to P_σ within the VP scheme). The conclusions derived from the empirical analysis reported at the beginning of this section, therefore, have a sounder physical basis.

The changes in VP nitrogen charges following deprotonation agree perfectly with the observed charge redistributions. QTAM allows one to investigate quantitatively these mechanisms, providing also a self-explanatory chemical description of them. Deprotonation of a planar tricoordinated nitrogen increases its σ charge, thereby allowing an efficient release of its π charge to the π-conjugated ring system. So the "increase in σ electron density can be associated with the observed ^{15}N low-field shift"[12] mainly because a greater amount of π charge is pushed away. In fact, the σ electron density made available upon deprotonation at nitrogen is to a great extent transferred to the whole molecular σ framework. Pushing away π charge enables the amino nitrogen to effectively conjugate to the ring π system or, in the case of **1** and **5c** systems, to set up π conjugation throughout all the heterocyclic ring. This is clearly indicated by the differences in the portrait of the Laplacian of the charge density for the protonated and the deprotonated forms.

This study demonstrates that useful and enlightening information is obtained by a combined analysis of changes in nuclear magnetic shielding tensors and charge density rearrangement mechanisms, despite the lack of a firm physical basis relating the two. Moreover, the study shows that apparently intriguing experimental behavior of chemical shift changes upon deprotonation can be rationalized in terms of plain concepts.

Acknowledgment. We thank a referee for his very helpful and stimulating comments. Thanks are also due to Dr. P. J. MacDougall for suggesting that we explore correlations involving the charge density quadrupole moment tensor. The help of Mr. M. Bandera in preparing the drawings is gratefully acknowledged.

Registry No. 1, 109-97-7; **1a**, 23303-09-5; **2**, 504-29-0; **2a**, 41458-22-4; **3**, 462-08-8; **3a**, 80287-52-1; **4**, 504-24-5; **4a**, 37062-09-2; **5**, 110-86-1; **5c**, 16969-45-2.

Substituent Effects. 4. Nature of Substituent Effects at Carbonyl Groups

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Abstract: The effect of substituents on the properties of acyl derivatives has been examined. Geometry optimizations were carried out at the MP2/6-31G* theoretical level, followed by calculation of energies at the MP3/6-311++G** level. The energies were studied via isodesmic reactions with ethane leading to acetone and a methyl derivative. The calculated energy changes were in good agreement with the available experimental data and showed that groups more electronegative than carbon stabilize a carbonyl group more than methyl, whereas the opposite is true with the more electropositive groups. The reasons for the energy changes were studied by examining bond dissociation energies for the acyl derivatives and for the corresponding methyl derivatives. The changes in electron populations, bond orders, and atom energies that result from changes in substituents were also studied. It is concluded that the stabilization of carbonyl groups by the substituents NH_2, HO, and F results from a combination of two interactions. The first is the interaction of the substituent lone pair with the electron deficient carbonyl carbon, which decreases on going from NH_2 to F. The second is the Coulombic stabilization of dipolar bonds, which increases on going from NH_2 to F. Similar effects are seen with the second-row substituents SH and Cl. The SiH_3 group, along with CN and CF_3, gives a different behavior which results from the positive charge at the substituent atom and the resultant repulsive interaction with the carbonyl carbon. Changes in hybridization also affect the bond dissociation energies, but in a different way than electronegativity.

1. Introduction

The carbonyl group is probably the most important functional group in organic chemistry, and it has received extensive study.[2] Nevertheless, there still remain important questions concerning the nature of the interaction of substituents with this group. One manifestation of this interaction may be seen in the isodesmic reactions in Table I which lists the experimental energies found in replacing a given substituent by a methyl group.[3] Some related reactions have been discussed by George, Bock, and Trachtman.[4] Replacement of a hydrogen by methyl leads to stabilization, whereas the replacement of atoms that are more electronegative than carbon by methyl leads to an endothermic reaction. Another manifestation is found in rotational barriers (Table II) for the bonds joining the carbonyl group to the substituent. Although the barriers are small with methyl groups, they can become quite large with other substituents.

We have carried out an investigation dealing with the ways in which the carbonyl group is affected by the substituents. Here, we have carried out geometry optimizations at the MP2/6-31G* level which is known to give structures close to those determined experimentally.[5] This was followed by MP3/6-311++G** single-point energy calculations. This large basis set is effectively triple-ζ with both diffuse and polarization functions on all atoms, and it includes correction for electron correlation via perturbation theory through the third order. Zero-point energies were estimated via HF/6-31G* frequency calculations. The MP2 wave functions

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(1) (a) Yale University. (b) Florida State University.

(2) Cf.: Falbe, J. *Methoden der Organische Chemie (Houben-Weyl)*; Vol. E3, G. Thieme Verlag: Stuttgart, 1983; Vol. E3. Müller, E. *Ibid.* 1973; Vol. 7/7.

(3) The data were taken from: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.

(4) George, P.; Bock, C. W.; Trachtman, M. *Molecular Structure and Energetics*; VCH Publishers, Florida, 1987; Vol. 4, p 163.

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

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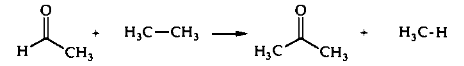
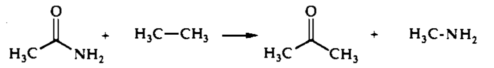
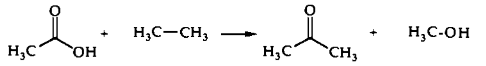
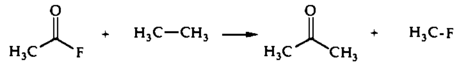
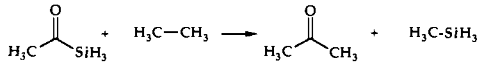
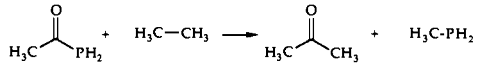
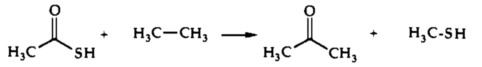
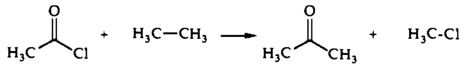
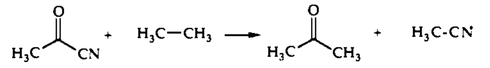
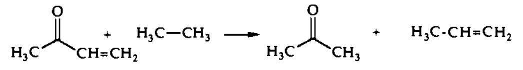
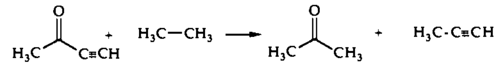
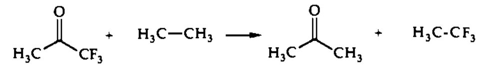
Table I. Isodesmic Reactions[a]

reaction	ΔH(obs), kcal/mol	ΔH(calc),[b] kcal/mol 6-31G*	MP2/6-31G*	MP3/6-311++G**
	−11.5 ± 0.2	−10.8	−11.4	−10.3
	−9.9 ± 0.3	−9.0	−10.4	−9.3
	+19.6 ± 0.3	+20.6	+21.2	+18.3
	+23.4 ± 0.4	+25.5	+26.8	+22.3
	+17.9 ± 1.3	+19.0	+21.1	+16.4
	na	−13.0	−12.0	−12.6
	na	−6.2	−3.5	−3.9
	+4.5 ± 2.0	+4.3	+7.3	+5.5
	+6.6 ± 0.3	+2.9	+7.9	+6.7
	na	−11.8	−9.3	−11.0
	−2.9 ± 1.1	+0.2	+0.7	−0.4
	na	−5.6	−3.6	−5.5
	na	−11.9	−11.0	−12.4

[a] The MP2 optimizations included all electrons, and the MP3 single-point calculations used the frozen core approximation. [b] Calculated ΔE corrected for the zero-point energy change.

Table II. Rotational Barriers (kcal/mol)

compd	HF/6-31G*	MP2/6-31G*	MP3[a]	ΔZPE[b]	MP3+ZPE	obs
acetamide	14.0	14.3	12.7	−0.19	12.5	16.7[c]
acetic acid	13.8	14.7	12.5	−1.11	11.4	~10–15[d]
acetyl phosphine	3.8	3.5	3.4	−0.21	3.2	
thioacetic acid	8.9	9.6	7.9	−0.53	7.4	
acetone	0.7	0.8	0.6	−0.08	0.5	0.8[e]

[a] "MP3" = MP3(fc)/6-311++G**[a]//MP2(fu)/6-31G*. [b] The HF/6-31G* zero-point energies were scaled by 0.8934. [c] The value was determined in acetone solution, and it is known that polar solvents increase the rotational barrier: Drakenberg, T. *Tetrahedron Lett.* **1972**, 1743. [d] This is the observed barrier for methyl acetate: Blom, C. E.; Günthard, Hs. H. *Chem. Phys. Lett.* **1981**, *84*, 267. [e] Reference 10.

have been analyzed by using Bader's theory of atoms in molecules[6] in order to obtain the charge densities at the bond critical points and the electron populations for each of the atoms. A particularly interesting quantity is the carbonyl bond order, and both the σ and π components of the bond order have been obtained by using an extension of a recently developed method of defining the bond orders.[7]

2. Energies and Structures

The calculated energies of the compounds in this study are given in Table A in the supplementary material, and the structural data are summarized in Table III. Formamide has a very flat potential surface for NH_2 wagging. At the MP2/6-311+G** level, there is essentially no difference in energy between the planar structure and one which has the amino hydrogens out of plane by 1.5°.[8] The planar structure was used in the present calculations. With acetamide, the minimum energy structure at the MP2/6-31+G* level had a 30° rotated methyl group and an amino group with the hydrogens 7° out of plane.[9] However, this was only 0.2

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(6) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893. Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, 1990.

(7) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142.

(8) Calculations by Wright et al. (Wright, G. M.; Simmonds, R. J.; Parry, D. E. *J. Comput. Chem.* **1988**, *9*, 600) at the MP2/DZP level found a slightly nonplanar amino group. Our calculations at a somewhat higher theoretical level (MP2/6-311++G**) gave $E = -169.562144$ hartrees for a nonplanar structure with the amine hydrogens ~1.5° out of plane and $E = -164.562137$ hartrees for the planar structure. They differ by only 2 cal/mol, too small to be of any significance at any practical theoretical level, and much smaller than the zero-point vibrational energy for the amino wagging mode (288 cm^{-1} = 400 cal/mol). This is in very good agreement with the more recent experimental study: Hirota, E.; Sugusaki, R.; Neilsen, C.; Sorensen, G. O. *J. Mol. Spectrosc.* **1974**, *49*, 251.

Table III. Structures of Carbonyl Compounds, MP2/6-31G*

compd A	compd B	conf	r(C=O), Å	r(AC), Å	r(BC), Å	∠ACO, deg	∠BCO, deg
H	H		1.2200	1.1039	1.1039	122.19	122.19
CH_3	H		1.2222	1.5017	1.1090	124.39	120.34
CH_3	CH_3		1.2265	1.5118	1.5118	121.75	121.75
CH_3	NH_2	planar	1.2281	1.5140	1.3674	123.32	122.14
CH_3	NH_2	90°	1.2199	1.5008	1.4555	123.94	123.19
CH_3	OH	*Z*	1.2170	1.5002	1.3610	126.40	122.60
CH_3	OH	90°	1.2096	1.5030	1.3947	125.39	121.74
CH_3	OCH_3	*Z*	1.2184	1.5027	1.3561	126.04	123.43
CH_3	OCH_3	*E*	1.2139	1.5102	1.3647	123.54	118.56
CH_3	F		1.1978	1.4937	1.3672	129.23	120.65
CH_3	SiH_3		1.2341	1.5126	1.9295	121.04	119.72
CH_3	PH_2[a]	C_1	1.2246	1.5108	1.8721	122.46	120.50
CH_3	PH_2	planar	1.2262	1.5124	1.7963	123.69	120.44
CH_3	PH_2	90°	1.2216	1.5069	1.9128	122.71	121.77
CH_3	SH		1.2169	1.5072	1.7978	124.39	122.45
CH_3	SH	90°	1.2106	1.5036	1.8579	124.45	120.92
CH_3	Cl		1.1996	1.4986	1.7997	127.43	120.64
CH_3	$CH{=}CH_2$[b]	trans	1.2320	1.5118	1.4832	121.30	119.30
CH_3	$C{\equiv}CH$		1.2281	1.5056	1.4590	123.25	120.95
CH_3	CN		1.2228	1.4992	1.4800	125.16	119.51
CH_3	CF_3		1.2197	1.4999	1.5362	125.61	119.25

[a] The PH_2 group is pyramidal, unlike the NH_2 group. The CPH angles are 95.7 and 97.5°. [b] MP2/6-31G* optimized geometry kindly provided by Dr. James Blake.

kcal/mol higher in energy than the planar structure, and the latter was used in this study. Acetylphosphine was found to be markedly nonplanar with CPH bond angles of 95.7 and 97.5°, and here the planar structure was 27 kcal/mol higher in energy. The planar form had the shorter C–P bond length suggesting an interaction similar to that for acetamide. Its higher energy must result from the much greater preference for placing the lone pair electrons in an s orbital with phosphorus than with nitrogen. Acetone is known to have two methyl hydrogens eclipsed with the carbonyl group and to have a rotational barrier of 0.8 kcal/mol.[10] Acetylsilane was calculated to have a very small rotational barrier for the SiH_3 group. The smaller basis set calculations found it to prefer a conformer in which a methyl hydrogen is eclipsed, and the silane hydrogens are staggered with respect to the carbonyl. However, at the MP3/6-311++G** level, the conformer in which both groups were eclipsed with the carbonyl was found to have the lower energy by a very small amount. Methyl vinyl ketone is known to prefer the *s-trans* conformation,[11] but both the HF and MP2 geometry optimizations gave the *s-cis* form as having the lower energy. However, at the MP3/6-311++G** level, the *s-trans* form was correctly calculated to have the lower energy by 0.6 kcal/mol.

The energies for isodesmic reactions based on the calculated energies are given in Table I. There is generally good agreement between the calculated and experimental energy changes. Replacement of a hydrogen attached to a carbonyl group by a methyl leads to an exothermic reaction, and it is known that a methyl group will stabilize a carbonyl by about 7 kcal/mol.[12] It was interesting to note that with substituents less electronegative than carbon the reactions are calculated to be exothermic whereas the more electronegative substituents generally give endothermic reactions. Thus the carbonyl carbon prefers to be substituted by electronegative groups, but not by electropositive groups. However, with electronegative groups that have carbon as the first atom in the substituent (i.e. $-CF_3$, $-CN$, and $-C{\equiv}CH$), the substituent prefers to be attached to methyl rather than a carbonyl group.

Another way in which to examine these compounds is to make use of decarbonylation reactions (i.e., acetone → ethane + CO), and they are given in Table IV. Here, a constant difference of 4.8 ± 0.8 kcal/mol was found between the MP3 and observed energies. This is probably due to the well-known difficulty in calculating the energy of carbon monoxide.[13] Making this empirical correction, the calculated results are in good agreement with the available experimental data. Again, it is clear that the unusual substituents are NH_2, OH, and F in one direction and Si, CN, and CF_3 in the other.

Table IV. Energies of Decarbonylation Reactions (kcal/mol)

compd	ΔH(calc)[a] MP2/6-31G*	ΔH(calc)[a] MP3/6-311++G**	ΔH corr[b]	ΔH obs
CH_3COCH_3	2.8	1.1	5.9	5.4 ± 0.2
CH_3CONH_2	23.9	19.4	24.2	25.0 ± 0.2
CH_3COOH	29.7	23.6	28.4	28.8 ± 0.4
CH_3COF	23.9	17.5	22.3	23.4 ± 2.0
CH_3COSiH_3	−9.2	−11.5	−3.7	na
CH_3COPH_2	−0.7	−2.9	1.9	na
CH_3COSH	10.1	6.6	11.4	9.9 ± 2.0
CH_3COCl	10.7	7.8	12.6	12.0 ± 0.2
$CH_3COCH{=}CH_2$	3.4	0.7	5.5	na
$CH_3COC{\equiv}CH$	−0.8	−4.4	0.4	na
CH_3COCN	−6.5	−9.9	−5.1	na
CH_3COCF_3	−8.3	−11.2	−6.4	na

[a] Calculated energy changes corrected for zero-point energy changes. [b] MP3 energies corrected for the 4.8 ± 0.8 kcal/mol constant deviation between the calculated and observed ΔH which probably results from the difficulty in calculating the energy of carbon monoxide (see text).

Table V. Isodesmic Reactions of Saturated Compounds (kcal/mol)

reaction	ΔH(obs)
$CH_2(OCH_3)_2 + CH_3CH_3 \rightarrow CH_3CH_2OCH_3 + CH_3OCH_3$	+7.7
$CH_2F_2 + CH_3CH_2F + CH_3F$	+9.7
$CH_2Cl_2 + CH_3CH_3 \rightarrow CH_3CH_2Cl + CH_3Cl$	−3.6

These energy changes are not a specific property of the carbonyl group, but also are found in saturated carbon derivatives (Table V). Carbon generally prefers to be substituted with electronegative first row elements, although multiple cyano groups are known to lead to destabilization.[14]

The energy changes for the isodesmic reactions may be due to changes in the energies of the carbonyl compounds in response to substitution, to changes in energies of the methyl derivative products of the reactions, or to both of the above. Since differences are involved, it is not possible to locate the origins of the energy changes from the above data. Therefore, we also have examined the bond dissociation energies of the acyl derivatives and of the

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(9) Wong, M. W.; Wiberg, K. B. *J. Phys. Chem.* **1992**, *96*, 668.

(10) Pierce, L.; Nelson, R. *J. Mol. Spectrsoc.* **1965**, *18*, 344.

(11) de Smedt, J.; Vanthouteghem, F.; van Ansenoy, C.; Geise, H. J.; van der Veken, B.; Coppens, P. *J. Mol. Struct.* **1989**, *195*, 227.

(12) Wiberg, K. B.; Crocker, L. S.; Morgan, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 3447.

(13) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry*; Macmillan: New York, 1982; pp 201 and 372.

(14) Salzner, U.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1992**, *190*, 401.

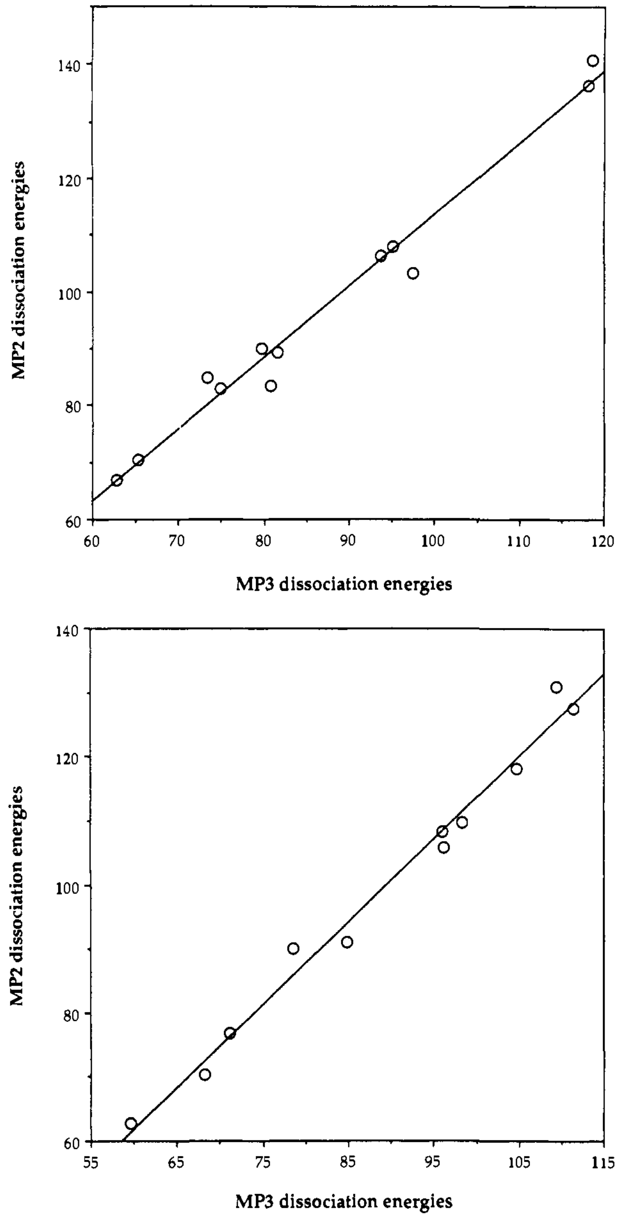

Figure 1. Relationship between MP2 and MP3 calculated bond dissociation energies (kcal/mol): (a, top) methyl derivatives; (b, bottom) acetyl derivatives.

methyl derivatives. The energies of the radicals are included in Table A in the supplementary material. Except for vinyl, acetylide, and cyano, spin contamination in the radicals was small ($s^2 \sim 0.76$). The MP3 energies were corrected for spin contamination.[15] For comparison with the experimental data, the values should be corrected for the change in zero-point energy on going to the radicals. The zero-point energies were estimated from vibrational frequencies calculated at the HF/6-31G* level and were scaled by the factor 0.893.[16] The calculated bond dissociation energies are summarized in Table VI. The MP2 dissociation energies are somewhat greater than the larger basis set MP3 energies. However, there is a fairly reasonable linear relationship between the MP2 and MP3 energies, especially for the carbonyl derivatives (Figure 1). There also is a rather good linear relationship between the calculated MP3 dissociation energies and the measured values (Figure 2). With the methyl derivatives, the only point that falls significantly off the line is that for methyl fluoride, and here the dissociation energy is based on a guessed heat of formation with an estimated uncertainty of 4 kcal/mol.[17] Therefore, it is unlikely that a higher level of theory would lead to significantly different conclusions.[18] It is seen that whereas the C–C bond dissociation energy for ethane is significantly greater than that for acetone, the relative energies are reversed when X = NH_2, OH, and F, and the MeCOX bond dissociation energy is now much larger than that for MeX.

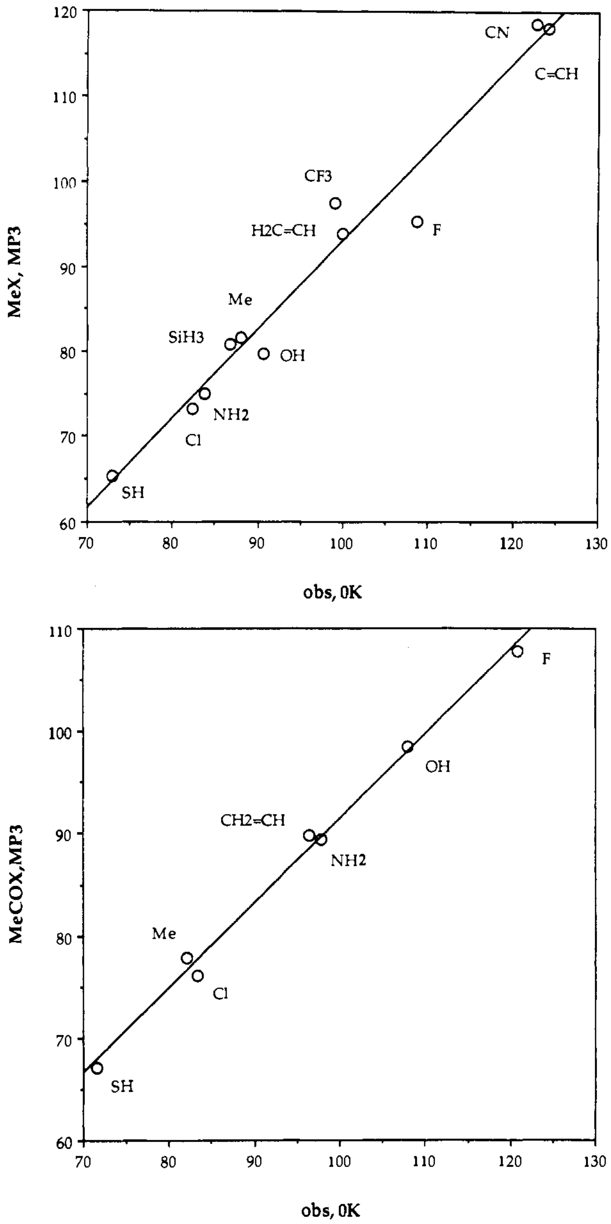

Figure 2. Relationship between observed (0 K) and MP3 calculated bond dissociation energies (kcal/mol): (a, top) methyl derivatives (slope = 1.044, intercept = −11.53, r^2 = 0.97); (b, bottom) acetyl derivatives (slope = 0.828, intercept = 8.55, r^2 = 0.99).

One possible explanation for the preference of an amino group to be attached to acetyl rather than methyl might be that in the former the N lone pair is donated to the C=O π^* orbital leading to stabilization. The magnitude of such an interaction should be related to the lone pair energy, which decreases rapidly in the series NH_2, OH, F. However, the observed stabilization of acetic acid is greater than that for acetamide, and acetyl fluoride is stabilized about as much as acetamide. Thus, this explanation cannot, at

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(15) Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530.

(16) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622.

(17) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Supp. 1.

(18) It is possible to obtain quite satisfactory bond dissociation energies for compounds such as these by going to QCISD(T) with a larger basis set such as 6-311+G** followed by a semiempirical correction for the remaining correlation energy (ref 16) or by a complete basis set extrapolation method (Montgomery, J. A., Jr.; Petersson, G. A. *Chem. Phys. Lett.* **1990**, *168*, 75).

Table VI. Calculated Bond Dissociation Energies[a] (kcal/mol)

compd	MP2/6-31G*	MP3/6-31++G**	obs 298 K[b]	obs 0 K
HCO–H	77.3	83.7	88.5 ± 1.9	87.1 ± 1.9
MeCO–H	79.2	84.7	88.8 ± 1.0	87.3 ± 1.0
Me–CHO	83.3	77.9	84.9 ± 1.9	83.3 ± 1.9
MeCO–Me	84.1	77.9	83.8 ± 1.0	82.2 ± 1.0
MeCO–NH_2	99.0	89.4	99.5 ± 1.8	97.8 ± 1.8
MeCO–OH	111.7	98.4	109.6 ± 1.1	108.0 ± 1.1
MeCO–F	124.0	107.8	121.2 ± 1.3	120.1 ± 1.3
MeCO–SiH_3	66.4	64.5		
MeCO–PH_2	58.2	55.1		
MeCO–SH	72.6	67.1	73.0 ± 2.3	71.5 ± 2.3
MeCO–Cl	87.6	76.2	83.6 ± 1.0	83.4 ± 1.0
MeCO–$CHCH_2$	101.8	89.8	97.6 ± 1.6	96.4 ± 1.6
MeCO–CCH	127.6	108.9		
MeCO–CN	126.4	104.8		
MeCO–CF_3	87.0	81.4		
HCO–$CHCH_2$	102.3	90.9	98.6 ± 2.5	97.3 ± 2.5
Me–H	94.6	97.8	105.0 ± 0.2	103.2 ± 0.2
Me–Me	89.2	81.6	89.8 ± 0.3	88.0 ± 0.3
Me–NH_2	83.0	74.9	85.8 ± 1.5	83.9 ± 1.5
Me–OH	90.0	79.7	92.3 ± 0.4	90.6 ± 0.4
Me–F	108.0	95.2	109.3 ± 2.0	108.7 ± 2.0
Me–SiH_3	83.5	80.8	88.5 ± 2.5	86.8 ± 2.5
Me–PH_2	66.8	62.8		
Me–SH	70.3	65.3	74.6 ± 0.8	73.0 ± 0.8
Me–Cl	84.7	73.3	83.1 ± 0.3	82.4 ± 0.3
Me–$CHCH_2$	106.3	93.9	101.8 ± 0.8	100.0 ± 0.8
Me–CCH	136.3	118.1	125.9 ± 0.8	124.1 ± 0.8
Me–CN	140.8	119.5	124.0 ± 1.8	122.7 ± 1.8
Me–CF_3	103.2	97.5	100.5 ± 1.1	99.0 ± 1.1

[a] The energies were corrected for the change in zero-point energies. [b] See Table XII for the source of the data.

least by itself, account for the observed isodesmic reaction or decarbonylation energies.

The information derived from the energy calculations leads to a set of questions:

1. Why do the bond dissociation energies in the MeCOX and MeX series generally increase with increasing electronegativity?
2. Why are the bond dissociation energies in the MeCOX series much larger than those in the MeX series when X = NH_2, OH, and F, but not in the series PH_2, SH, and Cl?
3. Why does CH_3SiH_3 give an apparently anomalous value of the bond dissociation energy (larger than for CH_3PH_2 or CH_3SH despite its lower electronegativity), and why is this not also found in the MeCOX series?
4. How are the bond length variations related to the energy changes and/or electronegativity?
5. What is the effect of conjugation (i.e., X = $CH{=}CH_2$ or CN) on the properties of the carbonyl group?

The answers to these questions should lie in the wave functions for the molecules, and therefore much of the remainder of this report will be concerned with such an analysis.

3. Analysis of the Electronic Wave Functions

The rigorous analysis of the electronic wave functions employs the topological theory of atoms in molecules[6] that provides a natural basis for partitioning first-order properties into atomic contributions. The necessary first-order reduced density matrices[19] are either computed from the HF spin orbitals or obtained as the total MP2 energy derivatives with respect to orbital perturbations.[20] Identification of atoms in molecules commences with locating the critical points in the electron density that serve as starting points for constructing zero flux surfaces demarcating the atomic basins, Ω_A. This is followed by evaluation of atomic properties such as the atomic charges and energies. The atomic overlap matrix (AOM) elements between natural spin orbitals, $\psi_i(\vec{x})$, that are obtained together with the corresponding occupation numbers n_i by diagonalization of the first-order density matrices, are computed at the same time as

$$\langle\psi_i|\psi_j\rangle_A = \int_{\Omega_A}\psi_i^*(\vec{x})\psi_j(\vec{x})\,d\vec{x} \qquad (1)$$

Like their Hartree–Fock counterparts, natural spin orbitals can be localized. The localized natural orbitals provide a chemically useful description of correlated electronic wave functions in terms of core orbitals, lone pairs, and two- and multicentered bonds. It is important that the orbital localization keeps as many of the electronic properties invariant as possible. For this reason, the localized natural spin orbitals, $\phi_i(\vec{x})$, that are related to the original natural spin orbitals through isopycnic (of equal density) transformations[21]

$$\phi_i(\vec{x}) = \sum_j C_{ij}\psi_j(\vec{x}), \quad C_{ij} = U_{ij}\sqrt{n_j/\nu_i}, \quad \nu_i = \sum_j n_j U_{ij}^* U_{ij} \qquad (2)$$

are of particular interest. Such orbitals leave the first-order density matrices invariant, i.e.

$$\Gamma(\vec{x},\vec{x}') = \sum_i n_i\psi_i^*(\vec{x})\psi_i(\vec{x}') = \sum_i \nu_i\phi_i^*(\vec{x})\phi_i(\vec{x}') \qquad (3)$$

This means that the values of the first-order one-electron properties remain unchanged upon isopycnic transformations.

In eq 2, **U** denotes a unitary matrix and ν_i stands for the occupation number of the *i*th localized natural orbital. The isopycnic transformations reduce to ordinary unitary transformations in the case of single-determinant wave functions. Many different localization procedures are possible in principle; however, the AOM-based localization scheme,[22] which involves finding **U** maximizing the localization sum

$$L(\mathbf{U}) = \sum_i \sum_{klmn} U_{ik}^* U_{il} U_{im}^* U_{in}\sqrt{n_k n_l n_m n_n}\sum_A \langle\psi_k|\psi_l\rangle_A\langle\psi_m|\psi_n\rangle_A \qquad (4)$$

has several advantages over others. In particular, it provides a

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(19) Davidson, E. R. *Reduced Density Matrices in Quantum Chemistry*; Academic Press: New York, 1976.

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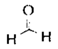
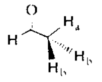
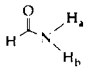
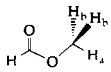
Table VII. Comparison of Atomic Charges with Levels of Electron Correlation and Basis Set[a]

		RHF		MP2		
compd	atom	6-31G**	6-311++G**	6-31G*	6-31G**	6-311++G**
formaldehyde (C_{2v})	O	−1.259	−1.207	−1.091	−1.089	−1.022
	C	1.282	1.168	0.992	1.103	0.976
	H	−0.011	0.020	0.049	−0.007	0.023
	sum	0.000	0.000	0.000	0.000	0.000
acetaldehyde (C_s)	O	−1.293	−1.243	−1.121	−1.119	−1.053
	C	1.216	1.127	1.016	1.074	0.977
	H	−0.031	0.001	0.035	−0.022	0.010
	C(Me)	0.174	0.094	−0.115	0.049	−0.045
	H_a	−0.010	0.021	0.068	0.013	0.045
	H_b	−0.031	−0.001	0.057	0.000	0.033
	sum	−0.006	−0.003	−0.003	−0.004	−0.001
formamide (C_s) (planar)	O	−1.361	−1.304	−1.193	−1.190	−1.120
	C	1.908	1.781	1.571	1.629	1.479
	H	−0.014	0.022	0.047	−0.010	0.026
	N	−1.463	−1.380	−1.319	−1.310	−1.226
	H_a	0.473	0.448	0.452	0.446	0.426
	H_b	0.457	0.435	0.442	0.435	0.417
	sum	−0.001	0.002	−0.001	0.000	0.002
methyl formate (C_s) (Z)	=O	−1.357	−1.296	−1.188	−1.186	−1.112
	C	1.953	1.833	1.630	1.683	1.543
	-O-	−1.319	−1.273	−1.141	−1.138	−1.083
	H	0.040	0.073	0.096	0.042	0.073
	C(Me)	0.710	0.607	0.391	0.550	0.440
	H_a	−0.018	0.014	0.064	0.011	0.044
	H_b	−0.008	0.022	0.069	0.016	0.047
	sum	−0.006	0.002	0.009	−0.006	0.000

[a] The sums are not exactly zero because of the small error associated with numerical integration of the charge density.

Table VIII. Comparison of Covalent Bond Orders Derived from RHF and MP2 Wave Functions[a]

		RHF		MP2		
compd	bond	6-31G**	6-311++G**	6-31G*	6-31G**	6-311++G**
formaldehyde (C_{2v})	C=O	1.388	1.430	1.456	1.441	1.488
	C—H	0.953	0.958	0.933	0.936	0.939
acetaldehyde (C_s)	C=O	1.339	1.379	1.406	1.400	1.445
	C—C	1.010	1.021	1.006	0.992	1.000
	C—H	0.939	0.946	0.922	0.922	0.927
	C—H_a	0.978	0.975	0.949	0.953	0.946
	C—H_b	0.972	0.972	0.941	0.945	0.941
formamide (C_s) (planar)	C=O	1.153	1.213	1.273	1.268	1.332
	C—N	0.911	0.954	1.007	0.996	1.042
	C—H	0.905	0.914	0.893	0.895	0.900
	N—H_a	0.774	0.779	0.764	0.770	0.788
	N—H_b	0.790	0.814	0.773	0.781	0.799
methyl formate (C_s) (Z)	C=O	1.159	1.225	1.277	1.272	1.343
	C—O	0.777	0.812	0.869	0.864	0.901
	C—H	0.901	0.907	0.881	0.887	0.890
	O—C(Me)	0.776	0.778	0.817	0.804	0.805
	C—H_a	0.955	0.957	0.932	0.933	0.932
	C—H_b	0.951	0.954	0.927	0.930	0.929

[a] Using the MP2/6-31G* optimized geometry.

rigorous definition of covalent bond orders which takes advantage of the fact that the contribution of the ith localized natural orbital to covalent bonding between two atoms A and B can be expressed as $2\nu_i^2\langle\phi_i|\phi_i\rangle_A\,\langle\phi_i|\phi_i\rangle_B$.[7] This gives rise to the following expression for the covalent bond order:[7]

$$P_{AB} = 2\sum_i \nu_i^2\langle\phi_i|\phi_i\rangle_A\langle\phi_i|\phi_i\rangle_B \qquad (5)$$

Since it does not involve any parametrization, such a definition is clearly preferable to the previous approach[23] which uses empirical correlations between the bond order and the value of the electron density at the respective bond point.

With the planar molecules it is possible to separate the σ and π components of the bond order by restricting the summation in the expression for the bond order to those orbitals ϕ_i which have the desired symmetry (σ or π). With out-of-plane atoms such as in methyl groups, it was necessary to combine the AOM elements for the symmetrically related atoms and consider them as a "superatom" possessing symmetry with respect to the molecular plane. This procedure was found to be satisfactory and gave components that added up to the total bond order with an error of less than 0.03.

One should note that all of the aforementioned interpretive tools are observable based,[24] which means that they can be derived directly from the wave functions in question with the help of *universal* quantum-mechanical operators. One can therefore regard the above analysis as free from bias inherent in those definitions of bond orders that attempt to identify the nuclei-centered basis functions as "atomic orbitals".

4. Results of the Analysis

Before considering the full set of compounds in this study, it would appear useful to present a comparison of the atomic charges derived using different basis sets and to examine the effect of electron correlation. The data are presented in Tables VII and VIII and were obtained consistently at the MP2/6-31G* geom-

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(23) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061.

(24) Cioslowski, J.; Surjan, P. R. *J. Mol. Struct.* (*THEOCHEM*). In press.

Table IX. Atomic Charges for Carbonyl and Substituent Groups (MP2/6-31G*)

Formyl Derivatives

X	H	C	O	$\sum XH_n$
H	0.049	0.992	−1.091	0.049
CH_3	0.035	1.016	−1.121	0.067
NH_2 (planar)	0.047	1.571	−1.193	−0.425
NH_2 (90°)	0.078	1.368	−1.137	−0.312
OH (*Z*)	0.103	1.648	−1.189	−0.559
OH (*E*)	0.067	1.652	−1.167	−0.551
OCH_3 (*Z*)	0.096	1.630	−1.188	−0.548
OCH_3 (*E*)	0.067	1.633	−1.164	−0.542
F	0.129	1.678	−1.151	−0.653

Acetyl Derivatives

X	CH_3	C	O	$\sum XH_n$
H	0.067	1.016	−1.121	0.035
CH_3	0.047	1.036	−1.140	0.047
NH_2 (planar)	0.066	1.569	−1.207	−0.428
NH_2 (90°)	0.111	1.360	−1.162	−0.312
OH	0.146	1.627	−1.206	−0.564
OCH_3 (*Z*)	0.133	1.618	−1.203	−0.553
OCH_3 (*E*)	0.104	1.623	−1.180	−0.541
F	0.188	1.638	−1.170	−0.655
vinyl (*s-trans*)	0.060	1.014	−1.119	0.042
vinyl (*s-cis*)	0.059	1.033	−1.134	0.044
C≡CH	0.100	1.130	−1.093	−0.135
CN	0.148	1.158	−1.070	−0.233
CF_3	0.137	1.083	−1.083	−0.141
SiH_3	0.055	0.349	−1.100	0.701
PH_2 (C_1)	0.081	0.531	−1.123	0.514
PH_2 (planar)	0.100	0.491	−1.132	0.541
PH_2 (90°)	0.087	0.607	−1.117	0.428
SH	0.127	0.969	−1.143	0.042
Cl	0.190	1.179	−1.126	−0.245

Methyl Derivatives

X	CH_3	$\sum XH_n$	X	CH_3	$\sum XH_n$
CH_3	0.000	0.000	CN	0.282	−0.282
NH_2	0.348	−0.347	CF_3	0.192	−0.192
OH	0.552	−0.550	SiH_3	−0.715	0.720
OCH_3	0.553	−0.553	PH_2	−0.518	0.517
F	0.667	−0.663	SH	0.013	−0.012
vinyl	0.040	−0.039	Cl	0.255	−0.255
CCH	0.202	−0.202			

Table X. Covalent Bond Orders for Substituent Groups (MP2/6-31G*//MP2/6-31G*)

Formyl Derivatives

	C═O		C—X	
X	total	π	total	π
H	1.456	0.689	0.933	0.005
CH_3	1.406	0.653	1.002	0.064
NH_2 (planar)	1.273	0.541	1.007	0.302
NH_2 (90°)	1.371	0.634	0.941	0.068
OH (*Z*)	1.348	0.552	0.925	0.229
OH (*E*)	1.372	0.566	0.933	0.220
OCH_3 (*Z*)	1.278	0.548	0.869	0.244
OCH_3 (*E*)	1.299	0.566	0.845	0.222
F	1.324	0.583	0.725	0.150

Acetyl Derivatives

	C═O		C—X		C—C	
X	total	π	total	π	total	π
H	1.406	0.653	0.922	0.005	1.002	0.064
CH_3	1.361	0.626	0.979	0.040	0.983	0.040
NH_2 (planar)	1.238	0.523	0.970	0.276	0.945	0.049
NH_2 (90°)	1.328	0.604	0.915	0.064	0.975	0.064
OH	1.242	0.531	0.821	0.207	0.992	0.046
OCH_3 (*Z*)	1.237	0.529	0.830	0.219	0.947	0.056
OCH_3 (*E*)	1.251	0.546	0.815	0.204	0.954	0.054
F	1.291	0.561	0.697	0.135	0.963	0.063
vinyl (*s-trans*)	1.353	0.619	1.006	0.081	0.983	0.056
vinyl (*s-cis*)	1.349	0.615	1.005	0.083	0.986	0.058
C≡CH	1.361	0.625	0.992	0.070	0.989	0.061
CN	1.379	0.637	0.905	0.037	0.996	0.067
CF_3	1.380	0.643	0.834	0.011	0.997	0.067
SiH_3	1.470	0.668	0.461	0.014	0.990	0.064
PH_2 (C_1)	1.429		0.867		0.974	
PH_2 (planar)	1.413	0.612	1.198	0.358	0.978	0.058
PH_2 (90°)	1.429	0.653	0.827	0.028	0.978	0.066
SH	1.394	0.614	1.144	0.214	0.996	0.061
Cl	1.409	0.612	0.984	0.140	0.992	0.067

Methyl Derivatives

X	C—X	X	C—X	X	C—X
NH_2	1.000	vinyl	1.034	SiH_3	0.479
OH	0.883	CCH	1.066	PH_2	0.841
OCH_3	0.862	CN	1.036	SH	1.109
F	0.786	CF_3	0.918	Cl	1.058

etries so that changes in charge would not result from changes in geometry.[25] The charges were obtained by subtracting from the atomic number (nuclear charge) the integrated populations for the atomic basins. It can be seen that there is a systematic decrease in the magnitudes of both the oxygen and carbon charges on going from 6-31G** to the larger basis set (~0.06 e), with smaller changes in the hydrogen populations. The MP2 wave functions lead to somewhat smaller charges, and again there are small systematic changes in charge on going to the larger basis set. The change in hydrogen populations on going from MP2/6-31G* to MP2/6-31G** was fairly consistently ~0.05 e as has been found previously with RHF wave functions[26] and results from a small shift in the bond critical point on going to the better balanced basis set.

The covalent bond orders (Table VIII) usually increase by a small amount on going from the smaller to the larger basis set in accord with the changes in calculated charges. With largely covalent bonds, such as C–H, they decrease somewhat on going from RHF to MP2 wave functions. On the other hand, with polarized bonds, the covalent bond orders increase on going to MP2. Inclusion of electron correlation results in effectively populating antibonding virtual orbitals which often causes a decrease in bond order.[27] However, the HF wave functions are known to exaggerate the ionicity of bonds, and so inclusion of electron correlation decreases the ionicity and increases the bond order. In the case of largely covalent bonds, the former is the more important effect, but with the polar bonds, the latter is more important.

In the following, the charges and bond orders derived from the MP2/6-31G* calculations will be reported since the times required for the numerical integration using the MP2/6-311++G** wave functions are quite long. It is clear from the above results that the conclusions derived from the smaller basis set would not be significantly different from those obtained with the larger basis set.

The atomic charges derived from the electron populations are summarized in Table IX and the full data are available as supplementary material. The bond orders for the carbonyl group and for its bond to the substituent are summarized in Table X. Again, the full data are available as supplementary material. In examining these data, it will be convenient to first consider the reason for the apparently anomalous C–Si bond dissociation energy of methylsilane.

The general trend of increasing bond strength with increasing electronegativity of the substituent was recognized by Pauling,[28] who concluded that the increased strength was due to the Coulombic attraction between the charged centers which increased with increasing difference in electronegativity. The increase in

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(25) Additional data are available as supplementary material.

(26) Wiberg, K. B.; Wendoloski, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 6561.

(27) Wiberg, K. B.; Hadad, C. M.; LePage, T. J.; Breneman, C. M.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 671.

(28) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1939.

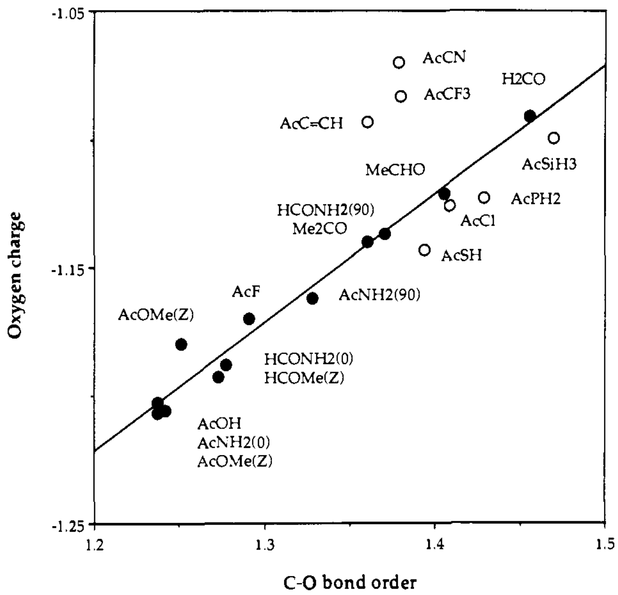

Figure 3. Relationship between C–O bond orders and O atomic charges. The line is defined by the dark circles which represent the simple first-row substituents.

the C–X BDE on going from methylamine to methanol and methyl fluoride presumably arises from the increasing charge separation in this series (cf. Table IX). There is a small decrease in BDE on going from ethane to methylamine. Here, the CH_3 group of ethane is forced to use $\sim sp^3$ orbitals, whereas the NH_2 group of the amine uses an orbital with relatively high p character in forming the bond to carbon. The decrease in bond strength with increasing p character accounts for the decrease in BDE.

The changes in BDE in the series methylsilane, methylphosphine, methanethiol, and methyl chloride may be rationalized in the same fashion. The decrease in BDE between methylsilane and methylphosphine has two components. Carbon is considerably more electronegative than silicon, and so the C–Si bond is more polar than the C–P bond, leading to a stronger bond. The C–P bond is further weakened by the change in hybridization on going from methylsilane with $\sim sp^3$ hybridized silicon to methylphosphine with a largely p hybridized bond to carbon. The difference in BDE between methylphosphine and methanethiol is more difficult to explain, but it may represent a change in hybridization.[29] The increase in BDE on going from methanethiol to methyl chloride probably results from the increased electronegativity of chlorine, leading to bond polarization and internal Coulombic stabilization. It is interesting to note that the BDE of methylsilane is somewhat larger than that for methyl chloride and that methylsilane has larger bond polarization than methyl chloride (Tables IX and X) although with the opposite sense.

It also may be noted that there is not a simple correlation between the BDE's and the covalent bond orders (Table X). In the series X = NH_2, HO, and F, the covalent bond orders decrease, but the BDE's increase. This is a result of the increasing ionic character that decreases the bond order but leads to stronger bonds. The BDE for methyl fluoride is considerably greater than that for methyl chloride, despite the greater bond order for the chloride. Bonds to second-row elements are generally weaker than those to first-row elements in part because of the greater bond lengths. The greater ionic character in the CF bond also contributes to the difference.

The changes in the C–C BDE's in the series ethane (88.0 kcal/mol), propene (100.0, and propyne (124.1 kcal/mol) must be a result of the change in hybridization for it corresponds to the changes in the C–H BDE's of ethane (98 kcal/mol), ethene (110 kcal/mol), and ethyne (131 kcal/mol). The large BDE for acetonitrile also must result from the sp hybridization of the carbon of the cyano group.

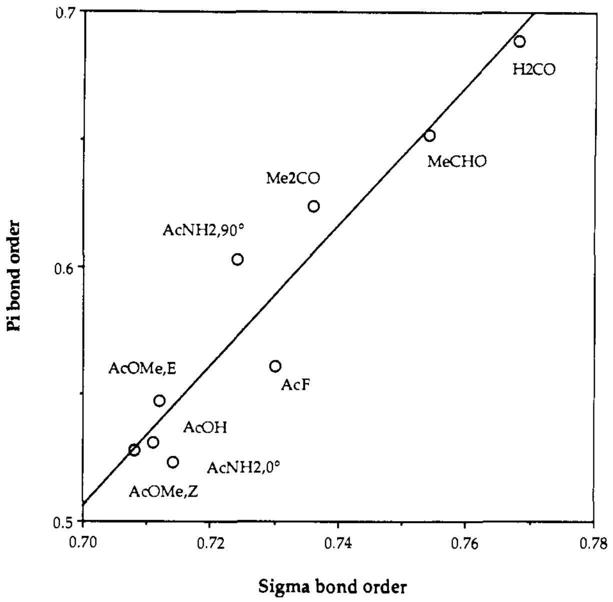

Figure 4. Relationship between σ and π bond orders for first-row substituents.

The C═O group is quite different than the methyl group with regard to substituent effects, first because it has both a σ and a π system, and second because it also involves an electronegative atom, the oxygen. If one examines the C═O bond orders and the O atomic charges, it can be seen that more electronegative substituents lead to smaller C═O covalent bond orders and larger O atomic charges. The two should be related since a decrease in covalent bond order should correspond to the formation of a more ionic bond. The relationship is tested in Figure 3, and it can be seen that except for X = CN and CF_3 there is a good linear relationship with a slope of about 2. It also should be noted that the oxygen charges cover a range of only 0.1 e. These data support our assertion that the oxygen is mainly a spectator as far as the properties of the carbonyl group are concerned and that its principal role is to polarize the C–O bond leading to an electron deficient carbon.[30] It should also be noted that the total bond order for the carbonyl group is composed of approximately equal σ and π components. The two components of the bond order are roughly linearly related (Figure 4), showing that both are similarly affected by changes in electronegativity. This illustrates a problem with drawing resonance structures such as

These structures are commonly thought to represent the π electrons, but as seen from the data in Table XI, the σ bond also is polarized.

It is useful to examine the MeCOX BDE's with reference to the corresponding MeX derivatives. Since a full set of experimental data is not available, the MP3 calculated values are compared in Figure 5. At first, the data appear to be quite scattered. However, it is possible to select a group of data that correspond to substituents having similar hybridization and increasing electronegativity, and they are shown as solid circles. The data for SH, NH_2, and OH are for the 90° rotated forms in which the π interaction is eliminated. The structure for acetylphosphine shows that there is no important π interaction, and with the electronegative F and Cl, one might expect the π interaction to be small. It can be seen that all of these substituents fall on a line with a slope if 1.63 and $r^2 = 0.99$. This is not an artifact of the use of calculated BDE's. The use of the experimental BDE's with correction for the rotational barriers in the acetyl series gives a slope of 1.54 with $r^2 = 0.99$.

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(29) It might be noted that acetyphosphine has a much different conformation than acetamide, whereas thioacetic acid and acetic acid are quite similar.

(30) Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 831.

Table XI. Total Electron Integration by Symmetry Class for Acetyl Derivatives, MP2/6-31G*[a]

XH_n	C	=O	X	C(Me)	H_a	H_b	H_c	H_d	ΣXH_n
				π-Molecular Orbitals					
CH_3	0.578	1.507	0.978	0.978	0.020	0.483	0.020	0.483	1.964
NH_2 (planar)	0.572	1.624	1.811	0.978	0.020	0.487	0.014	0.015	1.840
NH_2 (90°)	0.552	1.528	1.351	0.986	0.020	0.471	0.318		1.987
OH	0.544	1.609	1.894	0.991	0.020	0.473	0.070		1.964
F	0.535	1.576	1.952	0.994	0.020	0.467			1.952
$CHCH_2$[b]	0.609	1.495	0.963	0.980	0.020	0.483			1.950
C≡CH	0.607	1.487	0.997	0.988	0.020	0.475	0.014		1.973
CN	0.601	1.469	0.730	0.993	0.020	0.467			2.003
CF_3	0.581	1.472	0.368	0.995	0.020	0.466			12.003
SiH_3	0.623	1.477	2.246	0.977	0.020	0.479	0.045	0.835	3.960
PH_2 (planar)	0.742	1.571	3.561	0.988	0.020	0.481	0.078	0.078	2.186
PH_2 (90°)	0.606	1.495	2.589	0.982	0.020	0.474	0.692		3.973
SH	0.633	1.551	3.838	0.992	0.020	0.475	0.027		3.865
Cl	0.593	1.543	3.930	0.999	0.020	0.465			3.930
				σ-Molecular Orbitals					
CH_3	4.385	7.631	5.139	5.137	0.912	0.468	0.912	0.468	6.074
NH_2 (planar)	3.859	7.582	6.502	5.124	0.906	0.466	0.537	0.550	7.589
NH_2 (90°)	4.088	7.633	6.737	5.097	0.919	0.462	0.293		7.324
OH	3.829	7.599	7.265	5.077	0.908	0.456	0.400		7.664
F	3.828	7.595	7.702	5.060	0.901	0.452			7.702
$CHCH_2$[b]	4.377	7.623	5.101	5.134	0.909	0.466			13.007
C≡CH	4.264	7.606	5.146	5.113	0.907	0.460	0.779		11.163
CN	4.241	7.602	4.417	5.103	0.895	0.453			11.231
CF_3	4.336	7.612	3.802	5.114	0.897	0.451			21.134
SiH_3	5.029	7.625	8.995	5.145	0.913	0.467	1.654	0.846	12.340
PH_2 (planar)	4.767	7.561	10.099	5.113	0.901	0.458	1.314	1.328	14.667
PH_2 (90°)	4.787	7.624	11.088	5.125	0.912	0.463	0.757		12.602
SH	4.398	7.591	12.197	5.099	0.902	0.455	0.894		13.091
Cl	4.227	7.581	13.314	5.065	0.900	0.449			13.314

[a] In units of electrons. [b] For *s-trans*-methyl vinyl ketone.

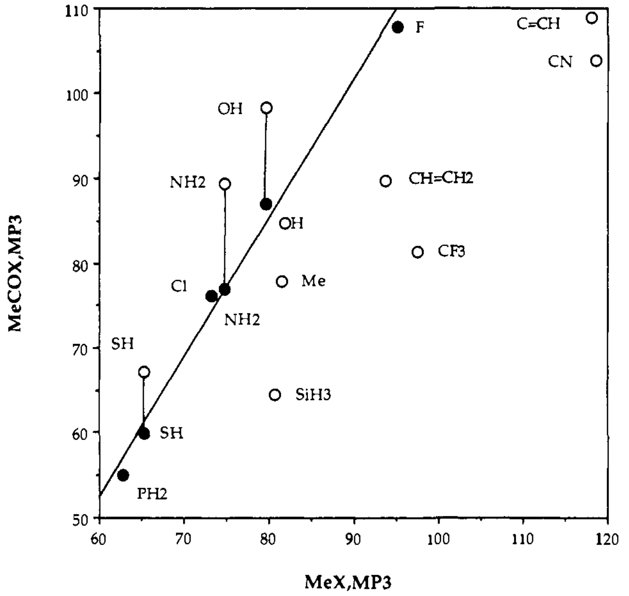

Figure 5. Relationship between MeCOX and MeX bond dissociation energies. The line is defined by the dark circles (slope = 1.63, r^2 = 0.99) and represents the effect of electronegativity with hybridization being relatively constant. The dark circles for X = SH, NH_2, and OH correspond to the 90° rotamers.

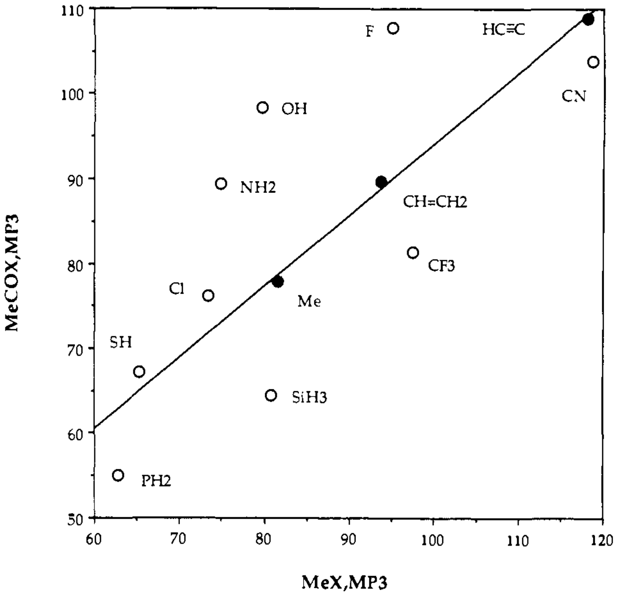

Figure 6. Relationship between MeCOX and MeX bond dissociation energies. The line is defined by the dark circles (slope = 0.83, r^2 = 0.99) and represents the effect of changing hybridization.

The greater than unity slope is to be expected for this case. Increasing electronegativity will increase the polar character of a bond, and this in turn will lead to internal Coulombic stabilization. In the case of the acetyl compounds, increasing charge at carbon will increase not only the strength of the C–X bond *but also the strength of the C–O bond.*

In the planar forms, the substituents SH, NH_2, and OH have MeCOX bond dissociation energies that lie above the line, and they have significant π bond orders from the substituents to the carbonyl carbons (0.214, 0.276, and 0.207 kcal/mol, respectively). They are in the expected order with NH_2 giving the largest π bond order for the first-row elements. Further, the π-bond order is reduced to a small value when the SH, NH_2, or OH group is rotated 90°. It is clear that these substituents have a significant interaction between their lone pairs and the electron deficient carbon of the carbonyl groups. The interaction is, of course, lost when the substituent is rotated 90°.

In contrast to the other substituents in this group, SiH_3 lies on the other side of the line in Figure 5. Because of its low electronegativity, silicon has a relatively large positive charge. As a result, the interaction with the positively charged carbonyl carbon will be repulsive, leading to a reduced BDE for acetylsilane. A similar effect is seen with CN and CF_3 where the carbons bear a positive charge.

Another factor that is important in determining bond dissociation energies is hybridization. It can be seen in Figure 6 that

Table XII. Heats of Formation and Zero-Point Energies (kcal/mol)

compd	ΔH_f(298 K)	ref[a]	ΔH_f(0 K)	ref[a]	ZPE obs	ZPE calc
methane	−17.8 ± 0.1	P	−15.9 ± 0.1	APl	27.1	26.8
ethane	−20.0 ± 0.1	P	−16.6 ± 0.1	APl	44.8	44.7
ethene	12.6 ± 0.1	P	+14.6 ± 0.1	J	30.9	30.7
ethyne	54.6 ± 0.2	P	54.7 ± 0.2	APl	16.2	16.5
propene	4.8 ± 0.2	P	8.4 ± 0.2	APl	48.2	47.9
propyne	44.2 ± 0.2	P	45.9 ± 0.2	APl	33.9	33.7
formaldehyde	−26.0 ± 0.1	P	−25.1 ± 0.1	J	16.1	16.4
formic acid	−90.5 ± 0.2	P	−88.8 ± 0.2	W	20.4	20.6
acetaldehyde	−39.7 ± 0.1	P	−37.2 ± 0.1	W	33.7	33.6
acetone	−51.9 ± 0.2	P	−48.0 ± 0.2	W	51.2	50.5
acetamide	−57.0 ± 0.2	P	−53.1 ± 0.2	W	44.7	44.3
acetic acid	−103.4 ± 0.4	P	−100.2 ± 0.4	W	37.9	37.5
acetyl fluoride	−105.7 ± 0.8	P	−103.4 ± 0.8	W	29.9	29.8
thioacetic acid	−41.8 ± 2.0	P	−38.9 ± 2.0	W		33.9
acetyl chloride	−58.0 ± 0.2	P	−55.9 ± 0.2	W	29.0	28.7
methylamine	−5.5 ± 0.1	P	−2.0 ± 0.1	W	39.1	38.6
methanol	−48.2 ± 0.1	P	−45.6 ± 0.1	W	31.0	31.0
methyl fluoride	−55.9 ± 4.0	J	−54.0 ± 4.0	J	24.0	23.8
methylsilane	−7.0 ± 2.0	D	−3.2 ± 2.0	W	37.2	36.6
methanethiol	−5.5 ± 0.2	P	−3.2 ± 0.2	W	27.8	27.8
methyl chloride	−19.6 ± 0.1	P	−17.7 ± 0.1	W	23.0	22.8
acetonitrile	15.4 ± 1.7	P	17.1 ± 1.7	W	27.5	27.4
acrolein	−16.6 ± 1.5	W1	−14.2 ± 1.5	W	37.1	37.3
methyl vinyl ketone	−28.9 ± 1.0	W1	−25.2 ± 1.0	W	53.8	54.2
1,1,1-trifluoroethane	−178.0 ± 0.4	P	−175.0 ± 0.4	W	32.2	31.9
$H^\bullet$	52.1 ± 0.0	J	51.6 ± 0.0	J	0.0	0.0
$CH_3^\bullet$	34.9 ± 0.2	J	35.7 ± 0.2	J	18.2	17.4
$NH_2^\bullet$	45.5 ± 1.5	J	46.2 ± 1.5	J	11.3	11.5
$HO^\bullet$	9.2 ± 0.3	J	9.3 ± 0.3	J	5.3	5.1
$F^\bullet$	18.5 ± 0.1	J	19.0 ± 0.1	J	0.0	0.0
$H_3Si^\bullet$	46.6 ± 1.5	D	47.9 ± 1.5	W		12.8
$HS^\bullet$	34.2 ± 0.7	N	34.1 ± 0.7	N	3.8	3.7
$Cl^\bullet$	28.6 ± 0.0	J	29.0 ± 0.0	J	0.0	0.0
$H_2C{=}CH^\bullet$	71.7 ± 0.8	E	72.7 ± 0.8	E		21.7
$HC{\equiv}C^\bullet$	135.3 ± 0.7	E	134.3 ± 0.7	E	9.2	8.4
formyl$^\bullet$	10.3 ± 1.9	J	10.4 ± 1.9	J	7.7	8.1
acetyl$^\bullet$	−3.0 ± 1.0	G	−1.5 ± 1.0	W		26.1
$N{\equiv}C^\bullet$	104.5 ± 0.5	H	104.1 ± 0.5	H	3.0	2.5
$CH_3O^\bullet$	4.2 ± 1.0	M	6.0 ± 1.0	W		21.7
$F_3C^\bullet$	−112.4 ± 1.0	J	−111.7 ± 1.0	J	7.6	7.6

[a] References: APl = American Petroleum Institute Research Project 44 tables of $H^\circ - H^\circ_0$. In the case of acetylene, the JANAF tables appear to be incorrect, but the API tables are correct. D = Doncaster, A. M.; Walsh, R. *Int. J. Chem. Kinet.* **1981**, *14*, 246. Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. E = Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750. G = Niiranen, J. T.; Krasnoperov, L. N.; Gutman, D. *J. Phys. Chem.* In press (report ΔH_f = −2.4 ± 0.3 kcal/mol); Nimlos, M. R.; Soderquist, J. A.; Ellison, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 7675 (report −5.4 ± 2.1 kcal/mol). A weighted average of the two values was used. H = Huang, Y.; Barts, S. A.; Halpern, J. B. *J. Phys. Chem.* **1992**, *96*, 425. J = JANAF thermochemical tables: Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Ref. Data* **1985**, *14*, Suppl. 1. In some cases the ΔH_f(298) were corrected to reflect more recent values. M = McMillan, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. N = Nicovich, J. M.; Kreutter, K. D.; van Dijk, C. A.; Wine, P. H. *J. Phys. Chem.* **1992**, *96*, 2518. P = Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986. W = this work. W1 = Wiberg, K. B.; Rosenberg, R. E.; Rablen, P. R. *J. Am. Chem. Soc.* **1991**, *113*, 2890. The values are based on the heats of formation of the saturated analogs and estimates of the heats of hydrogenation.

the points for CH_3, $CH_2{=}CH$, and $HC{\equiv}C$, corresponding to increasing s character, lie on a line with a slope of 0.84, or approximately half the slope in Figure 4. The increasing s character strengthens bonds without the degree of charge transfer found with increasing electronegativity. As a result, the slope is much smaller. The smaller bond dissociation energy for acetyl cyanide probably results from the positive charge at the carbon of the CN group, leading to a repulsive interaction with the carbonyl carbon, as was found with the SiH_3 group. The same is true with 1,1,1-trifluoroacetone.

The large positive isodesmic reaction energies for the first group of substituents then probably result from a combination of two factors. First, the lone pair electrons of the substituent interact with the electron deficient carbon, with the formation of a partial π bond. The net effect of this interaction is to lead to stabilization. The effect is largest with NH_2 and smallest with F. At the same time, the Coulombic stabilization increases on going from NH_2 to F, as was found with the methyl derivatives, but by a greater amount. The combination of these two effects then leads to the almost constant isodesmic energies recorded in Table I. These factors along with changes in hybridization will accommodate the changes in bond dissociation energies for the carbonyl compounds.

The above discussion has concentrated on the π interactions and their role in determining the rotational barriers and the energy changes for the isodesmic reactions. There also are important changes in the σ system. As we have noted previously, the nitrogen of the planar amide uses an $\sim sp^2$ orbital to form the bond to the carbonyl group so that a p orbital can be used to interact with the electron deficient carbon.[30] When the amino group is rotated 90° it chooses to place the lone pair in an orbital with high s character, and uses an orbital with high p character to form the bond to carbon. The change in hybridization at nitrogen results in a change in electronegativity, just as is found with carbon. Thus, the nitrogen in the planar amide is more electronegative than in the rotational transition state, and withdraws charge from the carbonyl carbon via the σ bond. According to the calculated charges (Table XI), the σ withdrawal is greater than the π donation. The same is seen with acetic acid, where again rehybridization occurs on rotation.

5. Conclusions

The chemistry of the substituted carbonyl group is dominated by lone pair interactions and changes in electronegativity. The role of the oxygen is to cause polarization of the C–O bond, leading to an electron deficient carbon. The remainder of the interactions are mainly local to the carbonyl carbon and its substituent. Atoms having lone pairs will adopt a bonding scheme that will minimize the energy of the lone pairs. For amides, carboxylic acids, and thioacids, this will involve placing the lone pair in a p orbital that can effectively interact with the electron deficient carbon of the carbonyl group. Rotation of the group leads to loss of this interaction, and rehybridization occurs so as to place the lone pair in an orbital having high s character. With acetylphosphine, the strong preference for placing the lone pair electrons in an s orbital minimizes the interaction of the lone pair with the electron deficient carbon of the carbonyl group.

The isodesmic reactions in Table I may be understood in terms of the differences in bond dissociation energies of MeCOX and MeX derivatives. The factors that control the dissociation energies may be summarized as follows:

1. An increase in the difference in electronegativity between MeCO or Me and the first atom in the substituent, X, will lead to increased polarity of the bond and an increase in bond dissociation energy as shown in Figure 5. The effect of substituents is larger in the MeCOX series than for MeX because increasing polarization of the C–X bond will also lead to increased Coulombic stabilization of the polar C–O bond as well as greater polarity in the C–X bond.
2. Lone pair interactions of substituents with the electron deficient carbon of the carbonyl group will lead to increased bond dissociation energies in the MeCOX series (Figure 5). This is a complex interaction having both σ and π components that result from the rehybridization needed to place the lone pair in a p orbital. The data also indicate that F and Cl are poor π donors.
3. Increased s character in the bond from the substituent also leads to increased bond dissociation energies (Figure 6). Here, the effect is slightly larger in the MeX series than for MeCOX. The high C–C bond dissociation energy for acetonitrile results from the sp hybridization of the CN group.
4. If the substituent has a positive charge on the atom attached to the carbonyl group ($-SiH_3$, $-CN$, $-CF_3$), the bond dissociation energy is reduced because of the Coulombic repulsion with the positively charged carbonyl carbon.

6. Calculations

The ab initio calculations were carried out using GAUSSIAN-91[31] and standard basis sets. Six cartesian d functions were used with all of

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the basis sets. The integration of the charge density was carried out using PROAIM,[32] and the bond orders were calculated using a modified version of BONDER.[7]

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Supplementary Material Available: Tables of calculated energies, structures, bond properties, and atom properties (35 pages). Ordering information is given on any current masthead page.

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Resonance Interactions in Acyclic Systems. 5. Structures, Charge Distributions, and Energies of Some Heterobutadiene Rotamers†

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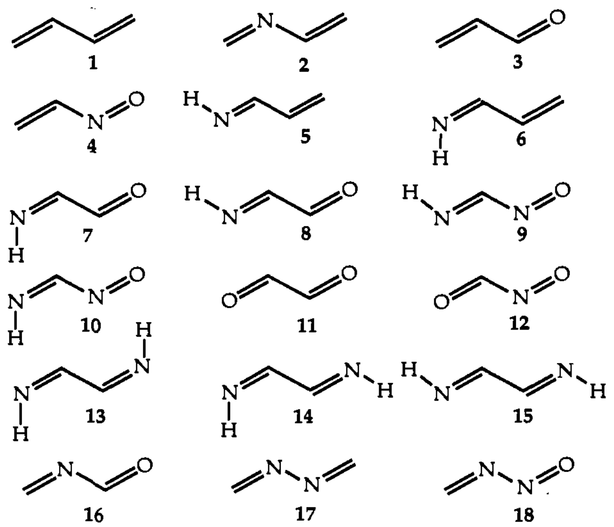
Abstract: The structures, energies, and rotational profiles of 17 heterobutadienes have been studied at the MP2/6-31G* theoretical level, with additional single point calculations at the MP3/6-311++G** level. The rotational profiles are, in part, determined by steric interactions between groups or between lone pairs. The magnitudes of these energies have been studied by examining the rotational profiles for some N-protonated derivatives which serve to minimize lone pair interactions. The conjugative interaction between the double bonds has been studied by examining the extent to which localized π orbitals have components at the other atoms and by calculation of bond orders as a function of torsional angle. The effect of a dipolar medium on the rotational barriers has been studied using reaction field theory. The atomic charges for the heterobutadienes have been calculated via numerical integration of the charge density within appropriately defined volume elements. In addition, the proton affinities and central bond dissociation energies have been calculated. The rotational barriers (s-trans to transition state) were largely a result of π-electron delocalization. However, shifts in π-electrons were compensated by shifts in σ-electrons so that the changes in total electron populations on rotation about the central bond were small.

1. Introduction

Butadiene and its heteroatom derivatives are common reagents in organic synthesis.[1] As such, it seemed useful to explore their structures and properties in greater detail than has been done so far. The magnitudes of the rotational barriers and the s-cis/s-trans relative energies were of particular interest to us because they may reveal the nature of the intramolecular interactions. The importance of π-resonance interactions also has been of special interest to us,[2] and these compounds present additional opportunities to examine these interactions.

The compounds included in this study are **1–18**, where only the trans forms are shown below. In the case of **5–10** and **13–15**, there are rotamers about the C=N bonds, and in each case both of the forms have been examined. This investigation is concerned with what may be learned about intramolecular interactions in these compounds via ab initio molecular orbital studies. The effect of replacing CH or CH_2 groups of butadiene by N, NH, or O will be examined by comparing structures, rotational barriers, degrees of π-electron delocalization, charge densities, and the effects of protonation and solvation in this series of compounds.



There have, of course, been many previous theoretical studies of these compounds. Butadiene (**1**)[2,3] and acrolein (**3**)[2,4] have been studied at a variety of theoretical levels, and the more recent calculations including correction for electron correlation in obtaining both the structures and energies are in very good agreement. Glyoxal (**11**) also has been studied at correspondingly high theoretical levels.[5] The azabutadienes (**2,5,6,13–15,17**) have

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† Dedicated to Professor William v. E. Doering on the occasion of his 75th birthday.

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