_3CN (**1**) has a normal C–N bond length (1.16 Å) and a normal sp^3–sp C–C bond (1.46 Å).[19] The STO-3G C–C bond is too long compared to the experimental value[20] while the C–N bond length shows excellent agreement. The PRDDO geometry for CH_3CN shows excellent agreement with experiment for both the C—C and C≡N bonds. For CH_3CH_2CN (**3**), the C_α–C_N bond lengthens slightly in comparison to this bond in **1**. The C–C–C angle opens up to 112° while the angle H–C_α–H contracts to 108°. The PRDDO structure is very similar except that the C_α–C_N bond length is shorter. For $(CH_3)_2CHCN$ (**7**), the C_α–C_N bond length increases slightly due to the added methyl, and the C_{H_3}–C_α–C_{H_3} angle is close to 112°.

The geometries of the cyano-substituted cations show some important changes in comparison with the neutral species. The C–N bond of $^+CH_2CN$ (**2**) lengthens while the C_α–C_N bond is appreciably shortened as compared to these quantities in **1**. The C–C bond has partial double bond character (an average C=C bond length is 1.34 Å)[18] while the C–N bond has lost some triple bond character. The PRDDO structure for **2** is similar, with the C–N bond being slightly longer and the C_α–C_N bond being slightly shorter. As discussed previously,[9a] the difference in geometry between **1** and **2** is due to a resonance effect. In order to demonstrate that these geometrical results were not due to the use of a minimum basis set, we performed a gradient optimization of **2** at the DZP level in C_{2v} symmetry. The C_α–C_N bond length is essentially the same at the DZP level as it is at the STO-3G level. The C–N bond at the DZP level is somewhat shorter for two reasons: (1) the minimal basis set tends to overestimate the resonance character in order to distribute the charge as extensively as possible and (2) large basis sets tend to give bond lengths that are too short in comparison with experimental structures. The general conclusion that can be drawn from all of the calculations is that the C–C bond is significantly shorter in **2** than in **1** and

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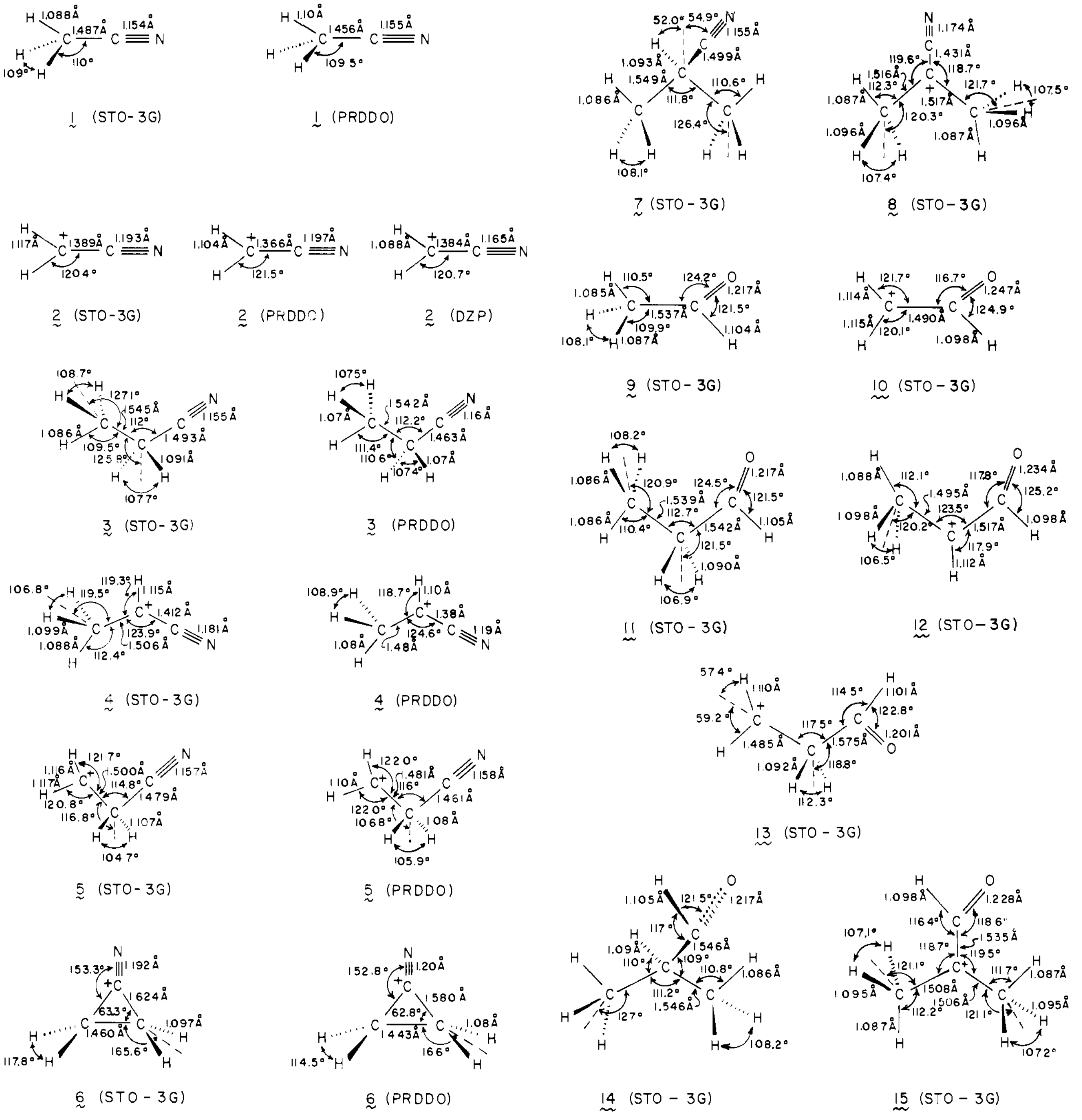

Figure 1. Optimized geometries of molecules and ions determined in this study.

that the C–N bond is longer in **2** than in **1**. The geometry of $CH_3{}^+CHCN$ (**4**) follows the trends seen in **2**. The C_α–C_β bond is slightly shorter than that found for a normal $C(sp^2)$–$C(sp^3)$ bond (1.52 Å) but is significantly longer than the value of the C–C bond in $CH_3{}^+CH_2$ (**16**), which is 1.49 Å (STO-3G basis), and is slightly longer than the C–C bond length found in $(CH_3)_2CH^+$ (**17**) of 1.50 Å (STO-3G basis).[18] The C_α–C_N bond lengthens in **4** in comparison to its value in **2**, while the C–N bond shortens. This follows since the CH_3 group is more effective at stabilizing the carbocationic center than H, and less resonance stabilization from the cyano group is required.

The structure of the other isomer, $^+CH_2CH_2CN$, is quite complicated and is similar to the 1-propyl cation (**18**), in this regard.[21-23] If the atoms, H_2CCCN, all lie in a plane, a typical carbocationic structure is found as indicated in **5**. The C_α–C^+ bond length is comparable to that found for the CH_3–C^+ bond in **4** and is slightly longer than the C–C bond in **16**, as is expected since CN is more electron withdrawing than H. The C_α–C_N and C–N bond lengths are similar to the values found in the corresponding neutral compound **3**. If the $^+CH_2$ group is rotated by 90°, a different type of structure is found. At the minimal basis set level, the optimum structure has the CN group bridging the two CH_2 groups, analogous to the bridging proton found for the nonclassical structure for $C_2H_5{}^+$.[21-23] The CH_2 groups are bent out of the plane by 15°, and the C–C bond lengthens from that of a C–C double bond (1.34 Å) but is still significantly shorter than a $C(sp^2)$–$C(sp^2)$ single bond (1.46 Å). A similar result is

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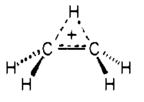
found for $C_3H_7^+$ where corner-protonated cyclopropane is of comparable stability to the classical carbocationic structure.[21-23] The CH_2–CH_2 bond in **6** is longer than the corresponding bond at the STO-3G level (1.40 Å) in proton-bridged $C_2H_5^+$ (**19**) or methyl-bridged $C_3H_7^+$ (**20**).[18]



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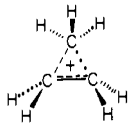
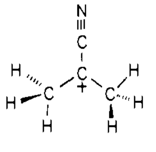


20

We note that the bridging cyano group forces a more cyclopropane-like structure than is found with a bridging methyl group. The C–C_N bonds in **6** (1.58 Å) are significantly shorter than the C–CH_3 bond found in **20** (1.80 Å). The C–N bond length in **6** is quite similar to that found for **2**. The structure for $(CH_3)_2{}^+CCN$ (**8**) follows the general trends established so far. The C_{H_3}–C^+ bonds lengthen slightly in comparison to **4** and are very close to the value of an sp^2–sp^3 single bond (1.52 Å). The C_α–C_N bond is longer and the C–N bond has shortened. The structure of **8** adopts the conformation where one C–H bond is cis (syn-periplanar) to the CN group and one is trans (anti-periplanar); we denote this as the cis–trans conformation. For propane (**21**) the



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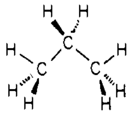

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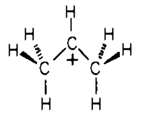
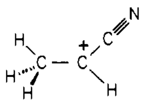
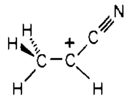


17

geometry is all trans, while for the 2-propyl cation (**17**) a trans–trans structure is found.[23] The cis–trans structure for **8** is only favored by a small amount over the cis–cis and trans–trans forms at the STO-3G level (0.5 and 0.3 kcal/mol, respectively). At the 4-31G//STO-3G level, the trans–trans structure only lies 0.1 kcal/mol above the cis–trans form. For comparison, we note that the rotational barrier in **4** for the CH_3 group is 2.5 kcal/mol, with the cis structure being the most stable form. The trans structure lies 0.9 kcal/mol higher in energy.



cis-4



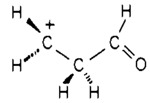
trans-4

Geometries—the Carbonyl Group. For the carbonyl-containing molecules, the geometries of the neutral structures with the CHO substituent (**9**, **11**, **14**) follow normal chemical expectations. The C_α–C_O bond distances tend to be more like a C(sp^3)–C(sp^3) single bond (1.54 Å) than like a C(sp^2)–C(sp^3) single bond (1.52 Å). The C–O bond distances are very close to that expected for a CO double bond (1.22 Å). For $^+CH_2CHO$ (**10**), the C_α–C_O bond is shorter than the comparable bond in **9**, as would be expected for an C(sp^2)–C(sp^2) bond whose average length is 1.46 Å. In fact, it is somewhat longer than this average value. The difference in the C_α–C_O bond lengths in **9** and **10** is 0.047 Å; this is a significantly smaller difference than that found by comparing C_α–C_N in **1** and **2** (0.098 Å). This shows that the resonance effect is larger for cyano substitution than for carbonyl substitution. The C–O bond is longer in **10** than in **9**, although this difference is probably exaggerated by the use of a minimum basis set.[24] In $CH_3{}^+$-CHCHO (**12**) the CH_3–C^+ bond shortens, more so than in the comparable CN substituted ion, **4**. As expected, the C_α–C_O bond lengthens while the C–O bond shortens with the addition of the CH_3 substituent. The compound $^+CH_2CH_2CHO$ (**13**) was first optimized in the conformation **13a**, which has a very long C_α–C_O bond. Rotation of the $^+CH_2$ group to place the hydrogen atoms in the C–C–CHO plane yields **13b**, which was partially optimized. The C_α–C_O bond shortens to 1.575 Å, but this value is still somewhat long in comparison to this bond in **11**. Following the results for the CN substituted compound, we would have expected this bond length to be the same in **11** and **13b**. The ^+C–C_α bond is now very similar to that in $CH_3CH_2{}^+$, in contrast to the case found for **4**. The C–O bond is slightly shortened.[25] Substitution of a second methyl group to give $(CH_3)_2{}^+CCHO$ (**15**) leads to the expected increase in the C_α–C_O bond length and a decrease in the C–O bond length. The CH_3–C^+ bond lengths are intermediate between those in **8** and in **17**. The favored conformation is the cis–trans structure with the cis hydrogen located on the same side as the carbonyl as shown below.

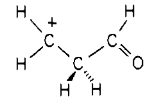
Table II. Isodesmic Energies (kcal/mol) for Reaction 1

ion	STO-3G	4-31G	DZP
2	0.1	−9.9	−15.8
4	25.9	15.2	9.4
5	12.6	7.4	4.3
6	13.7	−1.9	−5.3
8	47.2	35.1	(29.4)
10	15.5	−6.1	−9.7
10R	3.5	−10.8	−12.2
12	41.5	20.6	(17.0)
13b	26.5	13.3	(11.9)
15	62.5	42.5	(38.9)
16	30.7[a]	28.8[a,b]	30.2[c]
17	55.6[a]	50.6[a,b]	51.8[c]
18	34.6[a]	32.5[a,b]	33.0[c]
22[d]	−4.4	−37.3	

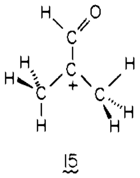
[a] Reference 18. [b] Calculated with a 3-21G basis set. [c] Calculated with a 6-311G** basis set (ref 23). [d] From ref 9b.



13a



13b



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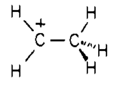

16

The other cis–trans isomer is 0.8 kcal/mol higher in energy. The cis–cis isomer lies 0.6 kcal/mol higher in energy while the trans–trans isomer is 1.0 kcal/mol higher. At the 4-31G//STO-3G level, the trans–trans isomer is 0.5 kcal/mol above the optimum form. These results suggest that there is a weak hydrogen bond between the hydrogen on the terminal CH_3 group and the oxygen.

Energetics. In order to compare the energies of various structures and to examine substituent effects, we have calculated energies for the following isodesmic reaction

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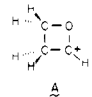
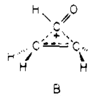
[24] For a more complete discussion of the $C_2H_3O^+$ surface see: Nobes, R. H.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 309.

[25] Two other possible structures, A and B, were not considered in this study although A may be the most stable ion on the hypersurface. However, it does not correspond to a carbonyl substituted carbocation.



A



B

[26] The experimental results demonstrate that the decrease in rates brought about by substitution of cyano for hydrogen tend to be more pronounced than those found for substitution of carbonyl for hydrogen. Therefore, cyano is more destabilizing than is carbonyl relative to hydrogen.

$$R_1R_2{}^+CX + CH_4 \rightarrow R_1R_2CHX + {}^+CH_3 \qquad (1)$$

$$X = CN, CHO, CH_3; R_1, R_2 = H, Me$$

We have chosen to make comparisons only to the CH_4/CH_3^+ pair due to the complications that are present in determining the structures of higher carbocations, such as $C_2H_5^+$.[21-23] These energies are given in Table II for various basis sets. We first discuss the basis set dependence for those structures where all three basis sets were employed. At the STO-3G level for $^+CH_2X$, we find that for X = CN, **2**, the effect of the cyano group is comparable to that of H, while for X = CHO, **10**, the aldehyde substituent is significantly more stabilizing than H. Addition of methyl groups to give **4** and **12** leads to a significant increase in the stabilization energy at the STO-3G level. At the 4-31G//STO-3G level, a reversal in the stabilization values for both cyano (**2**) and carbonyl (**10**) substitution is found. Both the CN group of **2** and the CHO group of **10** are now destabilizing with respect to H. Addition of polarization functions to the basis set shows an additional significant change. At the DZP level, the CN group of **2** is destabilizing by 15.8 kcal/mol with respect to H, while the CHO group of **10** is destabilizing by 9.7 kcal/mol. An estimate of the conjugative interaction of the CHO group in **10** can be made by examining the structure when the CHO group is rotated by 90° which prevents the overlap of the "vacant" orbital on C^+ with the π_{CO}. At the minimal basis set level, this rotational barrier is 12.0 kcal/mol, which shows the presence of a large resonance stabilization. This value decreases to 4.7 kcal/mol at the 4-31G level and is only 2.5 kcal/mol at the DZP level. Thus, there is apparently only a small resonance stabilization due to the CHO group in **10**. As shown by these results, the CHO group is less destabilizing than a CN group, as expected from experimental results. The results also demonstrate that the minimum basis set tends to significantly overestimate the amount of resonance stabilization, confirming the conclusion made from comparisons of geometries. Finally, we note that the CF_3 substituent of $CF_3{}^+CH_2$ (**22**) is very destabilizing.[9b] It is interesting to note that there is a large basis set effect in going from the STO-3G basis to the 4-31G basis. Again, the change is toward a larger destabilization as the size of the basis is increased.

The presence of methyl groups leads to ions that are more stable than $^+CH_3$. The basis set effects have been explored for **4**, and the same results as observed for **2** and **10** are observed. Thus, we have estimated the DZP result for **8** based on our values for **2** and **4**. The basis set effect in going from 4-31G to the DZP basis in **10** is somewhat smaller than that found in **2** and **4**. We have also estimated DZP results for **12** and **15** using the values from **10**. These estimates were made in order to compare with the work of Raghavachari et al.,[23] who have obtained stabilization energies for methyl, two methyls, and ethyl at the 6-311G** level, which is a basis set similar to our DZP level. Comparison of **4** with **16** shows that the CN group is destabilizing relative to H for this ion (20.8 kcal/mol). This agrees with the geometry results, which suggested a decrease in the resonance stabilization. For the dimethyl derivatives, **8** vs. **17**, the CN group is also destabilizing relative to H, again following the trend observed in the geometries. Thus, the CN in **2** is 7 kcal/mol more stabilizing than that in **8**. This is an estimate of additional stabilization, since even in **8** there is a significant stabilization energy as estimated from experimental results. Similar results are found for CHO as a substituent. For one CH_3 substituent (**12** vs. **16**) CHO is destabilizing by 13.2 kcal/mol with respect to H, while with two CH_3 substituents the CHO is destabilizing by 12.9 kcal/mol. These values are probably the same (~13 kcal/mol) due to our use of estimates. We can also estimate the effect of the CH_2CN group with respect to H, CH_3, and CH_2CH_3. The CH_2CN group is stabilizing with respect to H by 4.3 kcal/mol but is destabilizing with repect to CH_3 and CH_2CH_3 by 25.9 and 28.7 kcal/mol, respectively.

The relative energies of the ions **4**, **5**, and **6** can be compared with the analogous hydrocarbon ions **17**, **18** (1-propyl cation), and **20**. The most stable ion in both cases is the ion with maximum substitution at C^+, i.e., **4** and **17**. Ions **5** and **6** are unstable relative to ion **4** by 5.1 and 14.7 kcal/mol, respectively. At the 6-31G** level, **22** and **23** are higher in energy than **17** by 18.8 and 13.7 kcal/mol, respectively. The experimental energy difference for **17** and **22** is 23.5 kcal/mol.[27] The relative energies of the bridged structures are very similar, and it is apparent that the ^+CN and $^+CH_3$ group have comparable tendencies for bridging. An important difference between the CN series and the hydrocarbon series is that **5** is energetically much closer to **4** than **22** is to **17**.

In order to provide as complete a comparison as possible, we have calculated the energetics for the isodesmic reaction 1 for the alkyl cations **16**, **17**, and **18** from data given in ref 18. The calculations in ref 18 employed the STO-3G and 3-21G basis sets[28] where the latter basis set is essentially equivalent to the 4-31G basis set employed by us. The striking feature of these results is the remarkably good agreement found between the three basis sets. Thus, the minimum basis set gives good isodesmic energies for alkyl cations but not for the heteroatom cases.

The data in ref 23 for **17**, **18**, and **20** allow us to estimate the effect of correlation on the relative energies for **4**, **5**, and **6**. Inclusion of a correlation correction at the level of a MP 2/6-311G** calculation[29] shows little effect on the relative energies of **17** and **18**. Thus, we expect to find little effect of correlation on the relative energies of **4** and **5**. A large decrease in the energy of **20** relative to **17** is found at this level although the 2-propyl cation is still more stable. This gap is expected to increase if more accurate correlation corrections are employed. The increased stability of bridged species when correlation corrections are added is well-known and is due to the difficulty of treating a two-electron, three-center bond at the Hartree–Fock level. We thus expect the energy difference between **4** and **6** to decrease when correlation effects are included. It is unlikely, however, that the bridged species will become more stable than the open structure based on the results given in ref 23.

Charge Distributions. The charge distributions as determined from Mulliken population analyses are shown in Table III. We report group charges obtained by adding the charge at carbon to the charges of the attached hydrogens. Excellent agreement between the PRDDO and STO-3G charge distributions is found. The minimal basis set group charge distributions agree reasonably well with the DZP charges. The major differences are that the minimum basis set charges overestimate the polarity of the $C{\equiv}N$ bond and underestimate the polarity of the $C{=}O$ bond. For the neutral compounds with a cyano substituent, the nitrogen is observed to be strongly negative, and most of the positive charge is found on the α-carbon. In **2**, 0.28 e is delocalized onto the CN group, and the excess charge is divided approximately equally between the C_N and N. Thus, N has absorbed a significant amount of positive charge in comparison to C_N, resulting in a cyano group which is essentially nonpolar. The carbocationic center in **4** has just over 0.5 e, and the CH_3 group is quite positive. The CN group of **4** has lost some charge in comparison with **2**. At the DZP level, the polarity is shifted so that the nitrogen is more positive than C_N. In contrast, the minimum basis set results have the polarity of the C–N bond slightly reversed, due to the excess charge on C_N. For **5**, the carbocationic center has a charge comparable to that on C^+ in **2**, and there is significant charge on C_α. The CN group at the DZP level is essentially neutral and nonpolar, while its polarity is exaggerated at the minimal level. In **8**, the charge on C^+ is reduced over that in **4**, with most of the remaining charge found on the CH_3 groups. The charge on the cyano group is somewhat reduced from its value in **4**. In order to see if this delocalization of charge to the methyl group is typical of simple carbocations, we investigated the charge distributions in $CH_3CH_2^+$ (**16**) using STO-3G optimized geometries.[18] Comparison of **4** and **16** shows that the delocalization of charge to the methyl group is essentially the same. The remaining difference in the charges on C^+ between **4** and **16** is due to delocalization

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Table III. Mulliken Group Charges (e) for Various Molecules and Ions

molecule/	C_α			C			X			R = CH_3 or CH_2^+		
ion	PRDDO	3G	DZP	PRDDO	3G	DZP	PRDDO	3G	DZP	PRDDO	3G	DZP
1	0.14	0.12	0.13	0.08	0.08	0.04	−0.22	−0.20	−0.17			
2	0.71	0.72	0.72	0.15	0.14	0.13	0.14	0.14	0.15			
3	0.11	0.09	0.13	0.07	0.07	−0.02	−0.21	−0.20	0.17	0.04	0.05	0.06
4	0.52	0.49	0.54	0.12	0.11	0.04	0.07	0.09	0.11	0.29	0.31	0.31
5	0.30	0.28	0.30	0.07	0.08	0.02	−0.10	−0.07	−0.02	0.73	0.72	0.73
6	0.41	0.41	0.43	0.07	0.06	0.00	0.12	0.12	0.15			
7	0.11	0.07		0.07	0.06		−0.24	−0.21		0.03	0.03	
8	0.37	0.31		0.10	0.09		0.03	0.05		0.25	0.27	
9	0.02	0.02	0.03	0.22	0.19	0.33	−0.24	−0.21	−0.35			
10	0.68	0.66	0.72	0.31	0.30	0.40	0.02	0.04	−0.12			
10R	0.76	0.69	0.78	0.32	0.32	0.45	−0.08	−0.05	−0.23			
11	0.02	0.01		0.21	0.19		−0.24	−0.21		0.01	0.02	
12	0.48	0.45		0.29	0.28		−0.04	−0.01		0.26	0.28	
13b	0.21	0.19		0.26	0.25		−0.17	−0.13		0.70	0.68	
14	0.06	0.02		0.20	0.18		−0.25	−0.21		−0.01	0.00	
15	0.36	0.30		0.28	0.27		−0.07	−0.04		0.22	0.24	
16	0.71	0.70								0.28	0.30	
17	0.51	0.52								0.24	0.24	

Table IV. π-Overlap Populations, e[a]

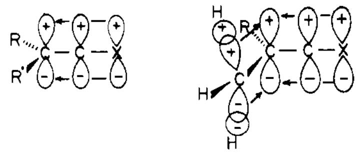
	C^+			C_X			X		
ion	PRDDO	3G	DZP	PRDDO	3G	DZP	PRDDO	3G	DZP
2	0.28	0.29	0.25	1.14	1.14	1.13	0.58	0.57	0.60
4	0.21	0.31	0.28	1.13	1.13	1.10	0.64	0.67	0.69
5	0.12	0.12	0.10						
8	0.34	0.32		1.12	1.11		0.71	0.73	
10	0.18	0.17	0.11	1.03	1.02	0.80	0.79	0.81	1.05
10R	0.06	0.06	0.05						
12	0.23	0.22		1.02	1.01		0.86	0.88	
13b	0.12	0.12							
15	0.26	0.25		1.01	1.00		0.90	0.92	
16	0.18	0.12							
17	0.18	0.18							

[a] Taken from a Mulliken population analysis. Obtained for the orbital perpendicular to the molecular plane.

to the CN group. A similar result is found in comparing **8** and **17**.

As discussed earlier, the minimum basis set tends to underestimate the polarity of the C=O bond, and this has some consequence on the charge distributions. The neutral molecule, **9**, is found to have very little charge on the CH_3 group in contrast to the result found for **1**. The charge on C^+ in **10** is comparable to that on C^+ in **2**. Most of the remaining positive charge has been absorbed by the oxygen, a result similar to that found for **2** where more charge is transferred to N. There is less charge effectively transferred in **10** than in **2**, especially when the charge distributions in the neutrals are accounted for. After rotation of the CHO group, the charge on C^+ increases. The remaining charge is evenly divided between the C and the O at the DZP level. At the minimal basis level, the O still absorbs slightly more charge. As found for **4** and **8**, there is significant delocalization of charge onto the methyls in **12** and **15**. A concomitant decrease in the delocalization of charge to the C=O group is also found following the trend found in the CN-substituted case. The charge distribution for $^+CH_2CH_2CHO$ (**13b**) is similar to that found for **5**. The positive charge is localized on C^+. Less charge is found on the CH_2 group in **13b** than in **5**, which demonstrates the ability of the CHO group to absorb charge.

π-Orbital Populations and Bond Orders. One measure of the amount of resonance stabilization is the electron density in the p orbital on C^+ perpendicular to the molecular plane and the corresponding decrease of charge density in the π-orbital of the C–X bond. These orbital populations are given in Table IV. Good agreement between the DZP and STO-3G results is found for the CN substituent. For **2**, there is a significant delocalization from the CN to the vacant orbital (0.25 e). Thus, there is a significant resonance interaction. Ion **4** has a significant population on C^+, even greater than that found for **2**. However, delocalization from the C and N has decreased. The increased charge at C^+ is due to interactions with the p-π CH_2 orbital of the CH_3 group, which for the nonbridged ethyl cation **16** is 0.12 e. A schematic of this orbital interaction is given below.



A similar result is found for **5**. Subtraction of this quantity gives a better estimate of the resonance interaction of the CN with ^+C, and the value decreases to 0.19 e at the STO-3G level. The delocalization from N is less for **8**, and we must subtract 0.18 e (the interaction of two methyl groups) from the p orbital, giving a population of 0.14 e at the STO-3G level. Thus, the resonance stabilization is decreasing with added methyl groups.

The results are somewhat more complicated for the CHO substituent. The minimum basis results for **10** show too much donation to C^+ and the wrong charge distribution on the CO group in comparison with the DZP result. This is probably due to the low polarity of the CO bond at the STO-3G level. However, the general trends seen at the minimum basis level for the population on C^+ do follow the results seen for the CN compounds, with **11** having a lower population (0.11 e) than **10**, while **15** is lower still (0.08 e) after accounting for the effects of the CH_3 groups. The population on C^+ for the rotated form of **10** is very low (0.05 e). The population on ^+C in **10** is much lower than that found for **2**, showing the expected decrease in resonance stabilization for CHO as compared to CN.

Another measure of the resonance interaction is provided by the bond order.[30] At present, these are only available for the

Table V. Bond Orders[a]

molecule	C_α–C_X	C_X–X	C_α–CH_2^+; C_α–CH_3
1	1.04	2.94	
2	1.42	2.52	
3	1.02	2.95	1.00
4	1.27	2.68	1.08
5	1.03	2.96	1.11
6	0.69	2.53	
7	1.00	2.95	1.00
8	1.20	2.75	1.06
9	0.99	2.02	
10	1.15	1.83	
10R	1.00	2.02	
11	0.98	2.02	1.01
12	1.07	1.91	1.11
13b	0.94	2.06	1.12
14	0.97	2.02	1.00
15	1.03	1.95	1.08
16			1.13
17			1.09

[a] Calculated in the PRDDO approximation for bond orders as defined in ref 29.

PRDDO wave functions and are given in Table V. As an example, the bond orders for **1** show a C–C bond with slightly more single bond character than a nominal single bond (bond order = 1.0) and slightly less of a C≡N triple bond (bond order = 3.0). In **2**, the C–N bond order is reduced by almost 0.5, while the C_α–C bond order is increased by ~0.4. Thus, there is significant double bond character in the C_α–C bond. The C_α–C bond order decreases significantly in **4** as expected from the previous discussion on charges and π-overlap populations while the C–N bond order increases. The C_α–C_{H_3} bond order is now greater than 1.0 due to the resonance stabilization of the CH_3 group. The ^+C–CH_2 bond order is increased in **5** since this is the only resonance stabilization available. Note, however, that it is less than the bond order in $CH_3CH_2^+$ (**16**). The bond orders in **8** follow the general trend of a decrease in the C_α–C_N order and an increase in the C–N order relative to **2**. However, even here, there is still an enhanced resonance stabilization of the ^+C moiety. The bond order C^+–CH_3 is decreased in **8** as compared to **17** due to the resonance interaction with the CN group. As expected, there is much less resonance stabilization in the CHO substituted ion, **10**, as denoted by the bond order. There is less than 0.2 of a bond transferred from the C═O to the C_α^+—C_0 bond on **10** relative to the neutral, as compared to the result found for **2** of ≳0.4 bond transfer. The C_α–C_0 bond orders in **12** and **15** decrease, as compared to **10**, to the point where in **15** there is only a very small amount of resonance stabilization (~0.06 of a bond) in comparison with the corresponding neutral. The bond orders to the CH_3 groups are comparable to the values found for **17** and are greater than those found in **8**. This is expected due to the small resonance interaction of the CHO group in **15**.

Conclusion

We have presented results at various theoretical levels on the structures and stabilities of cations substituted by electron-withdrawing CN and CO substituents. These substituents are σ-electron withdrawers but also act as π-electron donors, as revealed by geometries, stabilization energies, charge distributions, and bond orders.

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Registry No. 1, 75-05-8; **2**, 34430-18-7; **3**, 107-12-0; **4**, 74738-52-6; **5**, 38607-30-6; **6**, 90432-45-4; **7**, 78-82-0; **8**, 74738-53-7; **9**, 75-07-0; **10**, 41084-88-2; **11**, 123-38-6; **12**, 75279-61-7; **13**, 62130-89-6; **14**, 28-84-2; **15**, 75279-62-8; CH_3^+, 14531-53-4; CH_4, 74-82-8.

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Reactions of $FeCH_3^+$ and $CoCH_3^+$ with Aliphatic Alkanes in the Gas Phase

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Abstract: The gas-phase reactions of $FeCH_3^+$ and $CoCH_3^+$ with aliphatic alkanes up to C_6H_{14} were studied. $FeCH_3^+$ is completely unreactive with the aliphatic alkanes, while $CoCH_3^+$ reacts with all alkanes larger than ethane by initial insertion into a C–H bond resulting in CH_4 loss followed by dehydrogenation or alkane elimination forming $Co(allyl)^+$ products. The $Co(allyl)^+$ ions react rapidly with the alkanes (except methane) predominantly by dehydrogenation generating allyl–olefin complexes. The results indicate that the cobalt–allyl bond strength, $D°(Co^+–C_3H_5)$, is in excess of 72 kcal/mol while $D°(Co^+–\text{butadiene})$ appears to be less than 52 kcal/mol. $CoCH_3^+$ also abstracts a hydride from alkanes larger than ethane (except for 2,2-dimethylpropane) forming $C_nH_{2n+1}^+$ and implying $D°(CoCH_3^+–H^-) = 256 \pm 10$ kcal/mol which together with an earlier reported value of $\Delta H_f°(CoCH_3) = 256 \pm 4$ kcal/mol yields $D°(Co–CH_4) = 49 \pm 11$ kcal/mol and $\Delta H_f°(CoCH_4) = 35 \pm 11$ kcal/mol. Structures of the major primary product ions were investigated both by collision-induced dissociation (CID) and by specific ion–molecule reactions.

Transition-metal ions have proven to be highly reactive in the gas phase. This has been demonstrated by several recent investigations on the reactions of gas-phase transition-metal ions with a variety of organic species using ion cyclotron resonance (ICR) spectrometry,[1-3] Fourier transform mass spectrometry (FTMS),[4,5] and ion beam techniques.[6,7] The group 8 transition-metal ions, Fe^+, Co^+ and Ni^+, have received the most attention which has

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