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Carbanions 2. Intramolecular Interactions in Carbanions Stabilized by Carbonyl, Cyano, Isocyano, and Nitro Groups

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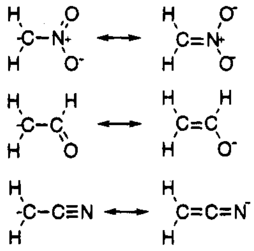
The effect of a cyano group, an isocyano group, an aldehyde group, and a nitro group on the acidity of methane, propane, and cyclopropane has been studied via ab initio geometry optimizations at the MP2/6-31+G* theoretical level. Relative energies also were calculated using the CBS-4 and G2(MP2) theoretical models. The experimental gas phase acidities are well reproduced. The effect of substituents on the parent molecules and on the anions was examined by the use of group transfer reactions. Whereas cyclopropanecarboxaldehyde and nitrocyclopropane are about 10 kcal/mol less acidic than their isopropyl counterparts, there is little difference in acidity with the nitriles and isonitriles. The rotational barriers for the anions were calculated, allowing the total stabilization energies to be partitioned into σ and π components. Charge transfer from a carbanion to a substituent was examined using the Hirshfeld charges; for the substituents the charge transfer was $NO_2 \sim CHO > CN > NC$, and for the carbanions it was $CH_3 \sim$ i-Pr > cyclopropyl.

1. Introduction

Carbanions that are stabilized by carbonyl, cyano and nitro groups have received wide use in synthesis,[1a] and some of them are important biochemical intermediates.[1b] The enhanced acidities of the parent compounds are seen in the gas phase acidities that have been determined experimentally (Table 1).[2] All of these energies are large because of the very high energy of a proton in the gas phase (366 kcal/mol). The effect of the substituent is better seen in the relative heats of ionization that are included in Table 1.

The acidity of these compounds is usually ascribed to a resonance interaction of the form:



The right hand structures are reasonable in that the negative charge is placed on an atom that is more electronegative than carbon. However, in each case, the atom directly attached to the methylene group has a partial positive charge (i.e., the carbonyl group is strongly polarized C^+-O^- and the cyano group is polarized C^+-N^-). As a result, there will be a stabilizing coulombic attraction in the left hand structures. To what extent is this important in stabilizing the carbanions? Although there is general agreement that charge transfer from the anionic carbon to oxygen is important in the nitro- and carbonyl-substituted anions, the nature of the interaction with the cyano group has been a subject of considerable controversy.[3] Attempts have been made to determine the extent of charge transfer to a cyano group using experimental methods such as ^{13}C NMR chemical shifts,[3] but in the absence of information on the tensor components of the shift, this method may prove to be unreliable. The chemical shift data, along with the results of the previous theoretical calculations,[4] do suggest that there is relatively little charge transfer. However, there is little quantitative information comparing charge transfer to the three stabilizing groups.

Table 1. Gas phase acidities, kcal/mol

compd	$\Delta H_{calc}{}^a$	$\Delta H_{obs}{}^b$	$\Delta\Delta H$
CH_4	416	416	0
CH_3-CH_3	419	420	4
cyclopropane	411	410	−6
CH_3-CN	373	372	−44
CH_3-CHO	366	365	−51
CH_3-NO_2	360	355	−61

[a] Based on G2(MP2) energies. [b] At 0K.

In order to obtain further information concerning the interaction of a carbanion with a cyano group, the corresponding isocyanides also were studied. Here, it would be possible to examine the effect of placing the more electronegative atom of the substituent adjacent to the carbanionic center.

It is known that some of these groups are much less effective in stabilizing carbanions on cyclopropane rings, and compounds such as nitrocyclopropane have a relatively small acidity[2c,5] despite the fact that cyclopropane is significantly more acidic than ethane.[2] This is commonly attributed to the energetic cost[6] of introducing a

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[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1995.

(1) (a) Trost, B. M., Ed. *Comprehensive Organic Synthesis, Vol. 3, Carbon−Carbon σ-Bond Formation*; Pergamon Press: Oxford, 1991. (b) Richard, J. P. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: New York, 1990.

(2) (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas-Phase Ion and Neutral Thermochemistry *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. (b) Kass, S. R.; Chou, P. K.; Dahlke, G. D. *J. Am. Chem. Soc.* **1993**, *115*, 315. (c) Peerboom, R. A. L.; de Koning, L. J.; Nibbering, N. M. M. *J. Am. Soc. Mass Spectrom.* **1994**, **5**, 159.

(3) For some recent NMR observations and a review of the literature concerning the stabilization of carbanions by cyano groups, cf. Abbalto, A.; Brademante, S.; Pagani, G. A. *J. Org. Chem.* **1993**, *58*, 449.

(4) Bühl, M.; Steinle, J.; Schleyer, P. v. R.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1160. Cioslowski, J.; Mixon, S. T.; Fleishmann, E. D. *J. Am. Chem. Soc.* **1991**, *113*, 4751. Gordon, M. S.; Davis, L. P.; Burggraf, L. W.; Damrauer, R. *J. Am. Chem. Soc.* **1986**, *108*, 7889. Edgecombe, K. E.; Boyd, R. J. *Can. J. Chem.* **1984**, *62*, 2887.

(5) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3113.

(6) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

0022-3263/95/1960-6327$09.00/0

trigonal center into the ring. However, in the parent acids electron deficient groups may be stabilized by a cyclopropane ring in much the same fashion as is found with the cyclopropylcarbinyl cation.[7] How important is ground state stabilization in determining the acidity of cyclopropyl derivatives?

In order to try to answer these and related questions, we have initiated a theoretical study of these compounds making use of ab initio MO theory. The energies, bond orders, and charge distributions will be examined. The simple enolate ions have been studied,[8] although generally at lower theoretical levels than used herein. Some of the cyclopropyl derivatives and anions have previously been studied by Chou, Dahlke, and Kass both experimentally and theoretically at the RHF/6-31+G* level with single point MP2/6-31+G* energies.[2b] Additional experimental data for cyclopropyl anions have very recently become available through the work of Peerboom, de Koning, and Nibbering.[2c]

2. Structures and Energies

The structures of methyl, isopropyl, and cyclopropyl derivatives were studied at the MP2/6-31+G* level that is known to satisfactorily reproduce experimental structures.[9] In order to have reliable relative energies, two recently developed model chemistries, CBS-4 and G2(MP2), were used. The CBS-4 method was developed by Ochterski, Petersson, and Montgomery[10] and is based on RHF/3-21G*-optimized geometries that are known to usually better represent experimental geometries than RHF/6-31G*.[11] It makes use of a RHF/6-311+G(3df,2p) calculation, a complete basis set extrapolation[12] applied to an MP2/6-31+G** calculation, corrections for electron correlation through MP4, and corrections for the zero-point energy and a higher level correction. In the present case, it was found that the RHF/3-21G* geometries for the nitro anions were not satisfactory,[13] and for these anions the CBS-4 energies were calculated using the MP2/6-31+G* geometries. The G2(MP2) method was developed by Curtiss, Raghavachari, and Pople[14] and gives essentially the same results as the computationally more demanding G2 model.[15] With the present compounds, when both G2 and G2(MP2) energies were available, the differences between calculated energy changes were on the order of 0.2–0.3 kcal/mol. G2(MP2) is effectively QCISD(T)/6-311+G(3df,2p) with correction for the zero point energy and a higher order correction. In the reactions to be considered in this report, the higher level corrections will in all cases cancel. Since we are concerned with anions, the G2(MP2) energies were obtained using MP2/6-31+G* geometries rather than the usual MP2/6-31G*.

With a fairly large set of test organic compounds, the CBS-4 method reproduces the heats of formation to ±2.0 kcal/mol[16] and G2(MP2) reproduces them to ±1.6 kcal/mol.[14] The use of both of these methods for the present calculations presents another opportunity to compare them.

The calculated energies are summarized in Table 2, and the bond lengths are given in Table 3. With the cyclopropyl derivatives, there is an important difference between the rotamers for the aldehyde and nitro derivative. As noted above, in the precursor molecules, the atom attached to the ring bears a positive charge. Therefore, it might interact with the ring in the fashion of cyclopropylcarbinyl cations, leading to some stabilization. It has been shown experimentally that cyclopropanecarboxaldehyde prefers the conformer in which the aldehyde group is perpendicular to the ring.[17] The two conformers of cyclopropanecarboxaldehyde with the carbonyl group either syn or anti with respect to the adjacent CH bond were calculated to differ in energy by less than 0.4 kcal/mol with the syn form favored, and the rotational barrier was 5.7 kcal/mol. Experimentally, the syn form was found to be the more stable by 0.9 kcal/mol, and the rotational barrier from the syn form was found by NMR spectroscopy to be 6.0 ± 0.2 kcal/mol in $CHClF_2/CHCl_2F/CF_2Cl_2$ solution.[18] In the case of nitrocyclopropane, the nitro group is perpendicular to the ring, and the calculated rotational barrier is 2.9 kcal/mol. The experimental barrier is 3.1 ± 1.4 kcal/mol.[19]

The conformational preference for the corresponding anions is opposite to the precursors. Thus, in each case the preferred conformation of the anion has its lone pair perpendicular to the NO_2 or CHO group in order to achieve the best interaction with the empty orbital of the substituent. The rotational barriers were calculated at the MP2/6-31+G* level, and they were found to be 14.2 kcal/mol for the anion derived from cyclopropanecarboxaldehyde and 14.8 kcal/mol for the anion from nitrocyclopropane. These values may be compared with the calculated rotational barriers for the anions derived from isobutyraldehyde (33.8 kcal/mol) and 2-nitropropane (33.7 kcal/mol).

The bond length changes on going from the parent acids to their anions are informative (Table 3). Charge transfer from the carbanion center to the substituent should lead to a decrease in the C–X bond length with the development of double bond character and an increase in the bond lengths in the substituent groups. With the nitriles, the C–CN bond shortens by 0.06–0.07 Å for acetonitrile and isobutyronitrile (0.03 Å for cyclopropyl cyanide), and the C≡N bond lengthens by 0.02 Å. These changes are smaller than those for the aldehydes and nitro compounds by a factor of 2. It is interesting to note that the C–X bond lengths in the cyclopropyl derivatives are shorter than those in the methyl or

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[7] Schleyer, P. v. R.; Van Dine, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 2321. Rhodes, Y. E.; Difate, V. G. *J. Am. Chem. Soc.* **1972**, *94*, 7582.

[8] Wiberg, K. B.; Breneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61. Mendez, F.; Gazquez, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 9298.

[9] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley: New York, 1986.

[10] Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.*, submitted.

[11] Reference 9, pp 174–175.

[12] Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081. Petersson, G. A.; Tensfeldt, T. G.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1991**, *94*, 6091.

[13] The 3-21G optimization gave for the nitromethane anion: r(C–N) = 1.294 Å and r(N–O) = 1.346 Å whereas MP2/6-31+G* gave r(C–N) = 1.348 Å and r(N–O) = 1.293 Å. The MP2 geometries are reasonable in comparison with that of nitromethane whereas the 3-21G geometries are not. The same trend was found with 2-nitropropane and nitrocyclohexane.

[14] Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

[15] Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

[16] Ochterski, J.; Petersson, G.; Wiberg, K. B. *J. Am. Chem. Soc.* submitted.

[17] Volltrauer, H. N.; Schwendeman, R. H. *J. Chem. Phys.* **1971**, *54*, 260.

[18] Pawar, D.; Noe, E. Jackson State University, private communication. An earlier measurement by microwave spectroscopy gave 4.4 ± 0.4 kcal/mol (ref 17).

[19] Boggs, J. E.; Britt, C. O.; Mochel, A. R. *J. Chem. Phys.* **1973**, *58*, 3221.

Table 2. Calculated Energies[a]

compound	ZPE	MP2(fc)/ 6-31+G*	CBS-4	G2(MP2)	ΔH_f, calc, 25 °C		ΔH_f obsd, 25 °C[b]
					CBS-4	G2(MP2)	
a. precursor molecules							
methane	26.7	−40.334 08	−40.428 21	−40.409 66	−18.6	−18.1	−17.8 ± 0.1
ethane	44.7	−79.497 60	−79.661 19	−79.628 93	−22.1	−19.9	−20.0 ± 0.1
acetonitrile	27.4	−132.345 36	−132.545 41	−132.519 83	19.4	18.5	17.6 ± 0.2
methyl isocyanide	27.3	−132.034 85	−132.510 54	−132.483 34	41.5	41.6	41.3 ± 0.2
acetaldehyde	33.6	−153.358 01	−153.609 59	−153.572 96	−41.2	−41.1	−39.7 ± 0.1
nitromethane	30.6	−244.351 76	−244.716 82	−244.672 16	−17.9	−21.4	−17.8 ± 0.1
propane	62.0	−118.664 88	−118.898 77	−118.853 06	−28.2	−24.5	−25.7 ± 0.1
isobutyronitrile	61.7	−210.682 70	−211.023 56		5.5		5.6 ± 0.3
isopropyl isocyanide	61.4	−210.646 96	−210.996 27		24.9		
isobutyraldehyde, gs	67.9	−231.694 49	−232.087 46		−54.5		−51.6 ± 0.2
isobutyraldehyde, TS	67.7	−231.692 98	−232.085 72				
2-nitropropane, gs	64.8	−322.696 86	−323.203 56		−36.2		−33.2 ± 0.2
2-nitropropane, TS	64.7	−322.694 34	−323.199 87				
cyclopropane	48.9	−117.455 12	−117.673 69	−117.628 91	6.9	14.2	12.7 ± 0.2
cyclopropyl cyanide	48.7	−209.472 95	−209.797 06		41.2		43.5 ± 0.3
cyclopropyl isocyanide	48.2	−209.431 95	−209.767 40		60.1		
cyclopropanecarboxaldehyde	55.0	−230.490 20	−230.867 43		−22.7		
cyclopropanecarboxaldehyde	55.1	−230.490 81	−230.867 04		−22.5		
cyclopropanecarboxaldehyde,TS	54.7	−230.480 81	−230.858 33				
nitrocyclopropane, gs	51.7	−321.483 48	−321.973 82	−321.90364	1.3	3.6	
nitrocyclopropane, TS	51.4	−321.475 49	−321.969 24				
b. anions							
CH_3	17.0	−39.654 43	−39.762 07	−39.746 57			
C_2H_5	34.6	−78.812 94	−78.991 52	−78.962 01			
CH_2CN	18.1	−131.736 74	−131.951 05	−131.925 14			
CH_2NC	18.2	−131.683 27	−131.898 02	−131.873 80			
CH_2CHO (gs)	25.4	−152.764 74	−153.024 48	−152.989 39			
CH_2CHO (TS)	23.6	−152.704 41	−152.971 61	−152.935 05			
CH_2NO_2 (gs)	22.1	−243.772 68	−244.149 10	−244.099 05			
CH_2NO_2 (TS)	21.2	−243.721 67	−244.102 17	−244.056 81			
Me_2CH	51.5	−117.983 77	−118.233 05	−118.189 74			
Me_2CCN	52.2	−210.069 60	−210.423 64				
Me_2CNC	51.9	−210.025 76	−210.382 38				
Me_2CCHO, gs	59.2	−231.103 36	−231.508 06				
Me_2CCHO, TS	57.7	−231.047 10	−231.452 57				
Me_2CNO_2, gs	55.6	−322.116 37	−322.632 99				
Me_2CNO_2, TS	55.0	−322.062 12	−322.579 31				
C_3H_5	38.9	−116.781 67	−117.015 86	−116.973 39			
C_3H_4CN	39.9	−208.861 06	−209.199 17				
C_3H_4NC	39.2	−208.817 15	−209.15978				
C_3H_4CHO, gs	46.1	−229.879 07	−230.266 81				
C_3H_4CHO, TS	45.5	−229.853 76	−230.244 10				
$C_3H_4NO_2$, gs	42.7	−320.887 83	−321.381 79	−321.316 64			
$C_3H_4NO_2$, TS	42.4	−320.864 79	−321.366 32				

[a] The total energies are given in Hartrees, and the heats of formation and zero-point energies are given in kcal/mol. The zero-point energies were derived from HF/6-31G* calculations using a scaling factor of 0.893. [b] The observed heats of formation were taken from: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986. For acetonitrile and methyl isonitrile they were taken from: Baghal-Vayjooee, M. H.; Collister, J. L.; Pritchard, H. O. *Can. J. Chem.* **1977**, *55*, 2634.

isopropyl derivatives corresponding to the higher *s* character of the cyclopropyl−X bonds.

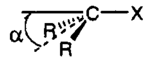
With the isocyanides, the C−NC bond shortens by 0.02−0.04 Å for the methyl and isopropyl derivatives on going to the anions, but there is no significant change for cyclopropyl isocyanide. The N=C length increases by only 0.01 Å. The changes in bond lengths are significantly smaller than for the other compounds.

With the aldehydes, the C−CHO bond shortens by 0.12 Å on going to their anions (0.08 Å for cyclopropanecarboxaldehyde) and the C=O bond lengthens by 0.06 Å. Rotation to the anion transition state leads to lengths that approach those of the parent acids, but the C−C bond remains somewhat smaller. This suggests a stabilizing coulombic interaction between the positively charged carbon of the aldehyde group and the negatively charged carbanionic center in the transition state structures.

In the case of the nitro compounds, formation of the anion leads to a 0.15 Å (0.1 Å for nitrocyclopropane) decrease in the C−N bond length and a 0.04−0.05 Å increase in the N−O length. Here, rotation to the anion transition state leads to C−N lengths that are greater in the anion than in the parent nitro compound, suggesting a repulsive interaction between the carbanionic center and the oxygens of the nitro group.

The changes in bond length imply that there is extensive charge transfer from the carbanionic carbon to the substituent via a π interaction with the aldehydes and nitro compounds, to a smaller extent with the nitriles, and least with the isonitriles. In all cases, the structural changes found with the cyclopropyl derivatives were significantly smaller than with the other compounds.

The pyramidalization of the carbanion center was of interest since one might expect a maximum π interaction when it is planar. The angle, α, is defined as follows:



where the solid line is the projection of the C−X bond

Table 3. Structural data, MP2/6-31+G*

compd	bond	neutral	anion	diff	anion TS[a]
ethane	C−C	1.528	1.532	+0.004	
propane	C−C	1.527	1.516	−0.011	
cyclopropane	C−C	1.506	1.524	+0.018	
	C−C	1.506	1.606	+0.103	
acetonitrile	C−C	1.464	1.401	−0.063	
	C≡N	1.181	1.203	+0.022	
isobutyronitrile	C2−C(≡N)	1.471	1.399	−0.072	
	C1−C2	1.533	1.510	−0.023	
	C≡N	1.183	1.205	+0.022	
cyclopropyl cyanide	C1−C(≡N)	1.442	1.408	−0.034	
	C1−C2	1.517	1.517	0.000	
	C2−C3	1.497	1.510	+0.013	
	C≡N	1.184	1.201	+0.017	
acetaldehyde	C−C	1.502	1.387	−0.115	1.474 (1.482)
	C=O	1.227	1.285	+0.058	1.244 (1.252)
isobutyraldehyde	C2−C(=O)	1.506	1.387	−0.119	1.468
	C1−C2	1.532	1.499	−0.033	1.520
	C=O	1.228	1.293	+0.065	1.239
cyclopropanecarboxaldehyde	C1−C(=O)	1.473	1.389	−0.084	1.456 (1.468)
	C1−C2	1.520	1.477	−0.043	1.541 (1.554)
	C2−C3	1.490	1.545	+0.055	1.487 (1.481)
	C=O	1.229	1.282	+0.053	1.243 (1.255)
nitromethane	C−N	1.490	1.348	−0.142	1.506
	N−O	1.244	1.293	+0.049	1.266 (1.255)
2-nitropropane	C−N	1.506	1.351	−0.155	1.507
	C−C	1.521	1.493	−0.028	1.524
	N−O	1.245	1.299	+0.054	1.264 (1.255)
nitrocyclopropane	C−N	1.465	1.370	−0.095	1.482
	C1−C2	1.504	1.475	−0.029	1.545
	C2−C3	1.500	1.543	+0.043	1.489
	N−O	1.245	1.285	+0.040	1.267
methyl isocyanide	C−N	1.428	1.404	−0.024	
	N=C	1.188	1.200	+0.012	
isopropyl isocyanide	C2−N	1.438	1.393	−0.045	
	C1−C2	1.525	1.513	−0.012	
	N=C	1.190	1.203	+0.013	
cyclopropyl isocyanide	C1−N	1.405	1.404	−0.001	
	C1−C2	1.507	1.524	+0.017	
	C2−C3	1.505	1.510	+0.005	
	N=C	1.190	1.200	+0.010	

[a] The values in parentheses are for the oxygen that is cis to the lone pair.

Table 4. Pyramidalization Angles for the Anions

anion	α	ΔE_{inv} (kcal/mol)
$CH_3CH_2^-$	51.3	3.3
CH_2NC^-	52.7	2.5
CH_2CN^-	33.6	0.15
$CH_2NO_2^-$	0.0	
CH_2CHO^-	0.0	
Me_2CH^-	55.1	6.4
Me_2CNC^-	54.4	8.6
Me_2CCN^-	39.3	2.3
$Me_2CNO_2^-$	17.6	0.03
Me_2CCHO^-	0.5	
$C_3H_5^-$	78.7	15.1
$C_3H_4NC^-$	66.2	20.3
$C_3H_4CN^-$	60.0	8.8
$C_3H_4NO_2^-$	50.9	5.9
$C_3H_4CHO^-$	30.0	0.7

and the dashed line is the bisector of the RCR group. It will be zero for a planar ion. The values of α are given in Table 4. Ethyl and isopropyl anions are strongly pyramidalized (α = 50−55°), and an even larger angle is found with cyclopropyl anion (79°). The anions from acetaldehyde and nitromethane are planar, but that from acetonitrile is pyramidal (34°). The inversion barrier was calculated and found to be only 0.15 kcal/mol, indicating no significant energy difference between the planar and pyramidal forms. The anions derived from the isocyanides are pyramidalized to about the same extent as the hydrocarbon anions, and they also have comparable inversion barriers.

The inversion barriers increase on going from ethyl to isopropyl and cyclopropyl anions, and the inversion barriers and pyramidalization angles for their derivatives increase in a corresponding fashion.[20] The larger barriers for the cyclopropyl derivatives are expected since angle strain should increase on going to the planar anions, and it is known that cyclopropyl anions have a relatively high configurational stability.[21]

The heats of formation of many of the compounds are known, and they are recorded in Table 2. The ΔH_f calculated from the CBS-4 and G2(MP2) energies, after correction to 25 °C, also are given in Table 2. The root mean square (rms) error for the CBS-4 derived energies is 2.5 kcal/mol (12 compounds) and that for G2(MP2) is 1.6 kcal/mol (eight compounds). The CBS-4 method has difficulty with cyclopropane, whereas G2(MP2) has difficulty with nitromethane.[22] If these two problem cases were eliminated, the rms errors would be reduced to 1.9 and 1.0 kcal/mol, respectively.

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(20) The pyramidalization angles for a variety of cyclopropyl derivatives have been examined (ref 2b,c).

(21) Walborsky, H. M. et al. *J. Am. Chem. Soc.* **1964**, *86*, 3283. Walborsky, H. M.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3288.

(22) It has been suggested that the ground state of nitromethane requires the use of a multireference determinant: Kaufman, J. J.; Hariharan, P. C.; Chabalowski, C.; Hotokke, M. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1985**, *19*, 221. However, it is likely that this is an artifact resulting from the use of a small basis set since a CBS-Q calculation which employs a much larger basis set and electron correlation through the QCISD(T) level with a single determinant reference reproduces the experimental heat of formation of nitromethane to within 1.5 kcal/mol (ref 16).

Table 5. Calculated gas phase acidities, 0K, kcal/mol

compd	MP2/6-31+G*	CBS-4	G2(MP2)	obsd	
				0K	298 K
methane	416.8	418.0	416.1	416	417 ± 2
ethane	419.5	420.2	418.5	420	421 ± 3
methyl isocyanide	380.1	384.4	382.5		
acetonitrile	373.5	373.0	373.2	372	373 ± 3
acetaldehyde	364.1	367.2	366.2	365	366 ± 3
nitromethane	354.9	356.3[b]	359.6	355	356 ± 3
propane	416.9	417.7	416.2	418	419 ± 2
isopropyl isocyanide	380.4	385.2			
isobutyronitrile	375.2	376.5		374	375 ± 3
isobutyraldehyde	362.2	363.6		365[a]	366 ± 4[a]
2-nitropropane	355.1	358.0[b]		355	356 ± 3
cyclopropane	412.6	412.8	411.3	411	412 ± 2
cyclopropyl isocyanide	376.9	381.3			
cyclopropyl cyanide	375.2	375.2		374	375 ± 3
cyclopropanecarboxaldehyde	375.0	376.9		374	375 ± 2
nitrocyclopropane	364.8	371.5[b]	368.3	365	366 ± 1

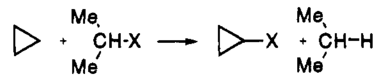
[a] Estimated value, see text. [b] The MP2/6-31+G* geometries were used for these calculations; see text.

It should be noted that the errors associated with the calculation of heats of formation will in most cases cancel when isodesmic reactions are considered, and it is the latter energies that will be the main focus of this report. The gas phase acidities that may be calculated from the energies of the parent acids and their anions provide a test of the ab initio calculations (Table 5). It can be seen that the deviations between the calculated and observed acidities are small in all cases, and average 1−2 kcal/mol, well within the stated uncertainties of the experimental data. This suggests that the relative error in the gas phase acidities may be less than the stated uncertainties (~2−3 kcal/mol). The accuracy of the MP2/6-31+G* calculations for the present series of compounds is also worth noting.

It appears that the gas phase acidities of isonitriles have not been determined experimentally. The data in Table 5 indicate that they are 6−10 kcal/mol less acidic than the corresponding nitriles. They are nevertheless over 30 kcal/mol more acidic than the parent hydrocarbons.

3. Energy Changes

One of the best ways in which to examine relative energies is via group transfer reactions. The possibility of stabilization of the cyclopropane ring may be explored by the reaction with the corresponding isopropyl derivative:



The energy changes for the reaction are summarized in Table 6. It can be seen that the cyano group does not have a significant preference between propane and cyclopropane. An aldehyde group prefers to be attached to a cyclopropane ring by 3 kcal/mol, and this presumably involves a stabilizing interaction between the electron deficient carbon of the carbonyl group and the cyclopropane ring. The reverse is found with a nitro group. Here, it prefers a 2-propyl group to cyclopropyl by 3 kcal/mol. This is reasonable if the main attribute of the nitro group is its inductive effect. It would then prefer an sp^3 orbital as offered by a 2-propyl group to the sp^2 orbital offered by the cyclopropyl ring. The same reversed preference is found with the isonitrile group, probably for the same reason.

Table 6. Energy Changes for Group Transfer Reactions, kcal/mol

substituent	MP2/6-31+G*	CBS-4
a. precursor molecules		
$(CH_3)_2CH_2 + C_3H_5X \rightarrow (CH_3)_2CHX + C_3H_6$		
CN	−0.1	−0.9
NC	−3.2	−2.4
CHO	+3.6	+3.2
NO_2	−2.2	−2.8
b. anions		
$(CH_3)_2CH_2 + C_3H_4X^- \rightarrow (CH_3)_2CX^- + C_3H_6$		
CN	0.0	0.4
NC	0.3	1.6
CHO	−9.1	−10.1
NO_2	−12.0	−16.4
c. proton exchange		
$(CH_3)_2CX^- + C_3H_5X \rightarrow (CH_3)_2CHX + C_3H_4X^-$		
CN	−0.1	−1.3
NC	−3.5	−3.9
CHO	+12.7	+13.3
NO_2	+9.7	+13.5

This type of reaction may also be used to examine the corresponding anions, and these data also are included in Table 6. Again, a cyano group does not have a significant preference between propyl and cyclopropyl, and the same is found with the isonitrile group. With both an aldehyde group and a nitro group, the substituted 2-propyl anion is preferred to the substituted cyclopropyl anion by about 10−15 kcal/mol, again suggesting less charge transfer in the latter case. It may be noted that there is a significant difference between the MP2 and CBS-4 anion group transfer energies for the nitro compounds. Throughout this study, the nitro compounds lead to larger deviations in energies than found with either the nitriles or aldehydes.

The other way of examining the interactions is to consider just the proton transfer to convert a substituted 2-propyl anion to the corresponding cyclopropyl anion (Table 6c). Again, no significant effect of a cyano group is found, and only a small effect is found with the isonitrile group. However, the 2-propyl anions are preferred when an aldehyde or nitro group is the substituent.

Further information about the interactions in the anions may be obtained by examining the rotational barriers for the C−X bonds (Table 7). The barriers give the energies associated with the π stabilization of the carbon centered anion by the substituent X. It is larger for the aldehyde enolates than for the nitro compounds, and for a given substituent it is much smaller for the

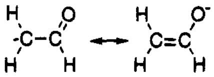
Table 7. Calculated rotational barriers

anion	MP2	CBS-4	G2(MP2)
CH_2CHO^-	36.1	33.2	34.1
Me_2CCHO^-	33.8	34.8	
$C_3H_4CHO^-$	14.2	14.3	
$CH_2NO_2^-$	32.9	29.5	26.5
$Me_2CNO_2^-$	34.6	33.7	
$C_3H_4NO_2^-$	14.8	9.7	

Table 8. σ and π Components of the Substituent Effect on Gas Phase Acidities, kcal/mol

compd	s	p	total
CH_3CHO	17	34	51
Me_2CHCHO	20	34	54
C_3H_5CHO	23	14	37
CH_3NO_2	33	28	61
Me_2CHNO_2	28	34	62
$C_3H_5NO_2$	31	14	45

cyclopropyl compounds than for the corresponding isopropyl derivatives. This suggests a markedly reduced double bond character in the bond between the cyclopropyl anion and the substituent. It is important to note that the rotational barriers should not be equated with resonance stabilization in these cases. The "resonance energy" of acetaldehyde enolate is the difference in energy between the ion and the more stable of the canonical structures below, which has the negative charge at the more electronegative oxygen:



Rotation about the C−C bond will force the negative charge to move to the less electronegative carbon, as in the left hand higher energy canonical structure, and will lead to a marked increase in energy.

The total effect of a substituent may be taken as the difference in acidity between the parent hydrocarbon (methane, propane, or cyclopropane) and the substituted derivative. The effect could be separated into σ and π terms for the anions derived from the aldehydes and nitro compounds by assigning the rotational barriers as the π term (Table 8). The π term is about the same for aldehydes and nitro compounds, and the difference between them results from the larger σ term for the nitro compounds.

4. Group Charges and Bond Orders

The data presented above suggests that there is a significant difference in double bond character between the anions derived from isopropyl derivatives vs cyclopropyl derivatives. In order to gain information on the bond orders, we calculated them using the method developed by Cioslowski and Mixon,[23] which is based on Bader's theory of atoms in molecules (AIM).[24] The data are shown in Table 9.

A comparison of the bond orders for the neutral compounds and the rotated anions (transition states) shows that there is not much change, indicating that the rotational transition states are well localized. On going from the acids to their conjugated anions in the methyl and isopropyl series, the C−X bond orders increase by about 0.15 when X = NC, by about 0.4 when X = CN, by about 0.6 when X = CHO, and by about 0.7 when X = NO_2. Smaller increases in bond orders are found with the cyclopropyl derivatives, but the trends were similar.

Table 9. Bond Orders

			anion	
compd	bond	neutral	gs	TS
ethane	C−C	1.021	1.093	
acetonitrile	C≡N	2.260	2.124	
	C−C	1.034	1.433	
methyl isocyanide	N≡C	1.838	2.006	
	C−N	0.854	1.013	
acetaldehyde	C−C	1.009	1.642	1.141
	C=O	1.401	1.191	1.348
nitromethane	N−O	1.834	1.464	1.810
	N−O[a]	1.834	1.464	1.749
	C−N	0.836	1.585	0.846
propane	C−C	1.001	1.075	
isobutyronitrile	C≡N	2.239	2.114	
	C1−C2	0.983	1.349	
	C2−C3	0.967	1.022	
isopropyl isocyanide	N≡C	1.838	1.970	
	C−C	0.959	0.991	
	C−N	0.798	0.941	
isobutyraldehyde	C1−C2	0.968	1.614	1.065
	C2−C3	0.973	1.034	1.013
	C=O	1.391	1.151	1.345
2-nitropropane	C−N	0.788	1.509	0.786
	C−C	0.968	0.989	0.999
	N−O	1.826	1.401	1.805
	N−O[a]	1.815	1.401	1.749
cyclopropane	C−C	1.003	1.045	
	C−C[b]	1.003	0.940	
cyclopropyl cyanide	C≡N	2.248	2.137	
	C1−C(≡N)	1.041	1.239	
	C1−C2	0.955	0.966	
	C2−C3	1.000	1.000	
cyclopropyl isocyanide	N≡C	1.791	1.945	
	C1−N	1.045	1.082	
	C1−C2	0.937	0.933	
	C2−C3	0.990	0.996	
cyclopropanecarboxaldehyde	C=O	1.382	1.219	1.323
	C1−C(=O)	1.021	1.545	1.104
	C1−C2	0.951	1.026	0.945
	C2−C3	1.013	0.964	1.030
nitrocyclopropane	N−O	1.832	1.596	1.774
	N−O[a]	1.807	1.596	1.695
	C1−N	0.846	1.403	0.964
	C1−C2	0.950	0.974	0.919
	C2−C3	0.994	0.958	1.026

[a] Oxygen that is cis to the lone pair. [b] Carbons not at the anionic site

Are the changes in bond lengths noted in Table 2 correlated with the changes in bond orders? This is examined in Figure 1. The solid circles represent the C−C bonds of the nitriles and aldehydes, and there is a good correlation with $r^2 = 0.96$. The line represents the best fit to the C−C bond data. The open circles give the corresponding changes for the C=O and C≡N bonds, the squares give the changes for the C−N bonds of the isonitriles, and the triangles give the changes for the C−N bonds of the nitro compounds. It can be seen that all of these data are reasonably well fit by the correlation line. This indicates that the changes in the above bond orders are meaningful quantities.

Another related question of interest is the extent of charge transfer from the carbanionic site to the substituent. In order to examine this question, we have made use of the Hirshfeld charges.[25] They are defined in terms of a set of spherically symmetrical proatoms that are

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[23] Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991,** *113,* 4142.

[24] Bader, R. F. W. *Atoms in Molecules. A Quantum Theory;* Clarendon Press: Oxford, 1990.

[25] Hirshfeld, F. L. *Theor. Chim. Acta* **1977,** *44* , 129.

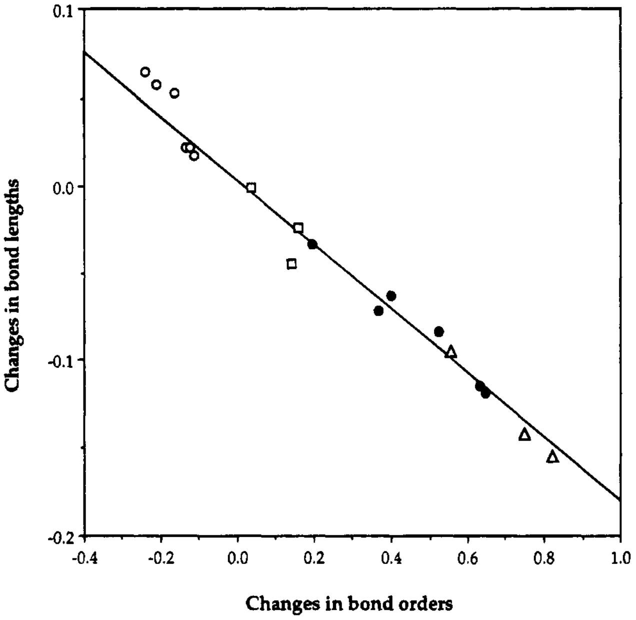

Figure 1. Relationship between the changes in bond lengths and the changes in bond orders for the bonds to carbon at the reaction site in the conversion of aldehydes, nitriles and isonitriles to their anions. The closed circles are for the C–C bonds, the open circles are for the C=O and C≡N bonds of the aldehydes and nitriles, the squares are for the C–N bonds of the isonitriles and the triangles are for the C–N bonds of the nitro compounds. The line is the best fit to only the changes for the C–C bonds.

Table 10. Charge Shifts to Individual Atoms of the Substituent Groups Based on Hirshfeld Charges[a]

	Compound		
atom	methyl	isopropyl	cyclopropyl
a. isonitriles[b]			
N	−0.048	−0.035	−0.029
C	−0.258	−0.231	−0.214
total	−0.306	−0.266	−0.243
b. nitriles			
C	−0.136	−0.109	−0.085
N	−0.248	−0.223	−0.194
total	−0.384	−0.332	−0.279
c. aldehydes			
C	−0.192	−0.189	−0.158
O	−0.277	−0.278	−0.238
H	−0.081	−0.075	−0.074
total	−0.550	−0.542	−0.470
c. nitroalkanes			
N	−0.095	−0.099	−0.080
O1	−0.257	−0.245	−0.200
O2	−0.257	−0.251	−0.206
total	−0.609	−0.595	−0.486

[a] In each case, the atoms gain electron density on going from the parent to the anion. [b] Charge shifts are given for the formation of the pyramidal anion.

placed at the locations of the atoms in the molecule in question. At any point in space, the charge density is calculated for the molecule and for each of the proatoms. The molecule's charge density is the apportioned among the atoms in proportion to their proatom's contribution. In this way, the electron populations are calculated for atoms with fixed sizes. This avoids questions about the volume element used to define a given atom.

The calculated charge shifts to the atoms of the substituent groups are summarized in Table 10. Large and comparable shifts are found with the aldehydes and nitro compounds, but with the cyano derivatives, the shift is only about 60% as large and with the isonitriles it is even smaller. It is interesting that the main recipient of the charge transfer is the terminal atom of the substituent even for the isonitriles where the carbon is less electronegative than the nitrogen. The shifts are about the same for the methyl and isopropyl derivatives, but are significantly smaller for the cyclopropyl derivatives (80–85% as large). This is in good accord with the larger pyramidalization angles found with these anions.

Table 11. Sigma-Pi Separation for Hirshfeld Electron Populations

		neutral		anion		shift[b]	
compd	atom[a]	σ	π	σ	π	σ	π
CH_3CN	N	6.151	1.106	6.182	1.323	+0.031	+0.217
	C	4.962	0.933	4.934	1.096	−0.028	+0.163
	C	4.971	1.018	5.044	1.291	+0.073	+0.273
	H	0.639	0.315	0.920	0.145	0.281	−0.170
	H	0.639	0.315	0.920	0.145	0.281	−0.170
	H	0.639	0.315			−0.639	−0.315
	total	18.001	4.002	18.000	4.000	−0.001	−0.002
CH_3NC[c]	C	5.411	0.719	5.443	0.973	0.030	0.254
	N	5.817	1.274	5.787	1.357	−0.030	0.083
	C	4.869	1.051	4.942	1.364	0.073	0.313
	H	0.634	0.319	0.914	0.153	0.280	−0.166
	H	0.634	0.319	0.914	0.153	0.280	−0.166
	H	0.634	0.319			−0.634	−0.319
	total	17.999	4.001	18.000	4.000	0.001	−0.001
CH_3CHO	C	5.063	0.747	5.017	0.984	−0.046	+0.238
	O	6.996	1.272	6.975	1.569	−0.021	+0.298
	H	0.936	0.046	0.993	0.070	+0.057	+0.024
	C	5.041	0.990	5.127	1.143	+0.086	+0.153
	H	0.906	0.067			−0.906	−0.067
	H	0.529	0.440	0.946	0.119	+0.416	−0.321
	H	0.529	0.440	0.942	0.115	+0.413	−0.325
	sum	20.000	4.002	20.000	4.000	−0.001	0.000
CH_3NO_2	N	5.524	1.263	5.508	1.373	−0.016	0.111
	O	6.806	1.398	6.822	1.639	0.016	0.241
	O	6.806	1.398	6.822	1.639	0.016	0.241
	C	4.935	1.012	5.017	1.134	0.082	0.122
	H	0.371	0.580			−0.371	−0.580
	H	0.781	0.175	0.916	0.108	0.137	−0.067
	H	0.781	0.175	0.916	0.108	0.137	−0.067
	sum	26.004	6.001	26.001	6.001	0.001	0.001

[a] The atoms are listed from right to left in the given formulas. [b] A positive sign indicates a gain in electron population on going from the parent to the anion. The large σ/π shift for the hydrogens results from the hydrogens moving into the plane in the anions, thereby losing their out-of-plane π contribution. [c] Populations are given for the planar anion in order to be able to carry out the σ/π separation.

The interpretation of these data would be assisted by a separation of the shifts into σ and π components. This is readily effected for the methyl derivatives since the anions derived from acetaldehyde and nitromethane are planar, and the planar anion from acetonitrile has an energy only slightly higher than the pyramidal form, and so the former may be used for the analysis. Although the inversion barrier for the anion from methyl isocyanide is somewhat larger, it still seemed reasonable to examine the planar form in order to separate the two terms. The components of the Hirshfeld charges are shown in Table 11.

With acetonitrile, there is no net σ shift to the cyano group, and the full 0.38 e shift is found in the π system. The isocyanides behave in the same fashion. The charge shifts for acetaldehyde and nitromethane also are essentially all in the π-systems. Thus, in this conservative view where the relative sizes of the atoms are not allowed to change on converting the parent compounds to their anions, the entire charge shift is found in the π system. If the atomic boundaries were allowed to shift in accord with changing electronegativity of the atoms, as in the atoms in molecules approach,[24] charge shifts would also be seen in the σ systems since the more electronegative atoms would occupy larger volume elements.[26]

Conclusions. The changes in bond lengths and bond orders, along with the charge shifts, present a consistent picture of the intramolecular changes that occur on converting the parent compounds to their anions. There is a relatively large degree of charge transfer from the carbanionic center to either a carbonyl or nitro group (~0.6 e). Although not in accord with previous studies of nitriles, it is now clear that whereas the charge shifts are smaller than for aldehydes and nitro compounds, they are still fairly large (~0.4 e). The isonitriles give a somewhat smaller charge shift (~0.3 e).

The cyclopropyl derivatives are different than the other compounds in that the changes in the above quantities are somewhat smaller, corresponding to less charge transfer and less double bond character in the anions. Despite the somewhat smaller charge transfer in the anion of cyclopropyl cyanide as compared to the ion of isobutyronitrile, it is interesting to note that the two nitriles have essentially the same acidity. This is in contrast to the aldehyde and nitro derivatives for which the cyclopropyl compounds are about 10 kcal/mol less acidic than the methyl or isopropyl compounds.

An examination of deformation density plots for the substituted cyclopropyl anions[27] showed that the anions from cyclopropane and cyclopropyl cyanide have well-developed lone pairs, whereas with nitrocyclopropane and cyclopropane carboxaldehyde the lone pairs are diminished and connected with the substituent orbitals. Thus, part of the acidity of cyclopropyl cyanide may be due to the inherent higher acidity of the cyclopropyl hydrogens, whereas this is lost when there is a stronger interaction between the lone pair and the substituent, and greater double bond character. The isonitriles were included in this study since, if the above explanation is correct, they also should lead to relatively small changes in acidity on going from methyl or isopropyl to cyclopropyl as the group to which it is attached. This was found to be the case.

Calculations

The ab initio calculations were carried out using Gaussian 92.[28] The bond orders were calculated using PROAIM[29] and BONDER.[23] The Hirshfeld charges were obtained using HIRSH.[30]

Acknowledgment. This investigation was supported by a grant from the National Science Foundation.

Supporting Information Available: Tables of MP2/6-31+G* structural data in z-matrix format and deformation density plots for cyclopropyl anions (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS; see any current masthead page for ordering information.

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[26] Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* **1994**, *14*, 1504.

[27] These plots are available as supporting information.

[28] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 92, Revision A, Gaussian, Inc., Pittsburgh PA, 1992.

[29] Biegler-König, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1982**, *3*, 317.

[30] Rablen, P. Yale University.