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Proton Transfers from Carbon Acids Activated by π-Acceptors. Changes in Intrinsic Barriers and Transition State Imbalances Induced by a Cyano Group. An ab Initio Study

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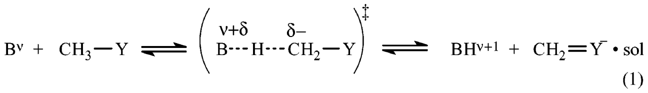
We report an ab initio study of the identity carbon-to-carbon proton-transfer $NCCH_2Y + NCCH{=}Y^- \rightleftarrows NCCH{=}Y^- + NCCH_2Y$ in the gas phase, where Y = H, $CH{=}CH_2$, $CH{=}O$, $CH{=}S$, CN, NO, and NO_2. The main focus is on a comparison with the previously reported systems $CH_3Y + CH_2{=}Y^- \rightleftarrows CH_2{=}Y^- + CH_3Y$, i.e., on the effect of the cyano group on acidities, proton-transfer barriers, and transition state structures. The conclusions of this study are as follows: (1) The transition state for the $NCCH_2Y/NCCH{=}Y^-$ systems is more imbalanced than that for the $CH_3Y/CH_2{=}Y^-$ systems. (2) The cyano group leads to an increase in the acidities but to a decrease in the proton transfer barriers. This barrier reduction results from the fact that the stabilizing effect of the cyano group on the transition state is greater than that on the anion. (3) Within a reaction series, the barriers are largely dominated by the π-acceptor strength of Y, i.e., the strongest π-acceptors lead to the highest barriers. This is similar to proton transfers in solution but quite different from the $CH_3Y/CH_2{=}Y^-$ systems in the gas phase; in these latter systems π-acceptor effects play a minor role while the barrier lowering field effect of Y is dominant.

Introduction

There has been an ongoing interest in the factors that determine the intrinsic barriers of proton transfers involving carbon acids activated by π-acceptors. The early work focused on reactions in solution and has been reviewed frequently;[1−5] more recently, several experimental[6−9] as well as ab initio[10−17] studies of proton transfer in the gas phase have been reported. The picture that emerges from this work is that close similarities as well as striking differences between solution and gas-phase reactivity patterns exist.

In solution the dominant factor that affects the intrinsic barrier is the strength of the π-acceptor, coupled, in some cases, with substantial solvation effects.[1−5] Weak π-acceptors lead to low intrinsic barriers while strong π-acceptors lead to high intrinsic barriers. The intrinsic barrier is further enhanced if there is strong specific solvation of the carbanion, e.g. hydrogen bonding of water to the oxygen atoms of enolate or nitronate anions.

The reason for these reactivity patterns is that the transition state of the proton transfer is imbalanced in the sense that delocalization of the incipient negative charge into the π-acceptor and its solvation lag behind proton transfer.[5] This is shown schematically and in exaggerated form in eq 1. The evidence for these imbalances has been established from Brønsted coefficients.[18]



$$B^{\nu} + CH_3{-}Y \rightleftharpoons \left(\overset{\nu+\delta}{B}\cdots H\cdots \overset{\delta-}{CH_2}{-}Y\right)^{\ddagger} \rightleftharpoons BH^{\nu+1} + CH_2{=}Y^{-}\cdot sol \qquad (1)$$

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[18] For a reaction of the type $ZC_6H_4CH_2Y + B^{\nu} \rightleftarrows ZC_6H_4CH{=}Y^- + BH^{\nu+1}$ the Brønsted α derived from the variation of the substituent Z is typically abnormally high because, at the transition state, the incipient negative charge is closer to Z than it is in the delocalized anion.[5] The best known example is the reaction of $ZC_6H_4CH_2NO_2$ with amines.[19] Conversely, for a reaction of the type $RCH_2YZ + B^{\nu} \rightleftarrows RCH{=}Y^-Z + BH^{\nu+1}$ the α value is abnormally low because, at the transition state, the incipient negative charge is farther away from Z than it is in the delocalized anion.[5] An example of this situation is the reaction of 2-NO_2-4-Z-$C_6H_3CH_2CN$ with amines.[20]

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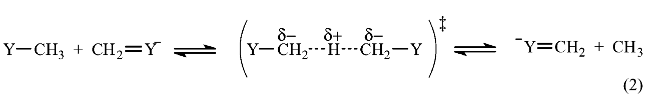
The increased barrier arises because the resonance stabilization found in the anion is disproportionately weakly developed at the transition state.[5] Or, if the reverse reaction is considered, most of the resonance energy that stabilizes the anion has to be lost in reaching the transition state. Hence for a given degree of imbalance, the stronger the π-acceptor, the higher the intrinsic barrier.

Similar transition state imbalances prevail in the gas phase, as demonstrated by ab initio calculations on identity carbon-to-carbon proton transfers of the type shown in eq 2,[21,22] as well as other gas-phase proton transfers.[15−17] In fact, because in eq 2 the *reactant* base is also a delocalized carbanion, the transition state is characterized by *two* imbalances, one in which the delocalization of the charge into the Y-group of the product anion lags behind proton transfer and one in which the localization of the charge onto the carbon of the reactant anion is ahead of proton transfer.[23] The ab initio evidence for imbalanced transition states is based on computed charge distributions as well as geometric parameters, especially the pyramidal angle, which is a measure of the loss of the tetrahedral geometry of the reactant and the development of the planar framework of the carbanion. These gas-phase calculations also reveal a proton in flight with substantial positive charge ($\delta+$ ca. 0.3), a point to which we will return below.



$$\mathrm{Y{-}CH_3 + CH_2{=}Y^-} \rightleftharpoons \left(\mathrm{Y{-}\overset{\delta-}{CH_2}{\cdots}\overset{\delta+}{H}{\cdots}\overset{\delta-}{CH_2}{-}Y}\right)^{\ddagger} \rightleftharpoons \mathrm{{}^-Y{=}CH_2 + CH_3} \quad (2)$$

The effect of the imbalances is qualitatively the same as in solution proton transfer, i.e., an increase in the intrinsic barrier with increasing π-acceptor strength.[21b,22c,d] However, in contrast to the situation in solution, the *actual* barriers do not correlate with π-acceptor strength. This is because the π-acceptor effect is more than offset by the field effect of the Y-group and by electrostatic effects.[22c,d] In fact, the field effect leads to a *reduction* of the actual barrier below that for the unactivated CH_4/CH_3^- systems, a finding that can be understood as follows. The positive charge on the proton in flight at the transition state implies that the sum of the negative charges on the two CH_2Y fragments is more than one unit charge. Hence the overall stabilization of these charges by the field effect of the Y-groups is greater than the stabilization of the unit charge in the reactant or product ion. This effect is so strong with some Y-groups that the barriers, defined as the difference in enthalpy between the transition state and the free reactants, actually become negative, e.g. with Y = CN, NO_2, CH=O, and NO.[22c,d]

A second factor that contributes to the lowering of the barriers in the gas phase is the polarizability effect of the Y-group.[22c,d] This factor is generally small but is sizable for Y = CH=S, and for Y = CH=CH_2, it is the most important factor.[22d]

A quantitative assessment of how the various factors affect the barriers was provided by a correlation of the barriers with Taft's gas-phase field and resonance and polarizability substituent constants[24] according to eq 3.

$$\Delta\Delta H^{\ddagger} = \Delta H^{\ddagger}(\mathrm{CH_3Y}) - \Delta H^{\ddagger}(\mathrm{CH_4}) = \rho^{\ddagger}_{\mathrm{F}}\sigma_{\mathrm{F}} + \rho^{\ddagger}_{\mathrm{R}}\sigma_{\mathrm{R}} + \rho^{\ddagger}_{\alpha}\sigma_{\alpha} \quad (3)$$

We obtained $\rho^{\ddagger}_{\mathrm{F}} = -22.6$, $\rho^{\ddagger}_{\mathrm{R}} = 9.81$, and $\rho^{\ddagger}_{\alpha} = 7.59$.[22d] These $\rho^{\ddagger}$ values show that the field and polarizability[25] effects are barrier reducing while the resonance effect is barrier enhancing. Incidentally, these results are in drastic contrast with how the gas-phase *acidities* of CH_3Y depend on the Y-group. These latter are dominated by the acidifying resonance effect; there is also a substantial contribution by the field effect while the polarizability effect is very small and acidity reducing. This was evident from a correlation of the acidities (relative to that of methane) with Taft's substituent constants according to eq 4 which yielded $\rho^{\circ}_{\mathrm{F}} = -43.0$, $\rho^{\circ}_{\mathrm{R}} = -192$, and $\rho^{\circ}_{\alpha} = -4.64$.[22d]

$$\Delta\Delta H^{\circ} = \Delta H^{\circ}(\mathrm{CH_3Y}) - \Delta H^{\circ}(\mathrm{CH_4}) = \rho^{\circ}_{\mathrm{F}}\sigma_{\mathrm{F}} + \rho^{\circ}_{\mathrm{R}}\sigma_{\mathrm{R}} + \rho^{\circ}_{\alpha}\sigma_{\alpha} \quad (4)$$

In the present paper we report results of an ab initio study of the gas-phase identity proton transfer of eq 5,

$$\mathrm{NCCH_2Y + NCCH{=}Y^-} \rightleftharpoons \mathrm{NCCH{=}Y^- + NCCH_2Y} \quad (5)$$

i.e., one of the hydrogens in CH_3Y has been replaced by a cyano group. The following Y-groups were investigated: CH=CH_2, CN, CH=O, CH=S, NO_2, and NO. Somewhat unexpectedly, our results indicate that the dependence of the intrinsic barrier on the Y-group is different than for the reactions of eq 2 and comes closer to the patterns observed in solution reactions.

Methods and Special Features of Individual Systems

Asymmetrically disubstituted methanes are pro-chiral structures. As a result, there are stereochemical considerations for the transition states being the subject of this current work. We have chosen to use the Prelog−Ingold convention with an arbitrary choice that a proton in flight takes precedence over a proton unaffected by a chemical reaction. Thus, RR, SS, and meso identity proton-transfer transition states are observed in the systems we consider here.

The $NCCH_2NO$ system allowed for complete exploration of stereochemistry. The theoretical methods employed gave consistent results: the meso transition state was higher in

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[23] The representation of the anion as having the entire negative on the Y group and of the transition as having the negative charge exclusively localized on the methylene group is an exaggeration.

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[25] Note that the σ_α values are defined as negative numbers[24] and hence a positive value of $\rho^{\ddagger}_{\alpha}$ implies a barrier *reducing* effect.

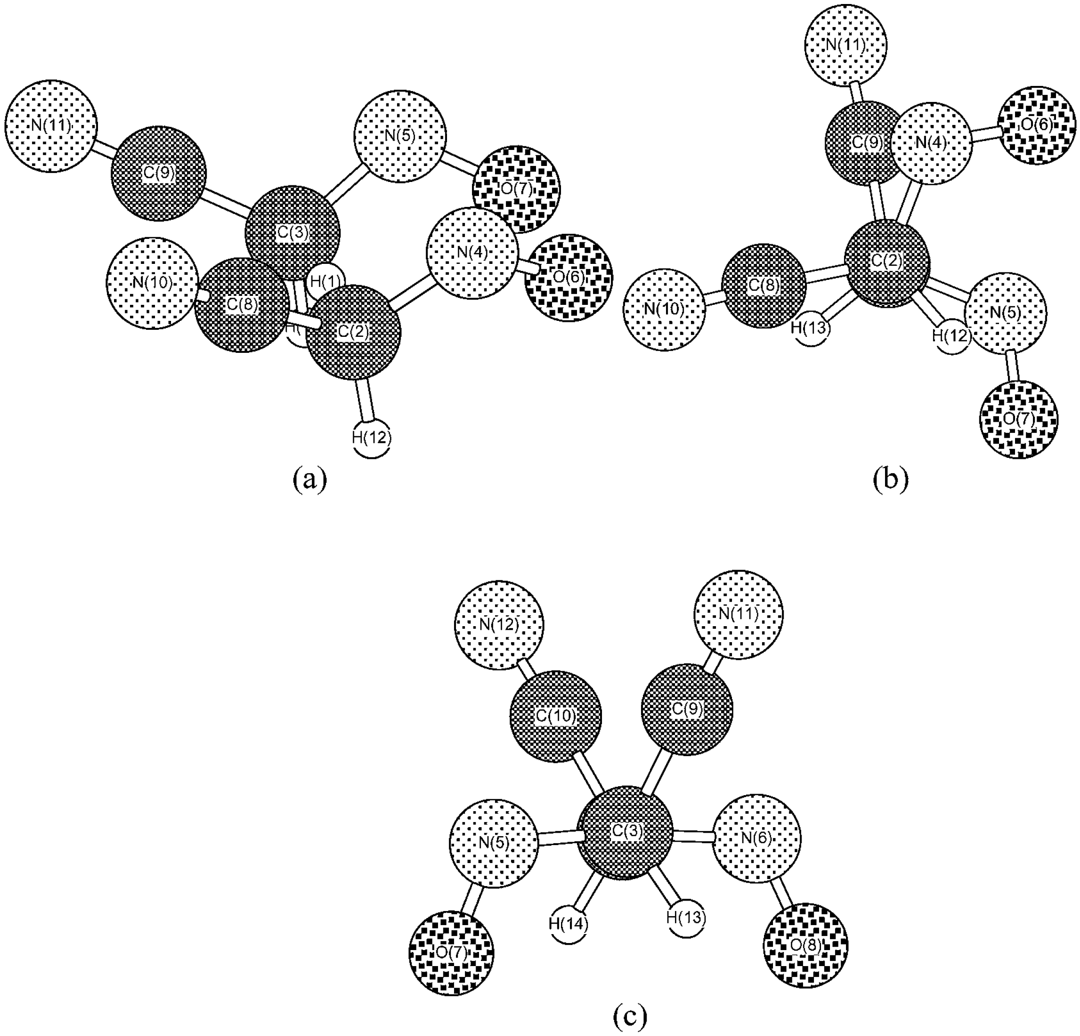

FIGURE 1. Transition states for the $NCCH_2NO$ system. (a) Meso transition state in the eclipsed conformation. (b) Optimized meso transition state. (c) SS transition state.

energy and the RR and SS transition states gave identical (to 1×10^{-7} Hartree) energies. As this was true for 3-21G* through MP2/6-311+G(d,p) calculations, 3-21G* calculations were used to determine whether the meso transition state or the chiral transition state was of lower energy. Once established at 3-21G*, the higher energy transition state was disregarded. For all systems the SS transition states were chosen for this study; this by chance was the result of the construction of the *Z*-matrix for the first system ($NCCH_2NO$) from which the other *Z*-matrix inputs for transition states were derived.

The explanation why chiral, not meso, transition states are of lower energy has most likely to do with the environment that a particular functional group is directed toward. Meso transition states were optimized by starting with an eclipsed arrangement, that is, viewing from one carbon atom, along the axis of the transferred proton, the functional groups of the closer carbon fragment will eclipse those of the more distant carbon fragment (Figure 1a). When optimized, the fragments move away from this eclipsed orientation, but each functional group is uniquely positioned (Figure 1b).

When the chiral transition state is constructed, the functional groups cannot be eclipsed. Upon optimization the groups are staggered, and the result is that each functional group is in the same environment, comparing one carbon fragment to the other. Figure 1, part c, shows the optimized SS transition state for the $NCCH_2NO$ identity proton transfer. Note that in Figure 1c, the odd number atoms are in exactly the same environment as the even numbered atoms. For example, the cyano group, C10 and N12, is flanked by the cyano group and the nitroso group from the odd numbered atoms, the opposite carbon fragment. The odd number cyano group, C9 and N11, is equivalently flanked by the nitroso and cyano groups of the even numbered carbon fragment.

All computations were performed by GAUSSIAN 98.[26] Transition state calculations were submitted as *Z*-matrix optimizations, symmetry was enforced by assignment of bond lengths, angles, and dihedrals as the same variable for each fragment. Anions and neutrals were submitted as *Z*-matrix optimizations, and geometries did not change when submitted as Cartesian coordinates. Standard basis sets (3-21G*, 6−31+G-(d,p), and 6-311+G(d,p)) were used. All our raw data are

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summarized in the Supporting Information.[27]Calculations were performed at the RHF, B3LYP, and MP2 levels of theory.

Frequency calculations were performed at each of these levels, and zero-point energies and contributions to the vibrational partition functions were scaled separately following Scott and Radom.[28] The acidities (barriers) were calculated as

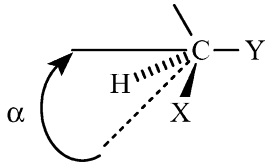
$$\Delta H^\circ\,(\Delta H^\ddagger) = \Delta E + \Delta \mathrm{ZPE} + \Delta C_{\mathrm{vib}}RT \qquad (6)$$

where ΔE is the difference in electronic energies between neutral and anion (transition state) at a given level of theory, ΔZPE the difference in the scaled zero-point energies, and $\Delta C_{\mathrm{vib}}RT$ is the difference in the scaled vibrational heat capacities. The barriers ($\Delta H^\ddagger$) were further corrected for the loss of translational and rotational freedom ($3RT$).

Results and Discussion

General Features. The focus of this paper is on how the cyano group in $NCCH_2Y$ modifies the main characteristics of CH_3Y, its anion, its gas-phase acidity, the transition state for the identity proton transfer, and the barrier for the proton transfer. For a discussion of a number of unique features of certain Y-groups and how they affect structure and reactivity the reader should consult ref 22d.

Anions: Geometries. Table 1 provides a summary of the bond lengths and angles that are most relevant to the questions addressed in this study; α refers to the pyramidal angle, defined as shown in **1** where the solid line is the projection of the C−Y bond and the dashed line is the bisector of the HCX group (X = CN in this study, X = H for the reactions of CH_3Y). Note that for the anions α is nearly zero in all cases, i.e., the anions are essentially planar.



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The changes in bond lengths that result from the ionization of $NCCH_2Y$ are qualitatively similar to those observed for the ionization of CH_3Y and consistent with charge delocalization into the Y-group. This is illustrated for two examples, one with a weakly electron-withdrawing Y-group ($CH{=}CH_2$) and one with a very strong one (NO). For $NCCH_2CH{=}CH_2$ the $C{-}CHCH_2$ bond is reduced by 6.2% while the C=C bond is elongated by 2.9%; the corresponding changes for $CH_3CH{=}CH_2$ are 6.9% and 4.3%, respectively.[29] For $NCCH_2NO$ the C−NO bond contracted by 11.9% while the N=O bond is elongated by 5.7%; the corresponding changes for CH_3NO are 10.8% and 3.9%, respectively. The percent C−Y bond contractions for all compounds studied is summarized in Table 2.

In the case of $NCCH_2Y$ there are also minor changes in the NC−C and C≡N bond lengths that indicate some degree of charge delocalization into the cyano group. For $NCCH_2CH{=}CH_2$ the NC−C bond contracts by 4.5% while the C≡N bond length increases by 1.4%; for $NCCH_2NO$ these values are 2.9% and 0.8%, respectively. These trends show that as the Y-group becomes more electron withdrawing, the effects on the C−C bond shortening and C≡N bond lengthening decrease, i.e., the resonance effect of the cyano group is attenuated by a more powerful Y-group. Similar conclusions were reached by Richard et al.,[30] i.e., addition of more cyano groups on cyanomethane decreases the resonance effect of each.

Anions: Charges. A complete summary of all atomic charges is given in Table S1 of the Supporting Information[27] while Table 3 reports a summary of group charges. The charges on the Y-group of the anions derived from $NCCH_2Y$ and CH_3Y as well as the charge on the cyano group of $NCCH{=}Y^-$ are reported in Table 2. The charge on the Y groups of $NCCH{=}Y^-$ follows the same qualitative trend as those for $CH_2{=}Y^-$ but they are considerably smaller, e.g. −0.312 for $NCCH{=}CHCH_2^-$ vs −0.539 for $CH_2{=}CHCH_2^-$, or −0.683 for $NCCH{=}NO^-$ vs −0.866 for $CH_2{=}NO^-$. The reduction in the charge on the Y-group is compensated for by placing a significant amount of charge onto the cyano group, e.g. −0.267 for $NCCH{=}CHCH_2^-$ and −0.198 for $NCCH{=}NO^-$. As is the case with the bond lengths, the trend toward a decrease in the charge on the cyano group and a concomitant decrease in the charge deficit on the Y-group as Y becomes more electron withdrawing is again consistent with the diminished role played by the cyano group in the delocalization of the anionic charge.

Gas-Phase Acidities. Table 4 summarizes the gas-phase acidities of $NCCH_2Y$ at the MP2 and B3LYP levels; the raw energy data are summarized in Table S2.[27] Also included are the acidities of CH_3Y at the same computational levels. On the basis of comparisons with experimental results and with CCSD(T)/6-311+G(2df,2p) calculations, the acidities of CH_3Y obtained at the MP2 level were deemed more reliable than the ones calculated at the B3LYP level.[22d] We shall assume the same to be true for the acidities of $NCCH_2Y$ and hence the emphasis of our further discussion will be on the MP2/6-311+G(d,p) results.

The following features are noteworthy.

(1) The order of the acidities of $NCCH_2Y$ ($CH{=}S > NO > NO_2 > CH{=}O > CN > CH{=}CH_2 > H$) is the same as that for CH_3Y at both computational levels but the cyano-substituted acids are all substantially more acidic than the corresponding CH_3Y. The change in the acidifying of the cyano group is presented in Table 4. As one would expect, the main reason for the acidifying effect is that in the anion part of the negative charge that is delocalized into the Y-group of $CH_2{=}Y^-$ is shifted into the cyano group of $NCCH{=}Y^-$. This is shown in Table 2, which reports the charge on the Y-group in $NCCH{=}Y^-$ and $CH_2{=}Y^-$ as well as the charge on the cyano group in $NCCH{=}Y^-$.

There is a trend toward a diminishing acidifying effect of the cyano group as the electron-withdrawing strength

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[27] See paragraph concerning Supporting Information at the end of this paper.

[28] Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

[29] These numbers as well as the ones discussed below refer to MP2 calculations. The B3LYP results are quite similar.

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TABLE 1. Bond Lengths and Pyramidal Angles of NCCH$_2$Y, NCCH=Y$^-$, and the Transition State

	MP2				B3LYP			
	neutral	anion	TS	% progress at TS	neutral	anion	TS	% progress at TS
NCCH$_3$ (Y = H)								
r_{C-C}	1.463	1.403	1.431		1.456	1.382	1.421	
Δr_{C-C}		−0.060	−0.032	53.3		−0.074	−0.035	47.5
$r_{C\equiv N}$	1.174	1.195	1.185		1.153	1.182	1.167	
$\Delta r_{C\equiv N}$		0.021	0.011	52.4		0.029	0.015	49.7
α	54.12	36.91	50.48		53.65	18.90	48.93	
		−17.21	−3.64	21.2		−34.75	−4.72	13.6
NCCH$_2$CH=CH$_2$ (Y = CH=CH$_2$)								
r_{NC-C}	1.469	1.403	1.430		1.465	1.392	1.426	
Δr_{NC-C}		−0.066	−0.039	59.1		−0.073	−0.039	53.4
r_{C-C}	1.510	1.417	1.465		1.513	1.416	1.466	
Δr_{C-C}		−0.093	−0.045	48.4		−0.097	−0.047	48.5
$r_{C=C}$	1.339	1.378	1.355		1.328	1.371	1.346	
$\Delta r_{C=C}$		0.039	0.016	41.0		0.043	0.018	41.8
$r_{C\equiv N}$	1.175	1.191	1.184		1.153	1.176	1.164	
$\Delta r_{C\equiv N}$		0.016	0.009	56.2		0.023	0.011	47.8
α	52.92	2.19	40.06		51.74	3.09	40.43	
$\Delta\alpha$		−50.73	−12.86	25.3		−48.65	−11.31	23.2
NCCH$_2$CN (Y = C≡N)								
r_{C-C}	1.469	1.401	1.439		1.465	1.393	1.434	
Δr_{C-C}		−0.068	−0.030	44.1		−0.072	−0.031	43.0
$r_{C\equiv N}$	1.174	1.189	1.181		1.151	1.172	1.160	
$\Delta r_{C\equiv N}$		0.015	0.007	46.7		0.021	0.009	42.9
α	51.14	1.50	45.61		51.02	2.57	44.65	
$\Delta\alpha$		−49.64	−5.53	11.1		−48.45	−6.37	13.1
NCCH$_2$CH=O (Y = CH=O)								
r_{NC-C}	1.463	1.411	1.432		1.457	1.400	1.428	
Δr_{NC-C}		−0.052	−0.031	59.6		−0.057	−0.029	50.9
r_{C-CO}	1.530	1.406	1.456		1.535	1.405	1.457	
Δr_{C-CO}		−0.123	−0.074	60.2		−0.130	−0.078	60.0
$r_{C=O}$	1.210	1.255	1.232		1.199	1.250	1.224	
$\Delta r_{C=O}$		0.045	0.022	48.9		0.050	0.026	52.0
$r_{C\equiv N}$	1.175	1.187	1.181		1.153	1.171	1.161	
$\Delta r_{C\equiv N}$		0.012	0.006	50.0		0.018	0.008	44.4
α	54.64	0.42	36.72		53.72	1.48	37.39	
$\Delta\alpha$		−54.23	−17.92	33.0		−52.24	−16.33	31.3
NCCH$_2$NO$_2$ (Y = NO$_2$)								
r_{NC-C}	1.459	1.401	1.433		1.451	1.394	1.428	
Δr_{NC-C}		−0.058	−0.026	44.8		−0.057	−0.023	40.4
r_{C-NO_2}	1.535	1.375	1.444		1.535	1.370	1.447	
Δr_{C-NO_2}		−0.160	−0.091	56.9		−0.165	−0.088	52.3
r_{N-O}	1.228	1.265	1.243		1.217	1.266	1.239	
Δr_{N-O}		0.037	0.015	40.5		0.049	0.022	44.9
$r_{C\equiv N}$	1.175	1.186	1.180		1.151	1.167	1.158	
$\Delta r_{C\equiv N}$		0.011	0.005	45.5		0.016	0.007	43.8
α	56.24	2.23	43.75		54.09	3.09	42.42	
$\Delta\alpha$		−54.01	−12.49	23.1		−51.00	−11.67	22.9
NCCH$_2$NO (Y = NO)								
r_{NC-C}	1.460	1.417	1.437		1.452	1.409	1.433	
Δr_{NC-C}		−0.043	−0.023	53.5		−0.043	−0.019	44.2
r_{C-NO}	1.517	1.337	1.398		1.541	1.331	1.407	
Δr_{C-NO}		−0.180	−0.119	66.1		−0.210	−0.134	63.8
$r_{N=O}$	1.213	1.282	1.250		1.190	1.276	1.233	
$\Delta r_{N=O}$		0.069	0.037	53.6		0.086	0.043	50.0
$r_{C\equiv N}$	1.175	1.184	1.179		1.152	1.167	1.159	
$\Delta r_{C\equiv N}$		0.009	0.004	44.4		0.015	0.007	46.7
α	53.11	0.94	37.77		52.08	0.19	38.22	
$\Delta\alpha$		−52.17	−15.35	29.4		−51.89	−13.86	26.7
NCCH$_2$CH=S (Y = CH=S)								
r_{NC-C}	1.466	1.417	1.437		1.463	1.409	1.434	
Δr_{NC-C}		−0.049	−0.029	59.2		−0.054	−0.029	53.7
r_{C-CS}	1.515	1.382	1.434		1.515	1.377	1.433	
Δr_{C-CS}		−0.133	−0.081	60.9		−0.138	−0.082	59.4
$r_{C=S}$	1.614	1.694	1.648		1.616	1.708	1.659	
$\Delta r_{C=S}$		0.080	0.034	42.5		0.092	0.043	46.8
$r_{C\equiv N}$	1.175	1.185	1.180		1.153	1.167	1.159	
$\Delta r_{C\equiv N}$		0.010	0.005	50.0		0.014	0.006	42.9
α	52.34	0.90	32.93		50.28	1.25	34.17	
$\Delta\alpha$		−51.44	−15.41	37.7		−49.03	16.11	32.8

TABLE 2. Anions: Relative C−Y Bond Contraction and Negative Charge on the Y-Group[a]

Y^b	$\sigma_R{}^c$	$100(\Delta r_{C-Y}/r_{C-Y})$	charge on Y	χ	charge on the CN group
			MP2		
$CH{=}CH_2$	0.16	6.16 (6.86)	−0.312 (−0.539)	−0.373 (−0.536)	−0.267
CN	0.10	4.63 (4.10)	−0.232 (−0.356)	−0.244 (−0.315)	−0.232
CH=O	0.19	8.04 (7.64)	−0.343 (−0.531)	−0.434 (−0.522)	−0.228
NO_2	0.18	10.4 (9.18)	−0.654 (−0.854)	−0.473 (−0.610)	−0.190
NO	0.26	11.9 (10.8)	−0.683 (−0.866)	−0.597 (−0.711)	−0.198
CH=S	≈0.33[d]	8.78 (8.94)	−0.544 (−0.756)	−0.604 (−0.735)	−0.175
			B3LYP		
$CH{=}CH_2$	0.16	6.41 (7.07)	−0.312 (−0.536)	−0.373	−0.288
CN	0.10	4.91 (5.08)	−0.246 (−0.391)	−0.254	−0.246
CH=O	0.19	8.47 (7.98)	−0.339 (−0.532)	−0.425	−0.248
NO_2	0.18	10.7 (10.8)	−0.659 (−0.871)	−0.473	−0.206
NO	0.26	13.6 (11.9)	−0.650 (−0.839)	−0.561	−0.216
CH=S	≈0.33[d]	9.11 (9.18)	−0.520 (−0.746)	−0.571	−0.194

[a] Numbers in parentheses refer to CH_3Y, see ref 22d. [b] Arranged in order of increasing electron withdrawing strength as indicated by the gas-phase acidities. [c] Reference 24. [d] Estimated (ref 22d)

TABLE 3. NPA Group Charges (MP2)

group	neutral	anion	difference[b]	TS	difference[c]
		$NCCH_2CH{=}CH_2$ ($CH_3CH{=}CH_2$)			
$NCCH(CH_2)^d$	−0.062 (0.003)	−0.688 (−0.461)	−0.626 (−0.464)	−0.567 (−0.376)	−0.505 (−0.379)
$CH(CH_2)$	−0.034 (0.003)	−0.420 (−0.461)	−0.386 (−0.464)	−0.416 (−0.376)	−0.382 (−0.379)
$CH{=}CH_2$	0.062 (−0.003)	−0.312 (−0.539)	−0.376 (−0.536)	−0.091 (−0.266)	−0.153 (−0.263)
H (transferred)				0.316 (0.285)	
		$NCCH_2CN$ (CH_3CN)			
$NCCH(CH_2)^d$	−0.012 (0.041)	−0.768 (−0.644)	−0.756 (−0.685)	−0.567 (−0.446)	−0.555 (−0.487)
$CH(CH_2)$	−0.024 (0.041)	−0.537 (−0.644)	−0.513 (−0.685)	−0.469 (−0.446)	−0.445 (−0.487)
CN	0.012 (−0.041)	−0.232 (−0.356)	−0.244 (−0.315)	−0.097 (−0.206)	−0.109 (−0.165)
H (transferred)				0.327 (0.303)	
		$NCCH_2CH{=}O$ ($CH_3CH{=}O$)			
$NCCH(CH_2)^d$	−0.091 (−0.021)	−0.657 (−0.469)	−0.566 (−0.448)	−0.563 (−0.384)	−0.472 (−0.363)
$CH(CH_2)$	−0.069 (−0.021)	−0.430 (−0.469)	−0.361 (−0.448)	−0.441 (−0.384)	−0.372 (−0.363)
CH=O	0.091 (0.021)	−0.343 (−0.531)	−0.434 (−0.552)	−0.101 (−0.266)	−0.192 (−0.287)
H (transferred)				0.327 (0.301)	
		$NCCH_2NO_2$ (CH_3NO_2)			
$NCCH(CH_2)^d$	0.181 (0.244)	−0.346 (−0.140)	−0.527 (−0.384)	−0.271 (−0.093)	−0.452 (−0.337)
$CH(CH_2)$	0.179 (0.244)	−0.156 (−0.140)	−0.335 (−0.384)	−0.190 (−0.093)	−0.369 (−0.337)
NO_2	−0.181 (−0.244)	−0.654 (−0.860)	−0.473 (−0.610)	−0.373 (−0.535)	−0.192 (−0.291)
H (transferred)				0.289 (0.253)	
		$NCCH_2NO$ (CH_3NO)			
$NCCH(CH_2)^d$	0.086 (0.155)	−0.317 (−0.134)	−0.403 (−0.289)	−0.273 (−0.082)	−0.359 (−0.237)
$CH(CH_2)$	0.103 (0.155)	−0.119 (−0.134)	−0.222 (−0.289)	−0.186 (−0.082)	−0.289 (−0.237)
NO	−0.086 (−0.155)	−0.683 (−0.866)	−0.597 (−0.711)	−0.373 (−0.548)	−0.287 (−0.393)
H (transferred)				0.293 (0.260)	
		$NCCH_2CH{=}S$ ($CH_3CH{=}S$)			
$NCCH(CH_2)^d$	−0.060 (0.021)	−0.456 (−0.244)	−0.396 (−0.265)	−0.441 (−0.233)	−0.381 (−0.254)
$CH(CH_2)$	−0.041 (0.021)	−0.281 (−0.244)	−0.240 (−0.265)	−0.351 (−0.233)	−0.269 (−0.254)
CH=S	0.060 (−0.021)	−0.544 (−0.756)	−0.604 (−0.735)	−0.221 (−0.413)	−0.281 (−0.392)
H (transferred)				0.323 (0.291)	

[a] Numbers in parentheses refer to CH_3Y, see ref 22d. [b] Difference between anion and neutral; on the Y-group this difference corresponds to $-\chi$ in eq 10. [c] Difference between TS and neutral; this value corresponds in eq 10 to $-\delta_C$ and $-\delta_Y$, respectively. [d] For the neutral this group corresponds to $NCCH_2(CH_3)$.

of Y increases (Table 4). This trend is reasonable as a stronger Y-group reduces the demand for additional carbanion stabilization by the cyano group. It is also consistent with the trend, mentioned earlier, toward a smaller portion of the negative charge being carried by the cyano group (Table 2).

(2) The influence of the Y group on the acidities of $NCCH_2Y$ in terms of contributions by field, resonance, and polarizability effects can be analyzed by using eq 7, which is similar to eq 4 applied to the acidities of CH_3Y. Plots according to eq 7 are shown in Figure 2 for the MP2 calculations;[31] a similar plot based on the B3LYP calculations is shown in Figure S1.[27] Table 6 reports the various $\rho°$ values from fitting the acidity data to the Taft plots.

$$\Delta\Delta H° = \Delta H°(NCCH_2Y) - \Delta H°(NCCH_3) = \rho_F^{\circ}\sigma_F + \rho_R^{\circ}\sigma_R + \rho_\alpha^{\circ}\sigma_\alpha \quad (7)$$

Resonance dominates the stabilization of the cyano carbanions as was true for the methylene carbanions but the presence of the cyano group leads to an approximately 30% reduction in ρ_R°. The diminished resonance effect is consistent with the reduced negative charge on the Y-group (Table 5).

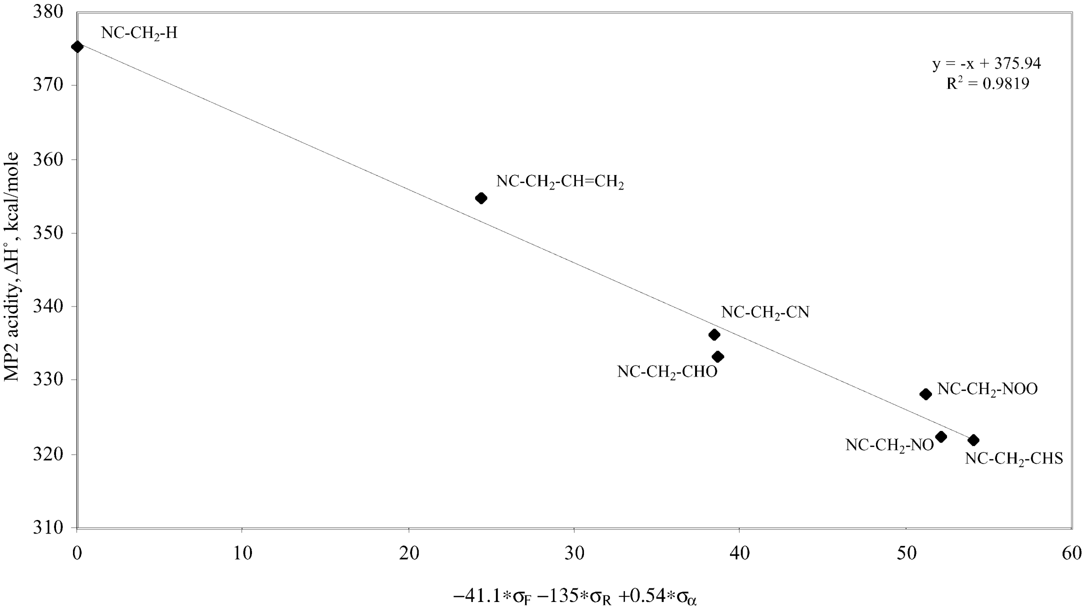

FIGURE 2. Plot of $\Delta\Delta H°$ according to eq 7 (MP2).

TABLE 4. Gas-Phase Acidities, $\Delta H°$, of CH_3Y and $NCCH_2Y$[a]

	MP2[b]			B3LYP[c]		
Y	CH_3Y	$NCCH_2Y$	diff[d]	CH_3Y	$NCCH_2Y$	diff[d]
H	418.1	375.4	(−42.7)	415.8	369.3	(−46.5)
$CH{=}CH_2$	390.2	354.9	(−35.3)	387.0	348.2	(−38.8)
CN	375.4	336.3	(−39.1)	369.9	328.4	(−41.5)
$CH{=}O$	367.2	333.5	(−33.7)	362.9	326.8	(−36.1)
NO_2	359.0	328.3	(−30.7)	354.0	318.6	(−35.4)
NO	351.9	322.5	(−29.4)	346.0	314.5	(−31.5)
$CH{=}S$	348.7	322.1	(−26.6)	344.4	313.5	(−30.9)

[a] In kcal/mol. [b] MP2/6-311+G(d,p)//MP2/6-311+G(d,p). [c] B3LYP/6-311+G(d,p). [d] $\Delta H°(NCCH_2Y) - \Delta H°(CH_3Y)$.

TABLE 5. Barriers, $\Delta H^‡$, for the Reactions of Eqs 2 and 5[a]

	MP2[b]			B3LYP[c]		
Y	CH_3Y	$NCCH_2Y$	diff[d]	CH_3Y	$NCCH_2Y$	diff[d]
H	8.1	−8.5	−16.6	6.7	−8.3	−15.0
$CH{=}CH_2$	4.7	−10.6	−15.3	5.2	−4.7	−9.9
CN	−8.5	−14.3	−5.8	−8.3	−10.5	−2.2
$CH{=}O$	−0.3	−8.4	−8.1	−1.8	−5.4	−3.6
NO_2	−6.2	−11.3	−5.1	−7.8	−7.2	0.6
NO	−1.1	−4.7	−3.6	−4.4	−3.6	−0.8
$CH{=}S$	0.3	−7.0	−7.3	−0.8	−1.8	−1.0

[a] In kcal/mol. [b] MP2/6-311+G(d,p)//MP2/6-311+G(d,p). [c] B3LYP/6-311+G(d,p). [d] $\Delta H^‡(NCCH_2Y) - \Delta H^‡(CH_3Y)$.

The field effect contributes significantly to the carbanion stabilization; interestingly, ρ_F° for $NCCH_2Y$ is only slightly smaller than that for CH_3Y, i.e., the cyano group only minimally reduces the influence of the field effect of the Y-group on carbanion stability. This finding is consistent with the fact that the negative charge on the CH-group of $NCCH{=}Y^-$ is only slightly smaller than the negative charge on the corresponding CH_2-groups of $CH_2{=}Y^-$ (Table 3).

TABLE 6. Analysis of Acidities and Barriers by Means of Taft Equations

	MP2		B3LYP	
ρ^c	CH_3Y	$NCCH_2Y$	CH_3Y	$NCCH_2Y$
		$\Delta\Delta H°$ [a]		
ρ_F°	−43.0	−41.1	−48.0	−45.1
ρ_R°	−192.5	−135	−197	−142
ρ_α°	−4.64	0.54	−5.96	0.62
r^2	0.992	0.982	0.995	0.990
		$\Delta\Delta H^‡$ [b]		
$\rho_F^‡$	−22.6	−7.01	−22.9	−6.48
$P_R^‡$	9.81	36.6	−3.85	31.0
$\rho_\alpha^‡$	7.59	11.9	0.78	2.95
r^2	0.995	0.925	0.985	0.992

[a] Equation 4 for CH_3Y, equation 7 for $NCCH_2Y$. [b] Equation 3 for CH_3Y, equation 11 for $NCCH_2Y$. [c] A negative ρ_F° or ρ_F° implies stabilization of the anion by the field and resonance effects, respectively (σ_F and σ_R are defined as positive numbers for electron-withdrawing substituents) while a negative ρ_α implies *de*stabilization of the anion (σ_α is defined as a negative number for polarizable groups). A negative $\rho_F^‡$ or $\rho_R^‡$ and a more positive $P_\alpha^‡$ mean that the transition state is more strongly stabilized than the anion.

Transition States: Geometries. The changes in bond lengths and the pyramidal angle upon conversion of the reactants to the transition state are summarized in Table 1. The most interesting feature is the percent progress in the bond and angle changes along the reaction coordinate from the carbon acid to its anion. Note that, due to the symmetry of the transition state, progress in the C−H bond cleavage/C−H bond formation is 50% by definition in all cases. For all bonds that undergo changes due to an increase/decrease in π-bond character the progress is typically in the 50 ± 10% range with the exception of the $NCCH_2NO$ system where this progress is 66% for the C−NO bond contraction.

A key point with respect to the question of imbalance is the fact that the progress in planarization as measured by α is significantly smaller than the progress in the bond changes. This is illustrated in Table 7 where the progress

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(31) Multiparameter fits were prepared by using the "solver" tool in Microsoft Excel. A linear least-squares fit was performed by varying each of the ρ values.

TABLE 7. Percent Progress in the C−Y Bond Contraction and Planarization (α) at the Transition State and Imbalance Parameter (*n*)

	CH_3Y			$NCCH_2Y$		
Y	C−Y	α	n^a	C−Y	α	n^a
			MP2			
$CH{=}CH_2$	56.3	22.6	1.61	48.4	20.0	2.14
C≡N	53.3	21.2	1.51	44.1	11.1	1.94
CH=O	65.2	34.1	1.52	60.2	33.0	1.99
NO_2	57.7	26.8	1.59	56.9	23.1	2.06
NO	70.0	44.0	1.28	66.1	29.4	1.67
CH=S	64.2	41.0	1.42	60.9	37.7	1.85
			B3LYP			
$CH{=}CH_2$	55.2	22.6	1.53	48.5	20.0	2.05
C≡N	47.5	13.6	1.56	43.0	13.1	1.99
CH=O	64.2	33.9	1.44	60.0	31.3	1.89
NO_2	57.1	18.1	1.48	53.3	22.9	1.82
NO	65.3	41.5	1.27	63.8	27.6	1.66
CH=S	52.1	42.4	1.44	59.4	32.8	1.90

[a] Equation 8.

in the planarization is compared with the progress in the C−Y bond contraction. The results are consistent with the notion of an imbalanced transition state.

There are some trends in the various progress variables as well as important parallels between the $NCCH_2Y$ and CH_3Y systems which are noteworthy. The progress in the C−Y bond contraction becomes greater with increasing electron-withdrawing strength of the Y-group. The same trend was observed for CH_3Y (Table 7). However, the progress in the C−Y bond contraction is somewhat smaller in the $NCCH_2Y$ systems compared to the corresponding CH_3Y systems, e.g. 48.4% vs 56.3% for Y = $CH{=}CH_2$, 60.2% vs 65.2% for Y = CH=O, and 66.1% vs 70.0% for Y = NO. This smaller progress in the C−Y bond contraction, i.e., the greater delay in π-bond development, decreases charge delocalization into the Y-group, implying a greater transition state imbalance. The charge distributions discussed below confirm this conclusion.

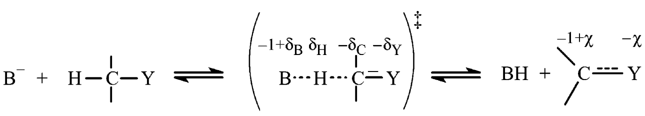
Just as for the C−Y bond contraction, there is a trend toward greater progress in the planarization as the Y-group becomes more electron withdrawing, with the notable exception of the nitro compound. This parallels the trend for the CH_3Y systems although the progress in reducing α is not uniformly smaller for the $NCCH_2Y$ systems. The asymmetry of the H−C−N group versus the H−C−H group makes interpretation of the pyramidal angle α less precise in the $NCCH_2Y$ versus the CH_3Y systems.

Transition States: Charges. Relative to the anion, there is a disproportionately large charge buildup on the NCCH group and a disproportionately small charge buildup on the Y group (Table 3), indicating the presence of a significant transition state imbalance. This is the same pattern observed for the CH_2 and Y groups, respectively, in the CH_3Y systems. However, for the $NCCH_2Y$ systems the *actual* charges on the NCCH-groups are larger than those on the CH_2-groups of the CH_3Y systems, while the *actual* charges on the Y-groups are smaller for the $NCCH_2Y$ than for the CH_3Y systems. This is the same pattern observed for the anions and is the result of the cyano group carrying part of the negative charge.

From a comparison of the charge distribution in the transition state with that in the anion one can calculate the imbalance parameter *n*, which is defined in eq 8. Equation 8 is the logarithmic form of eq 9 solved for *n*; δ_Y, δ_C, and χ are defined in eq 10.[32] The *n* values are

$$n = \frac{\log(\delta_Y/\chi)}{\log(\delta_C + \delta_Y)} \tag{8}$$

$$\delta_Y = \chi(\delta_C + \delta_Y)^n \tag{9}$$



(10)

summarized in Table 7. They are all significantly higher than those for the corresponding CH_3Y systems, indicating a stronger imbalance for the cyano derivatives. This finding of a stronger imbalance is consistent with the geometric measures of imbalanced discussed above. The larger imbalance may be attributed to the strong field effect of the cyano group which, because of its close proximity and its ion−dipole like interaction, strongly stabilizes the localized carbanion when that charge is close to the cyano group. This allows a disproportionately greater accumulation of the negative on the carbon in the $NCCH_2Y$ than in the CH_3Y system.

As observed for the CH_3Y systems, the proton that is being transferred carries a significant positive charge. For the $NCCH_2Y$ systems this charge is about 0.30 ± 0.03, slightly larger than the 0.275 ± 0.025 charge for the CH_3Y systems (Table 3). The slightly larger positive charge in the $NCCH_2Y$ systems may be related to the larger negative charges on the NCCH groups and provide greater electrostatic stabilization of the transition state, a point to be elaborated in the Intrinsic Barriers subsection below.

Intrinsic Barriers. Due to the symmetry of the proton-transfer reactions ($\Delta G° = \Delta H° = 0$, eqs 2 and 5), the barriers correspond to *intrinsic* barriers. These barriers,[33] which are defined as the difference in enthalpy between the transition state and the free reactants, are summarized in Table 5, while the raw energy data are in Table S2.[27] In comparing the reactions of $NCCH_2Y$ with those of CH_3Y we note that the cyano group has a barrier lowering effect. The degree by which the barriers are lowered is substantial in most cases but does not follow the regular pattern seen for the effect of the cyano group on the acidities. In fact, at the B3LYP level, the barriers for Y = NO_2, NO, and CH=S are barely affected by the presence of the cyano group. The latter results seem intuitively unreasonable and raise questions regarding the reliability of the B3LYP transition state calculations. Hence our focus will again be on the MP2/6-311+G(d,p) results.

The apparent randomness of the barrier lowering effect of the cyano group as a function of Y leads to a change

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(32) For a derivation of eq 9 see ref 22a.

(33) In previous papers[22c,d,e] we have also reported barriers calculated to include BSSE counterpoise corrections.[34] In all cases we noted that these corrections were relatively small, showed very little dependence on the Y group, and hence did not affect any of the conclusions. In view of these observations and due to the controversy as to whether at the MP2 level the counterpoise method may lead to an overcorrection,[35] we have not included such corrections in the present study.

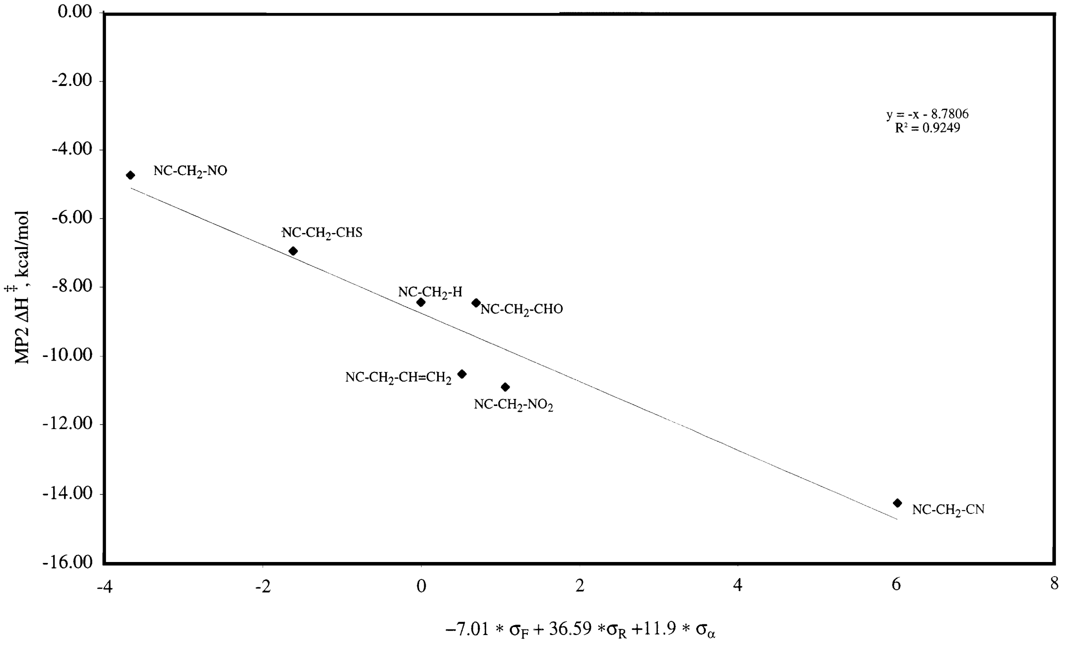

FIGURE 3. Plot of $\Delta\Delta H^{\ddagger}$ according to eq 11 (MP2).

in the order of the barriers from H(8.1) > $CH{=}CH_2$ (4.7) > $CH{=}S$ (0.3) > $CH{=}O$ (−0.3) > NO (−1.1) > NO_2 (−6.2) > CN (−8.5) for the reactions of CH_3Y, to NO (−4.7) > $CH{=}S$ (−7.0) > $CH{=}O$ (−8.4) > H (−8.5) > $CH{=}CH_2$ (−10.6) > NO_2 (−11.3) > CN (−14.3) (values in kcal/mole) for the reactions of $NCCH_2Y$. The latter order is more consistent with patterns observed in solution,[1−5] i.e., there is a better correlation between increasing barriers and increasing π-acceptor strength of the Y-group than in the CH_3Y series. For example, in the $NCCH_2Y$ systems, the two strongest π-acceptors, NO and $CH{=}S$, lead to the highest barriers while in the CH_3Y systems NO and $CH{=}S$ give rise to relatively low barriers.

The fact that the barriers are lowered indicates that the electron-withdrawing effect of the cyano group stabilizes the transition state to a greater extent than the anion. This is not unexpected. The lag in the charge delocalization into the Y-group results in placement of the center of charge closer to the cyano group at the transition state and more distant as the center of charge shifts to the Y-group in the anion. Furthermore, each $NCCH_2Y$ fragment of the transition states carries more than half a negative charge that can interact with the cyano groups (since the proton in flight bears an ca. +0.30 charge, each $NCCH_2Y$ bears an ca. −0.65 charge). Since the positive charge on the proton in flight is somewhat higher for the $NCCH_2Y$ systems than for the CH_3Y systems (Table 3), there is some extra electrostatic stabilization of the transition state of these reactions which contributes to additional lowering of the barriers for the $NCCH_2Y$ systems.

The order of the barriers is determined by the relative contributions of the field, resonance, and polarizability effects of the Y-group to the barriers. These contributions can be evaluated based on the Taft equation, eq 11, which is the analogue to eq 3 for the CH_3Y systems. Plots according to eq 11 are shown in Figure 3[31] for the MP2 calculations; a similar plot for the B3LYP calculations is shown in Figure S2.[27] The various $\rho^{\ddagger}$ values are summarized in Table 6. The following points are noteworthy.

$$\Delta\Delta H^{\ddagger} = \Delta H^{\ddagger}(\mathrm{NCCH_2Y}) - \Delta H^{\ddagger}(\mathrm{NCCH_3}) = \rho_{\mathrm{F}}^{\ddagger}\sigma_{\mathrm{F}} + \rho_{\mathrm{R}}^{\ddagger}\sigma_{\mathrm{R}} + \rho_{\alpha}^{\ddagger}\sigma_{\alpha} \quad (11)$$

(1) The negative $\rho_{\mathrm{F}}^{\ddagger}$ value (−7.01) indicates that the field effect of the Y-group is barrier lowering. This means that the field effect has a greater net stabilizing effect on the transition state than on the anion. This net effect can be quantified: transition state stabilization arises from $\rho_{\mathrm{F}}^{\circ}\sigma_{\mathrm{F}} + \rho_{\mathrm{F}}^{\ddagger}\sigma_{\mathrm{F}}$,[22d] anion stabilization from $\rho_{\mathrm{F}}^{\circ}\sigma_{\mathrm{F}}$, hence the field effect on the transition state is $(\rho_{\mathrm{F}}^{\circ}\sigma_{\mathrm{F}} + \rho_{\mathrm{F}}^{\ddagger}\sigma_{\mathrm{F}})/\rho_{\mathrm{F}}^{\circ}\sigma_{\mathrm{F}} = (\rho_{\mathrm{F}}^{\circ} + \rho_{\mathrm{F}}^{\ddagger})/\rho_{\mathrm{F}}^{\circ} = (-44.1 - 7.01)/(-44.1) = 1.17$-fold stronger than that on the anion. As discussed above for the effect of the cyano group, the greater stabilization of the transition state compared with that of the anion by the field effect of the Y-group results from the interaction with the greater negative charge on each NCCHY fragment of the transition state caused by the highly positive proton in flight. We note, however, that the degree of *enhanced* field effect stabilization of the transition state is much smaller for the $NCCH_2Y$ system than for the CH_3Y systems; in these latter systems $\rho_{\mathrm{F}}^{\ddagger} = -22.6$, $\rho_{\mathrm{F}}^{\circ} = -43.0$ and $(\rho_{\mathrm{F}}^{\circ} + \rho_{\mathrm{F}}^{\ddagger})/\rho_{\mathrm{F}}^{\circ} = (-43.0 - 22.6)/(-43.0) = 1.52$.[22d] The CH_2Y fragments of these transition states do not allow charge dispersion as extensive as the $NCCH_2Y$ fragments of the corresponding transition state.

This reduced influence of the Y-group in lowering the barrier by its field effect is a consequence of the cyano group being positioned adjacent to the α-carbon which, at the transition state, carries a larger negative charge in the $NCCH_2Y$ systems than in the CH_3Y systems. In other words, the cyano group takes over part of the role played by the Y-group. This contrasts with the fact that $\rho_{\mathrm{F}}^{\circ}$ for the *acidities* of $NCCH_2Y$ is not significantly different than ρ_F° for the acidities of CH_3Y, i.e., the field effect on the acidities of $NCCH_2Y$ and CH_3Y is quite similar.

(2) The positive $\rho_F^\ddagger$ value (36.6) indicates that the barrier is increased by the resonance effect. This does not mean that the transition state is destabilized by the resonance effect, it only means that the resonance stabilization of the transition state is weaker than that of the anion. In quantitative terms, transition state resonance stabilization is given by $\rho_R^\circ\sigma_R + \rho_R^\ddagger\sigma_R$,[22d] which gives $(\rho_R^\circ\sigma_R + \rho_R^\ddagger\sigma_R)/\rho_R^\circ\sigma_R = (\rho_R^\circ + \rho_R^\ddagger)/\rho_R^\circ = (-135 + 36.6)/(-135) = 0.73$ as the fraction of transition state stabilization relative to resonance stabilization of the anion. The relatively small resonance stabilization of the transition state is a direct consequence of the larger imbalance in the $NCCH_2Y$ systems. For the CH_3Y systems the $\rho_R^\ddagger$ value (9.81) is lower than for the $NCCH_2Y$ systems, i.e., the resonance stabilization of the transition state is only slightly less than that of the anion, with $(\rho_R^\circ + \rho_R^\ddagger)/\rho_R^\circ = (-192.5 + 9.81)/(-192.5) = 0.95$.

(3) The positive $\rho_\alpha^\ddagger$ value (11.9) implies a reduction of the barrier due to polarizability effects having a greater stabilizing influence on the transition state than on the anion.[25] As discussed previously,[22d] this factor is more effective when the charge is concentrated on the α-carbon rather than on the Y-group. The polarizability effect falls off with the fourth power of distance between the center of charge and the polarizable group.[24a] This short-range effect manifests itself at the transition state ($\rho_\alpha^\ddagger = 11.9$) but nearly vanishes as the charge moves into the Y-group ($\rho_\alpha^\circ = 0.54$). The $NCCH_2Y$ systems give a slightly larger $\rho_\alpha^\ddagger$ value due to the greater amount of charge developing on the $NCCH_2$ group compared to the CH_2 group on the CH_3Y systems.

Conclusions

(1) For a given Y-group, $NCCH_2Y$ is substantially more acidic than CH_3Y because the electron-withdrawing effect of the cyano group increases the stability of the anion by shifting part of the anionic charge to the cyano group. This is clearly evident from the calculated group charges on the anion. The resulting effects on acidity for the $NCCH_2Y$ systems are a decrease in the resonance effect (ρ_R°), virtually no effect on the field effect (ρ_F°), and a decrease in the polarizability effect (ρ_α°) of the Y-group compared to the CH_3Y systems.

(2) As is the case for the anions, the cyano group significantly changes the charge distribution at the transition state, with more charge accumulating on the NCCH group and correspondingly less charge on the Y-group. The π-bond to the Y-group, measured by the contraction of the C−Y bond length, is less developed in the $NCCH_2Y$ systems compared to the CH_3Y systems. The overall effect is an increase in the imbalance (*n* value) compared to that in the CH_3Y systems. The larger imbalance also manifests itself in a smaller degree of planarization (α) of the transition state.

(3) The intrinsic barriers for the $NCCH_2Y$ systems are lower than those for the CH_3Y systems but the barrier lowering effect of the cyano group does not correlate with the π-acceptor strength of the Y-group. This leads to a reordering of the relative intrinsic barriers with respect to the Y-group from H > $CH{=}CH_2$ > CH=S > CH=O > NO > NO_2 > CN for the CH_3Y systems to NO > CH=S > CH=O > H > $CH{=}CH_2$ > NO_2 > CN for the reactions of $NCCH_2Y$. This latter order of reactivity shows a better correlation between increasing barriers and increasing π-acceptor strength of the Y-group than is the case for CH_3Y, an order for $NCCH_2Y$ more reminiscent of solution-phase proton-transfer reactivity patterns.

(4) The barrier-lowering effect of the cyano group means that the transition state is more strongly stabilized by the cyano group than the anion. This is because at the transition state the negative charge is more concentrated on the NCCH group than on the Y-group compared to the situation with the anion. Because of the positive charge on the proton in flight, there is also more than half a negative charge on each NCCHY fragment of the transition available to interact with the cyano group.

(5) The change in the *order* of the barriers caused by the cyano group is attributed to the change in the relative contributions of the field and resonance effects to the barriers. The barrier-lowering field effect ($\rho_F^\ddagger$) is much smaller for the cyano derivatives while the barrier-enhancing resonance effect is much stronger than with the CH_3Y systems. The importance of the field effect of the Y-group in stabilizing the transition state is reduced because the cyano group takes over part of the role played by the Y-group in stabilizing the negative charge. The reduced resonance stabilization of the transition state which leads to a greater barrier-enhancing effect is the result of the larger imbalance in the $NCCH_2Y$ systems. This shift toward a greater role played by the resonance effect in determining the barrier is responsible for the change in order of the barriers.

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Supporting Information Available: Structures **S1**−**S7**, Tables S1 (charges) and S2 (energies), Figure S1 ($\Delta\Delta H^\circ$, B3LYP), and Figure S2 ($\Delta\Delta H^\ddagger$, B3LYP). This material is available free of charge via the Internet at http://pubs.acs.org.

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