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Evaluation of AM1 Calculated Proton Affinities and Deprotonation Enthalpies

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Abstract: Proton affinities (PA) were calculated for 60 compounds and deprotonation enthalpies (DPE) for 80 compounds by using the AM1 semiempirical molecular orbital model. With few exceptions, the errors in the calculated DPEs and PAs, as well as in the calculated heats of formation of deprotonated and protonated species, are comparable with those in the calculated heats of formation of neutral precursors. Intramolecular hydrogen bonding in bifunctional bases is also effectively reproduced. The main problems involve anions in which the charge is largely concentrated on one atom and anions formed by the deprotonation of oximes. Systematic errors are indicated in the extension of alkyl chains by addition of methene groups and in substitution of amine and hydroxyl groups for methyl groups bonded to secondary or tertiary carbons in neutral molecules.

Proton transfer reactions play a basic role in chemistry, in particular in biochemistry. A knowledge of the proton affinities (PA) of bases and of the deprotonation enthalpies (DPE) of acids is therefore essential. While major progress has been made in recent years in the development of experimental techniques for measuring PAs, these have necessarily been limited to the gas phase, and results are available only for a very limited number of ions and molecules.[1] If PAs could be calculated theoretically with sufficient accuracy by some quantum chemical procedure, this would be of major value, because calculations, if feasible, can be carried out much more quickly and at much less cost than experiments, and they are, of course, not limited by the physical properties of the species being studied.

In connections such as this, the only theoretical procedures that need to be considered are ab initio ones based on Roothaan–Hall[2] SCF MO approximation and the semiempirical SCF MO methods (MINDO/3,[3] MNDO,[4] AM1[5]) developed here. Other alternatives (e.g., CNDO/2) are too inaccurate and unreliable.[6]

Numerous ab initio calculations of absolute and relative DPEs and PAs have been reported for compounds derived from carbon, hydrogen, nitrogen, and oxygen.[7-9] Many of these can, however, be eliminated from consideration because of failure to optimize geometries. As would be expected, the results from the others depend greatly on the basis set used and on the allowance (if any) made for electron correlation. While the number of calculations

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(1) For a recent review including discussion of experimental aspects and results, see: (a) Aue, D. H.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 9. (b) Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T.; Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

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(9) DPEs and PAs are frequently approximated by the difference between the total energies of the neutral and deprotonated or protonated molecules in ab initio studies.

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Table I. Comparison with Experiment of AM1 Heats of Formation and Proton Affinities (kcal/mol)

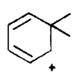
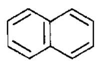
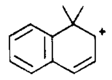
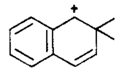
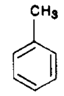
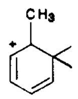
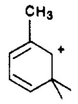
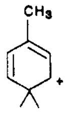
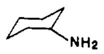
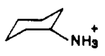
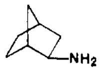
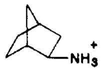
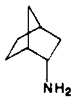
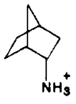
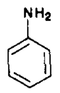
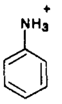
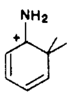
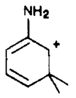
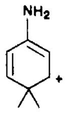
		calcd ΔH_f		proton affinity			exptl	error in calcd ΔH_f	
B	HB^+	B	HB^+	calcd	exptl[b]	error	ΔH_f(B)[d]	B	HB^+
			Carbon Bases						
CH_4	CH_5^+	−8.8[a]	224.4	134.0	132.0	2.0	−17.8	9.0	7.0
					134.7[c]	−0.7			9.7
CH_3CH_3	$CH_3CH_4^+$	−17.4[a]	208.4	141.4	143.6	−2.2	−20.0	2.6	4.8
					146.9[c]	−5.5			8.1
$CH_2{=}CH_2$	$CH_3CH_2^+$	16.5[a]	216.8	166.9	162.6	4.3	12.5	4.0	−0.3
$CH_3CH{=}CH_2$	$CH_3{}^+CHCH_3$	6.6[a]	191.9	181.9	179.5	2.4	4.8	1.8	−0.6
	$CH_3CH_2CH_2^+$		211.7	162.1					
		22.0[a]	206.0	183.2	181.3	1.9	19.8	2.2	0.3
		40.6[a]	213.2	194.6	194.7	−0.1	35.9	4.7	4.8
			216.7	191.1					
		14.5[a]	193.7	188.0					
			197.0	184.7					
			192.6	189.1	189.8	−0.7	12.0	2.5	3.2
$HC{\equiv}CH$	$H_2C{=}CH^+$	54.8[a]	261.5	160.5	153.3	7.2	54.5	0.3	−6.9
$CH_3C{\equiv}CH$	$CH_3C^+{=}CH_2$	43.4[a]	233.7	176.9	182	−5	44.2	−0.8	4
			Nitrogen Bases						
NH_3	NH_4^+	−7.3[a]	150.6	209.3	204.0	5.3	−11.0[g]	3.7	−1.6
CH_3NH_2	$CH_3NH_3^+$	−7.4[a]	148.7	211.1	214.1	−3.0	−5.5	−1.9	1.1
$CH_3CH_2NH_2$	$CH_3CH_2NH_3^+$	−15.1[a]	138.7	213.4	217.0	−3.6	−11.3	−3.8	−0.2
$CH_3(CH_2)_2NH_2$	$CH_3(CH_2)_2NH_3^+$	−22.1[a]	130.8	214.3	217.9	−3.6	−16.8	−5.3	−1.7
$(CH_3)_2CHNH_2$	$(CH_3)_2CHNH_3^+$	−19.2[a]	131.1	216.9	218.6	−1.7	−20.0	0.8	2.5
$CH_3(CH_2)_3NH_2$	$CH_3(CH_2)_3NH_3^+$	−28.9	124.0	214.3	218.4	−4.1	−22.0	−6.9	−2.8
$(CH_3)_2CHCH_2NH_2$	$(CH_3)_2CHCH_2NH_3^+$	−25.2	125.2	216.8	218.8	−2.0	−23.6	−1.6	0.4
$(CH_3)_3CNH_2$	$(CH_3)_3CNH_3^+$	−21.2	125.6	220.4	220.8	−0.4	−28.9	7.7	8.1
$(CH_3)_3CCH_2NH_2$	$(CH_3)_3CCH_2NH_3^+$	−30.5	120.9	215.8	219.3	−3.5	−30[f]	−1	3
		−31.9	115.1	220.2	221.2	−1.0	−25.1	−6.8	−5.8
		−8.9	137.4	220.9	221.7	−0.8	−8[f]	−1	0
		−8.2	138.2	220.8	221.7	−0.9	−7[f]	−1	0
		20.7[a]	176.5	211.4	209.5	1.9	20.8	−0.1	−2.0
			181.5	206.4					
			203.5	184.4					
			178.9	209.0					

Table I (Continued)

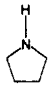
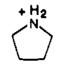
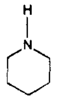
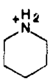
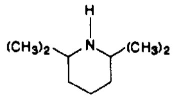
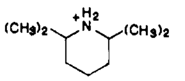
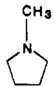
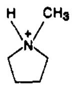
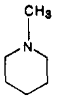
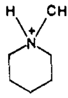
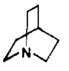
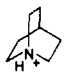
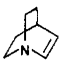
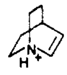
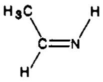
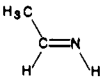
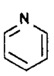
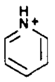
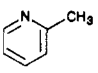
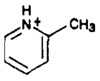
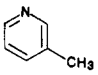
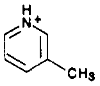
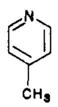
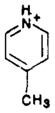
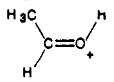
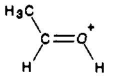
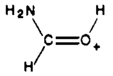
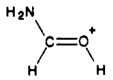
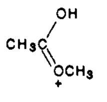
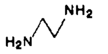
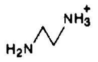
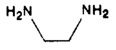
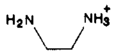
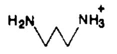
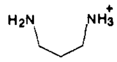
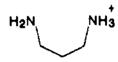
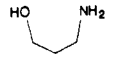
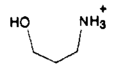
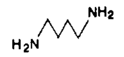
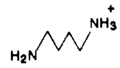
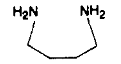
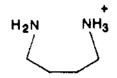
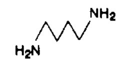
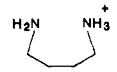
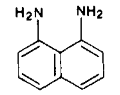
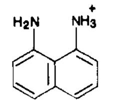
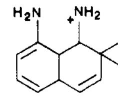
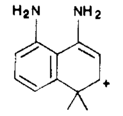
		calcd ΔH_f		proton affinity			exptl	error in calcd ΔH_f	
B	HB^+	B	HB^+	calcd	exptl[b]	error	$\Delta H_f(B)$[d]	B	HB^+
$(CH_3)_2NH$	$(CH_3)_2NH_2^+$	-5.6[a]	150.7	210.9	220.6	-9.7	-4.4	-1.2	8.5
$CH_3CH_2N(CH_3)H$	$CH_3CH_2{}^+N(CH_3)H_2$	-12.6	140.3	214.3	222.8	-8.5	-11[f]	-2	7
$(CH_3CH_2)_2NH$	$(CH_3CH_2)_2NH_2^+$	-17.8	131.5	217.9	225.9	-8.0	-17.3	-0.5	7.5
		-10.4	139.9	216.9	225.2	-8.3	-0.8	-9.6	-1.3
		-19.0	128.4	219.8	226.4	-6.6	-11.3	-7.7	-1.1
		-30.0	109.4	227.8	231.7	-3.9	-38[h]	8	12
$(CH_3)_3N$	$(CH_3)_3NH^+$	-1.7[a]	152.0	213.5	225.1	-11.6	-5.7	4.0	15.6
$(CH_3)_2NC_2H_5$	$(CH_3)_2N^+(C_2H_5)H$	-6.7	143.4	217.1	227.5	-10.4	-11[e]	4	14
$CH_3N(C_2H_5)_2$	$CH_3N(C_2H_5)_2H$	-11.6	135.0	220.6	230.0	-9.4	-17[e]	5	14
		-6.4	142.9	217.9	228.7	-10.8	-0.5[e]	-5.9	4.9
		-15.2	131.5	220.5	229.7	-9.2	-12[f]	-3	6
		-8.2	139.5	219.5	232.1	-12.6	-1.0	-7.2	5.4
		25.9	174.1	219.0	228.5	-9.5	37[f]	-11	-2
	$CH_3CHNH_2^+$	8.5	160.4	215.3	213.9	1.4	2[h]	7	6
		10.9		217.7					
		32.1[a]	184.2	215.1	220.8	-5.7	33.6	-1.5	4.2
		25.7	173.9	219.0	225.0	-6.0	23.7	2.0	8.0
		24.1	174.6	216.7	224.1	-7.4	25.4	-1.3	6.1
		24.2	173.3	218.1	225.2	-7.1	24.9	-0.7	6.4
HCN	$HCNH^+$	31.0[a]	214.8	183.4	171.4	12.0	32.3[e]	-1.3	-13.3
CH_3CN	CH_3CNH^+	19.3[a]	196.1	190.4	188.4	2.0	15.4	3.9	1.9
			Oxygen Bases						
H_2O	H_3O^+	-59.2[a]	143.5	164.5	166.5	-2.0	-57.8[g]	-1.4	0.6
					166.4[c]	-1.9			0.5
CH_3OH	$CH_3OH_2^+$	-57.0[a]	138.3	171.9	181.9	-10.0	-48.2	-8.8	1.2
CH_3CH_2OH	$CH_3CH_2OH_2^+$	-62.7[a]	125.8	178.7	188.3	-9.6	-56.2	-6.5	3.1
$CH_3)_3COH$	$(CH_3)_3COH_2^+$	-71.6[a]	107.8	187.8	193.7	-5.9	-74.7	3.1	9.0
$(CH_3)_2O$	$(CH_3)_2OH^+$	-53.2[a]	136.6	177.4	192.1	-14.7	-44.0	-9.2	5.5
$(C_2H_5)_2O$	$(C_2H_5)_2OH^+$	-64.4[a]	114.1	188.7	200.2	-11.5	-60.3	-4.1	7.4
$(CH_3)_3COCH_3$	$(CH_3)_3CO^+(CH_3)H$	-64.8	111.5	190.9	202.2	-11.3	-67.8	3.0	14.3
CO_2	CO_2H^+	-79.8[a]	147.8	139.6	130.9	8.7	-94.1[g]	14.3	5.6
					133.2[c]	6.4			7.9
H_2CO	H_2COH^+	-31.5[a]	161.3	174.4	171.7	2.7	-26.0[g]	-5.5	8.2
CH_3CHO		-41.6[a]	140.7	184.9	186.6	-1.7	-39.7	-1.9	-0.2

Table I (Continued)

		calcd ΔH_f		proton affinity				error in calcd ΔH_f	
B	HB^+	B	HB^+	calcd	exptl[b]	error	exptl $\Delta H_f(B)$[d]	B	HB^+
			142.3	183.3					
NH_2CHO		-44.7[a]	122.1	200.4	198.4	2.0	-44[h]	-1	-3
			122.7	199.8					
	NH_3^+CHO		132.5	190.0					
$CH_3CO_2CH_3$		-96.4[a]	76.0	194.8	197.8	-3.0	-98.4	2.0	5.0
			Bifunctional Bases						
H_2NNH_2	$H_2NNH_3^+$	13.7[a]	184.0	196.9	204.7	-7.8	22.8	-9.1	-1.3
		-9.1	143.3						
		-11.9	136.2	219.1	225.9	-6.8	-4.2	-7.7	-0.9
		-19.7	135.5						
		-18.1	127.8						
				219.7	234.1	-14.4	-8[f]	-12	2
		-68.7	88.9						
			121.6						
		-69.6	80.2	217.4	228.6	-11.2	-52[f]	-18	-7
		-26.5	127.8						
		-24.2	115.9						
				224.8	237.6	-12.8	-13[f]	-14	-1
		42.3	188.5	221.0	223.8	-2.8	46[f]	-4	-1
			188.9	220.6					
			186.5	223.0		-0.8			-3

[a] Reference 5. [b] Unless otherwise noted, experimental PAs are from ref 36a. [c] Reference 37. While reported in ref 36b, these values are not incorporated into the evaluated scale of PAs of ref 36. [d] Unless otherwise noted, experimental heats of formation are from ref 38. [e] Reference 15. [f] Estimated in ref 36a. [g] Reference 39. [h] Reference 36a and references therein.

is too large for the results to be compared here in detail, it seems clear that a reasonably large basis set must be used if the average errors in DPEs and PAs are to be kept within reasonable limits, e.g., 10 kcal/mol. In the case of anionic bases, it is also necessary to include diffuse AOs in the basis set.[7] Calculations at this level become very expensive for larger molecules, and the results are still by no means exact.

MNDO[4] is now a well-established procedure for calculating molecular properties.[10] While it was parametrized to reproduce ground-state properties of neutral closed-shell molecules, it also gives good results for radicals, carbenes, and positive and negative

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[10] (a) Dewar, M. J. S. *J. Phys. Chem.* **1985**, *89*, 2145. (b) Dewar, M. J. S.; Storch, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 3898.

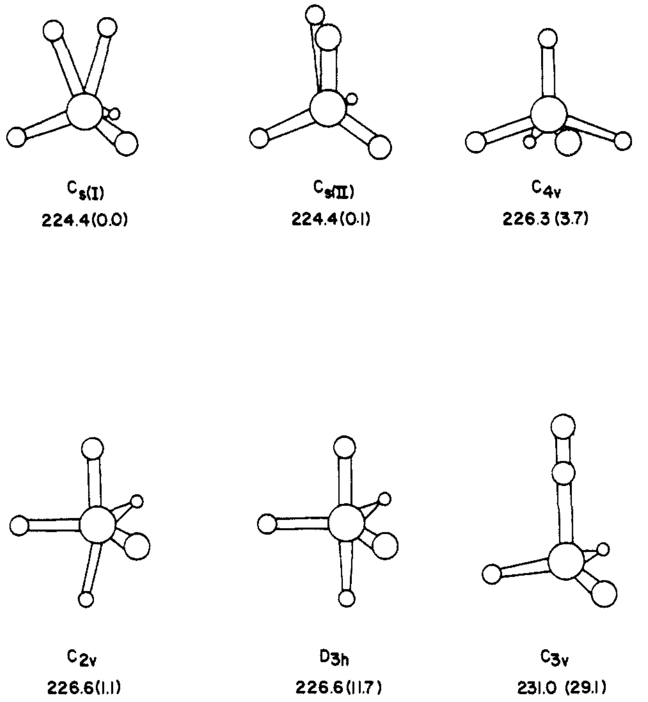

Figure 1. Six structures were optimized for CH_5^+ with AM1. AM1 heats of formation, in kcal/mol, are given below each structure. Values in parentheses are ab initio relative energies from ref 8p, also in kcal/mol.

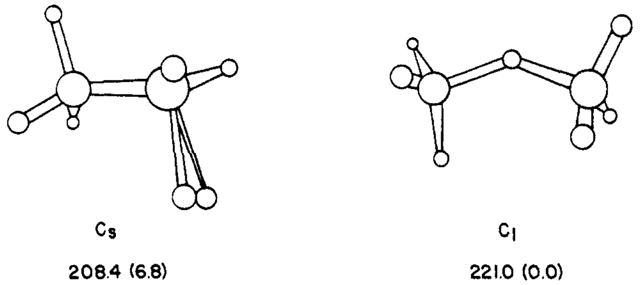

Figure 2. Two structures were optimized for $C_2H_7^+$ with AM1. AM1 heats of formation, in kcal/mol, are given below each structure. Values in parentheses are ab initio relative energies from ref 17, also in kcal/mol.

ions. The only exceptions are anions in which the charge is concentrated on a single atom, where the calculated heats of formation are much too positive.[11] This error is probably[11] due to failure to allow for orbital expansion accompanying large localized negative charges. It was therefore reasonable to hope that MNDO might provide satisfactory estimates of DPEs and PAs, and two recent studies[7,11] have indeed shown that the results are comparable with those from ab initio procedures that require a thousand times more computing time. The errors were, however, larger than desirable, particularly in the case of certain molecules involving features known to present problems in MNDO. These problems have now been mostly overcome in a new "third generation" semiempirical model, AM1,[5] so we decided to test its performance in calculations of DPEs and PAs. Here we present calculations for a large number of molecules for which we have been able to find apparently satisfactory experimental values.

Procedure

The calculations were carried out by using the standard AM1[5] procedure, as implemented in the AMPAC package of computer programs.[12] All geometries were optimized by minimizing the energy with respect to all geometrical variables by using the DFP method[13] incorporated in AMPAC and without making *any* assumptions. Various geometries of protonated methane and ethane were characterized as either true minima, transition states, or "hilltops" by diagonalizing their Hessian (force constant) matrices and looking for zero, one, or two or more negative eigenvalues, respectively.[14]

Table II. Comparison with Experiment of AM1 Hydrogen Bonding Stabilization in the Conjugate Acids of *n*-Alkyl Bifunctional Bases with Experimental and ab Initio Results (kcal/mol)

conjugate acid	AM1	exptl	ab initio[e]
$H_2N(CH_2)_2NH_3^+$	4.3	6.7,[a] 9.1,[b] 12.6[c]	24.8,[f] 7.7[g]
$H_2N(CH_2)_3NH_3^+$	9.3	14.2,[a] 14.2,[b] 20.5[c]	
$HO(CH_2)_3NH_3^+$	7.7[d]	8.8,[a] 15.2[b]	
$H_2N(CH_2)_4NH_3^+$	14.2	17.9,[a] 19.8[b]	

[a] Reference 28. [b] Reference 29. [c] Reference 30. [d] Hydrogen bonding stabilization in this acid is underestimated due to hydrogen bonding interaction in the neutral base. See text. [e] Reference 8jjj. [f] STO-3G//STO-3G. [g] 4-31G//STO-3G.

DPEs and PAs were found by difference from the calculated heats of formation of the parent molecule and the derived cation or anion, all of course with full geometry optimization. Since AM1 gives a very poor estimate of the heat of formation of H^+ (calcd 314.9; obsd 367.2[15] kcal/mol), the experimental value was used in calculating DPEs and PAs.

Results and Discussion

A. Proton Affinities. The PA of a compound (B) is defined as *minus* the heat of reaction for its combination with a proton

$$B + H^+ \rightarrow HB^+;\quad PA(B) = \Delta H_f(H^+) + \Delta H_f(B) - \Delta H_f(HB^+) \quad (1)$$

Table I lists calculated and experimental PAs for 60 compounds together with errors ($\delta\Delta H_f(HB^+)$) in the heats of formation calculated for the ionic species, these being found by using eq 2

$$\delta\Delta H_f(HB^+) = \delta\Delta H_f(B) - \delta PA(B) \quad (2)$$

where $\delta\Delta H_f(B)$ and $\delta PA(B)$ are, respectively, the errors in the heat of formation and in the PA of B. Included are nine carbon bases (the highest calculated PA is for protonation of a carbon atom), 33 nitrogen bases, 12 oxygen bases, and six bifunctional bases considered separately because they involve hydrogen bonding.

(1) Carbon Bases. The average unsigned error in the PAs calculated for the carbon bases is 2.9 kcal/mol,[16] while that in the heats of formation of the conjugate acids is 3.9 kcal/mol.[16] These are similar to the corresponding error (3.1 kcal/mol) in the heats of formation calculated for the parent hydrocarbons.

Heats of formation were calculated for six geometries of CH_5^+ cation (Figure 1). In agreement with high level ab initio calculations,[8p,nnn,17,18] the $C_{s(I)}$ structure is predicted to be most stable. AM1 calculates the $C_{s(II)}$ structure to be essentially equivalent in stability, its heat of formation differing from that for $C_{s(I)}$ by only 0.001 kcal/mol. While the AM1 results agree with the ab initio calculations as to the C_{3v} structure being the least stable isomer and the D_{3h} structure being the second least stable isomer, the magnitudes of the differences in heats of formation between these isomers and $C_{s(I)}$ are significantly less for AM1 than for the ab initio calculations. Additionally, the C_{2v} structure calculated by AM1 is a very slightly distorted trigonal bipyramid, its heat of formation being essentially the same as that of the D_{3h} structure. The calculated force constants indicate that only the $C_{s(I)}$ and C_{4v} structures correspond to minima on the potential energy (PE) surface, each of the others having at least one negative eigenvalue. Raghavachari et al. found only the $C_{s(I)}$ structure to be a true minimum.[17,19]

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(11) Olivella, S.; Urpi, F.; Vilarrasa, J. *J. Comput. Chem.* **1984**, *5*, 230.

(12) Available from Quantum Chemistry Program Exchange (QCPE).

(13) (a) Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163. (b) Davidon, W. C. *Comput. J.* **1968**, *10*, 406.

(14) Komornicki, A.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

(15) Stull, D. R.; Prophet, J. *JANAF Thermochemical Tables*; NSRDS-NBS37, 1971.

(16) In cases where two experimental values are quoted for the PA or DPE of a molecule, the average of the two values is used for calculating average unsigned errors.

(17) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649 and references therein.

(18) Dyczmons, V.; Kutzelnigg, W. *Theor. Chim. Acta* **1974**, *33*, 239.

Table III. Comparison of Errors in AM1 Heats of Formation for *n*-Alkanes, *n*-Alkylamines and *n*-Alkyl Alcohols (kcal/mol)

	$CH_3(CH_2)_nCH_3$			$CH_3(CH_2)_nNH_2$			$CH_3(CH_2)_nOH$		
	AM1 ΔH_f	exptl ΔH_f[b]	error	AM1 ΔH_f	exptl ΔH_f[b]	error	AM1 ΔH_f	exptl ΔH_f[b]	error
$n = 0$	-17.4[a]	-20.0	2.6	-7.4[a]	-5.5	-1.9	-57.0[a]	-48.2	-8.8
$n = 1$	-24.3[a]	-25.0	0.7	-15.1[a]	-11.3	-3.8	-62.7[a]	-56.2	-6.5
$n = 2$	-31.1[a]	30.0	-1.1	-22.1[a]	-16.8	-5.3	-70.6[a]	-61.0	-9.6
$n = 3$	-37.9[a]	-35.1	-2.8	-28.9	-22.0	-6.9	-77.3	-65.7	-11.6
$n = 4$	-44.1	-39.9	-4.2	-35.1	-26[c]	-9	-84.1	-70.4	-13.7

[a] Reference 5. [b] Reference 38. [c] Estimated in ref 36a.

Table IV. Comparison of ab Initio and AM1 Proton Affinities[9] (kcal/mol)

	6-31G*//3-21G		AM1
molecule	PA[a]	error[b]	error[c]
NH_3	218.4	14.4	5.3
CH_3NH_2	228.5	14.4	-3.0
$(CH_3)_2NH$	235.2	14.6	-9.7
HCN	178.1	6.7	12.0
CH_3CN	194.0	5.6	2.0
H_2O	173.3	6.9[d]	-2.0[d]
CH_3OH	189.5	7.6	-10.0
$(CH_3)_2O$	198.6	6.5	-14.7
H_2CO	181.4	9.7	2.7
CH_3CHO	194.0	7.4	-1.7
Av Unsigned Error		9.4	6.3

[a] Reference 8jj. [b] Errors are calculated by using experimental values from Table I. [c] From Table I. [d] Based on the average of the two experimental values given in Table I.

Two structures were calculated for $C_2H_7^+$ (Figure 2). In contrast to ab initio results[8hh,17] and conclusions based on pulsed high pressure mass spectrometry,[20] AM1 predicts the C_s structure alone to correspond to a minimum. The C_1 structure had one negative force constant. Similar results were obtained by using MINDO/3.[8hh,21]

The calculated heats of formation for protonated alkenes in Table I are for classical structures. AM1 fails to predict a nonclassical structure as a true minimum for the ethyl cation.[5] Protonation sites for asymmetric alkenes and alkynes are predicted correctly, as are the preferred para and ortho protonation of toluene.

(2) Nitrogen Bases. The average unsigned errors in the PAs calculated for neutral nitrogen bases and for the heats of formation calculated for them and for their conjugate acids are 5.8, 3.9, and 5.3 kcal/mol, respectively. The errors in the calculated PAs and in the heats of formation calculated for the conjugate acids are again similar to those for the neutral bases.

The conjugate acids for all amines except aniline are calculated to be unstable relative to the corresponding bases; i.e., $\delta\Delta H_f(HB^+) - \delta\Delta H_f(B) > 0$. Furthermore, these differences and the errors in the PAs generally increase in the sequence $1^0 < 2^0 < 3^0$. The former trend is probably due to AM1 being parametrized for ground-state neutral molecules, in each of which nitrogen has a localized lone pair of electrons. The latter trend can be attributed to the fact that ammonium ions have four atoms bonded to nitrogen, whereas the molecules included in the basis set had a maximum of three. Moreover, few of the latter had more than one alkyl group bonded to nitrogen.

As a result of these factors, the PAs of amines are underestimated by AM1 in an irregular manner, much as they were by MNDO.[11] The errors are less with AM1 than with MNDO, however, and some relative basicities predicted incorrectly by MNDO are now predicted correctly. For example, AM1 now correctly predicts trimethylamine to be more basic than methylamine, though dimethylamine is still predicted to be less basic than methylamine.

AM1 predicts preferential N-protonation of aniline, in agreement with experiment[22] and theory.[23] AM1 results do disagree with the results of Del Bene's high level ab initio calculations[8e] in predicting *cis*-ethanimine to be more stable than the trans isomer.

AM1 correctly predicts quinuclidine to be more basic than its unsaturated analogue. The difference between the two calculated PAs is significantly less than the experimental results, however, indicating that AM1 underestimates the inductive effect of the sp^2-carbon in the unsaturated compound.

(3) Oxygen Bases. The average unsigned error in the calculated PAs of the oxygen bases is 6.8 kcal/mol,[16] while that in the calculated heats of formation of the cations is 5.4 kcal/mol,[16] the corresponding error for the neutral bases being 5.1 kcal/mol.

Experimental trends within each group of compounds (i.e., alcohols, ethers, and carbonyl compounds) are accurately reproduced by AM1. As a whole, however, alcohols and ethers are predicted to be weaker bases than the experiment indicates by approximately 10 kcal/mol. As in the case of ethanimine, AM1 again differs from Del Bene's ab initio results[8g] in predicting preferential cis protonation of acetaldehyde and formamide.

(4) Bifunctional Bases. The unsigned average error in PAs for the six bifunctional bases listed is 9.3 kcal/mol, compared with 10.8 and 2.2 kcal/mol, respectively, for the heats of formation of the bases and conjugate acids. Thus, for these compounds, the heats of formation of the conjugate acids of the bifunctional bases are calculated more accurately than those of the neutral bases. Note that the errors for the neutral bases are all negative and that the errors for three of four *n*-alkyl bifunctional bases are exceptionally large (see below).

As mentioned previously, these bifunctional bases are of particular interest in that the PAs for five of the six compounds are much larger than those of alkyl amines of comparable polarizability, the exception being hydrazine. The high PAs can be attributed to intramolecular hydrogen bonding in the conjugate acids.[1a,24] For hydrogen bonding to play a role in the protonation of hydrazine, the conjugate acid would have to have a structure analogous to the nonclassical structure of the ethyl cation. No such structure was found to be a minimum on the AM1 PE surface.

Two geometries were calculated for each of the four *n*-alkyl bifunctional bases listed in Table I, one a "cyclic" structure (chain dihedral angles ~0°) and the other an "extended" structure (chain dihedral angles ~180°). It was assumed that hydrogen bonding would play a role only in the cyclic structure. Heats of formation are given for both optimized geometries. PAs are calculated by using the heats of formation of the more stable conformers.

In the more stable conformer of 1,2-diaminoethane, one amino group is gauche to the other. However, the relative orientation of the two amino groups in the optimized structure precludes hydrogen bonding between them. The lower heat of formation

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(19) The C_{3v} structure was not included in the force constant analysis of ref 17.

(20) Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6119.

(21) Bischof, P. K.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1975**, *97*, 2278.

(22) (a) Lau, Y. K.; Nishizawa, K.; Brown, R. S.; Kebarle, P. *J. Am. Chem. Soc.* **1981**, *103*, 6291. (b) Cavell, R. G.; Allison, D. A. *Ibid.* **1977**, *99*, 4203. (c) Martinsen, D. P.; Buttrill, S. E., Jr. *Org. Mass Spectrom.* **1976**, *11*, 762.

(23) (a) Pollack, S. K.; Devlin, J. L., III.; Summerhays, K. D.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4583. (b) Catalán, J.; Yáñez, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 741. (c) Catalán, J.; Yáñez, M. *Ibid.* **1979**, 1627.

(24) Alder, R. W.; Sessions, R. B. In *The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives*; Patai, S., Ed.; Wiley: Chichester, 1982; Vol. 2, pp 785–9.

calculated for this conformer relative to that for the conformer in which the two amino groups are anti to each other is a manifestation of the gauche effect.[25,26]

If no hydrogen bonding is involved in the protonated base, the difference between the heats of formation calculated for the cyclic and extended conformers of the acid should be approximately the same as for the neutral base, i.e., ΔH_f of the cyclic structure of $H_2NCH_2CH_2NH_3^+$ should be 140.5 kcal/mol. Consequently, AM1 calculates hydrogen bonding to stabilize the cyclic structure of the conjugate acid by 4.3 kcal/mol.

The stabilization due to hydrogen bonding in the conjugate acids of 1,3-diaminopropane, 3-aminopropan-1-ol, and 1,4-diaminobutane was calculated in the same manner as for 1,2-diaminoethane. The AM1 results are given in Table II, along with experimental estimates by Meot-Ner et al.,[28] Buschek et al.,[29] and Yamdagni et al.[30] and the ab initio results of Houriet et al.[8jjj] The AM1 values are similar to the most recent experimental values, i.e., those of Meot-Ner,[28,31] the N–H···N hydrogen bond being somewhat underestimated by AM1. The calculated value for 3-aminopropan-1-ol does not indicate the full extent of hydrogen bonding in the acid since hydrogen bonding is also involved in the neutral base.[29,32] The preferred N-protonation as opposed to O-protonation is in agreement with previous theoretical calculations and experimental results.[8jjj]

Despite the good predictions of the strengths of the hydrogen bonds, the errors in the calculated PAs for the *n*-alkyl bifunctional bases are exceptionally large. The errors in the corresponding PAs are moreover due largely to errors in the calculated heats of formation of the neutral bases rather than in those of the conjugate acids. The reason for this is a combination of systematic errors, one reflecting increasing alkyl chain lengths and the other substituting nitrogen or oxygen for a primary carbon atom. Table III lists the errors in AM1 heats of formation for a series of *n*-alkanes, *n*-alkylamines, and *n*-alkyl alcohols. The errors for the alkanes change by an average of −1.7 kcal/mol for each additional methylene group in the alkyl chain.[33] Likewise substitution of a nitrogen atom for a primary carbon changes the error for an *n*-alkylamine by an average of −4.4 kcal/mol relative to the error for the corresponding alkane. The corresponding change in the error due to replacement of a primary carbon by oxygen is −9.1 kcal/mol. These errors are approximately additive, and the large errors in the heats of formation of the bifunctional bases can be explained in terms of them. The corresponding errors for substitution for a primary carbon bonded to a tertiary carbon are less, being −1.8 and −5.2 kcal/mol for amino and hydroxyl substitution, respectively.[34] No such correlation exists for substitution for a secondary or tertiary carbon or for substitution for a primary carbon bonded to a quaternary carbon.

Catalán concluded in a recent INDO study[35] that 1,8-diaminonaphthalene is a nitrogen base, the PA calculated as 231.1 kcal/mol for amine protonation as opposed to 216.2 kcal/mol for ring protonation. The actual magnitude of the preference for protonation on nitrogen remained uncertain, due to the well-known tendency of INDO to overestimate the strengths of hydrogen bonds.[35] AM1, however, predicts a higher proton affinity for ring protonation. Neither the AM1 results for naphthalene nor those for aniline provide any indication that AM1 overestimates the stabilities of the ring protonated cations or underestimates those of the amine protonated ones. However, AM1 underestimates the strength of the N–H···N intramolecular hydrogen bond by at least 2.4–4.9 kcal/mol, as indicated by the calculations for the *n*-alkyldiamines. Consequently, the proton affinity for amine protonation is probably 0.4–2.9 kcal/mol higher than that for ring protonation. The small difference between N-protonation and ring protonation seems quite reasonable, given that aniline undergoes N-protonation[22] in the gas phase while *m*-diaminobenzene[22a,c] and 1-aminonaphthalene[24] protonate in the ring.

(5) Ab Initio Calculations. The results of high level ab initio calculations[8jj] of PAs for ten of the molecules listed in Table I are summarized in Table IV. While the errors naturally fluctuate, the AM1 values are, on average, more accurate by a significant margin.

B. Deprotonation Enthalpies. The deprotonation enthalpy (DPE) of compound HB is the heat of reaction for loss of a proton to form the conjugate base (eq 3). The DPE of a compound is thus equal to the PA of its conjugate base. The choice between them depends on the charges present, PA and DPE being regarded primarily as properties of neutral molecules.

$$HB \rightarrow H^+ + B^- \qquad \mathrm{DPE(HB)} = \Delta H_f(H^+) + \Delta H_f(B^-) - \Delta H_f(HB) \quad (3)$$

Calculated DPEs for 80 compounds are given in Table V, along with corresponding experimental values. Also included are the errors in the calculated heats of formation of the conjugate bases, $\delta\Delta H_f(B^-)$, calculated by using the equation

$$\delta\Delta H_f(B^-) = \delta\mathrm{DPE(HB)} + \delta\Delta H_f(HB) \quad (4)$$

where δ DPE(HB) and δ ΔH_f(HB) are the errors in the calculated DPE and heat of formation of HB, respectively. The listed compounds included 46 carbon acids (the lowest DPE is for a hydrogen bonded to a carbon), 10 nitrogen acids, and 24 oxygen acids.

(1) Carbon Acids. The average unsigned error in calculated DPEs for the carbon acids is 8.0 kcal/mol.[16] The values for CH_4, C_2H_4, HCN, and the alkynes are exceptionally poor as a result of large errors in the calculated heats of formation of the corresponding anions. When these eight compounds are excluded from the statistical analysis, the average unsigned error is reduced to 5.7 kcal/mol.[16] The average unsigned error in the heats of formation of the 38 anions is also 5.7 kcal/mol.[16] These errors compare favorably with the error of 5.1 kcal/mol for the 38 corresponding neutral acids.

The poor results for the CH_3^- and CN^- anions can be attributed to the failure of AM1 to allow for orbital expansion on atoms bearing large negative charges.[5] Similar problems were encountered in calculations for anions by using MNDO.[11] The calculated heats of formation are expected to be, and are, too positive whenever the formal charge in an anion is largely concentrated on a single atom. This is also the case for HO^- [5] and H_2N^- anions (see below). The same problem arises, as expected, in the case of allenyl anion[40] and propynyl anion. Both are incorrectly[41] predicted to be less stable than propargyl anion ($^-$

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(25) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102.

(26) After this manuscript had been submitted, an ab initio study[27] of 1,2-diaminoethane appeared in which the hydrogen bonded gauche conformer was found to be 1.28 kcal/mol more stable than the conformer predicted by AM1. This work was, however, carried out by using the 4-21G model. Reexamination at a higher level of theory would be of interest.

(27) Van Alsenoy, C.; Siam, K.; Ewbank, J. D.; Schäfer, L. *J. Mol. Struct. Theochem* **1986**, *136*, 77.

(28) Meot-Ner (Mautner), M.; Hamlet, P.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1980**, *102*, 6393.

(29) Buschek, J. M.; Jorgenson, F. S.; Brown, R. S. *J. Am. Chem. Soc.* **1982**, *104*, 5019.

(30) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 3504.

(31) Meot-Ner[28] has discussed the discrepancies between his values and those of Yamdagni and Kebarle.[30] The third set of values were derived indirectly from the experiment. It may be noted that Yamdagni and Kebarle obtained identical proton affinities (±0.005 kcal/mol) for the α, ω-diamines from propane, pentane, and heptane and also almost identical values (20.6, 20.0, 20.0 eu) for the entropies of cyclization. This would certainly not be expected in view of the known steric problems in medium-sized rings.

(32) Buschek et al. indicate hydrogen bonding between the hydroxyl hydrogen and nitrogen in the neutral molecule.[29] AM1 optimization of the neutral structure leads to hydrogen bonding between an amine hydrogen and oxygen.

(33) A value of −1.9 kcal/mol was reported previously based on results for ethane, propane, *n*-butane, and *n*-pentane.[5]

(34) These values are based on the AM1 results for isobutane, isopropylamine, and 2-propanol[5] and additional unpublished results for 2-methylbutane, 2-aminobutane, and 2-butanol.

(35) Catalán, J.; dePaz, J. L. G.; Yáñez, M. *J. Mol. Struct. Theochem* **1984**, *107*, 257.

(36) (a) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695. (b) Lias, S. G.; Levin, R. D., unpublished update to ref 32a.

(37) McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 2612.

(38) Pedley, J. B.; Rylance, G. *Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*; Sussex University: 1977.

Table V. Comparison with Experiment of AM1 Heats of Formation and Deprotonation Enthalpies (kcal/mol)

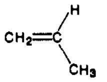
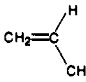
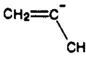
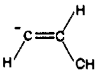
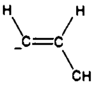
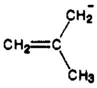
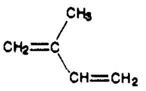
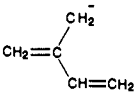
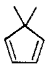
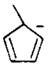
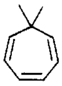
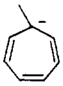
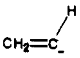
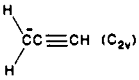
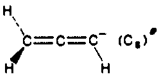
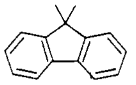
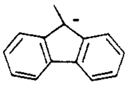
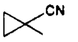
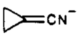
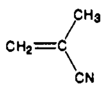
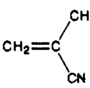
		calcd ΔH_f		deprotonation enthalpy			exptl	error in calcd ΔH_f	
HB	B^-	HB	B^-	calcd	exptl[b]	error	ΔH_f(HB)[c]	HB	B^-
				Carbon Acids					
CH_4	CH_3^-	−8.8[a]	57.7	433.7	416.6	17.1	−17.8	9.0	26.1
CH_3CH_3	$CH_3CH_2^-$	−17.4[a]	34.5	419.1	421.0	−1.9	−20.0	2.6	0.7
$CH_3CH_2CH_3$	$CH_3C^-HCH_3$	−24.3[a]	16.7	408.2	419.0	−10.8	−25.0	0.7	−10.1
$(CH_3)_3CH$	$(CH_3)_3C^-$	−29.4[a]	3.1	399.7	414.0	−14.3	−32.1	2.7	−11.6
		17.8[a]	67.6	417.0	412.0	5.0	12.7	5.1	10.1
		6.6[a]	27.6	388.2	390.7	−2.5	4.8	1.8	−0.7
			50.6	411.2					
			56.4	417.0					
			56.7	417.3					
$CH_2{=}C(CH_3)_2$		−1.2[a]	20.7	389.1	390.3	−1.2	−4.0	2.8	1.6
		23.3	42.5	386.4	385.0	1.4	18.0	5.3	6.7
		37.1[a]	25.2	355.3	356.1	−0.8	32.1	5.0	4.2
		38.3[a]	39.6	368.5	373.9	−5.4	43.2	−4.9	−10.3
$CH_2{=}CH_2$		16.5[a]	67.8	418.5	406.0	12.5	12.5	4.0	16.5
$HC{\equiv}CH$	$HC{\equiv}C^-$	54.8[a]	89.1	401.5	375.4	26.1	54.5	0.3	26.4
					384.5	17.0			17.3
$CH_3C{\equiv}CH$	$CH_3C{\equiv}C^-$	43.4[a]	74.9	398.7	379.7	19.0	44.2	−0.8	18.2
			64.5	388.3					
			73.1	396.9[f]					
$CH_3(CH_2)_2C{\equiv}CH$	$CH_3(CH_2)_2C{\equiv}C^-$	30.6	60.8	397.4	378.4	19.0	34.7[g]	−4.1	14.9
$(CH_3)_3CC{\equiv}CH$	$(CH_3)_3CC{\equiv}C^-$	30.8	60.3	396.7	376.7	20.0	25.1[g]	5.7	25.7
$C_6H_5C{\equiv}CH$	$C_6H_5C{\equiv}C^-$	76.5	94.3	385.0	370.4	14.6	78.3[g]	−1.8	12.8
C_6H_6	$C_6H_5^-$	22.0[a]	57.4	402.6	398.8	3.8	19.8	2.2	6.0
$C_6H_5CH_3$	$C_6H_5CH_2^-$	14.5[a]	20.8	373.5	379.4	−5.9	12.0	2.5	−3.4
$4\text{-}CH_3C_6H_4CH_3$	$4\text{-}CH_3C_6H_4CH_2^-$	6.8	12.2	372.6	380.5	−7.9	4.3	2.5	−5.4
$C_6H_5CH_2CH_3$	$C_6H_5C^-HCH_3$	8.8[a]	10.2	368.6	378.3	−9.7	7.2	1.6	−8.1
$C_6H_5CH(CH_3)_2$	$C_6H_5C^-(CH_3)_2$	4.7	2.5	365.0	377.5	−12.5	1.0	3.7	−8.8
$(C_6H_5)_2CH_2$	$(C^{\cdot}{}_6H_5)_2CH^-$	42.1	29.2	354.3	364.5	−10.2	33.2	8.9	−1.3
		54.4	36.1	348.9	353.3	−4.4	45[h]	9	5
HCN	CN^-	31.0[a]	44.0	380.2	353.1	27.1	32.3[i]	−1.3	25.8
CH_3CN	CH_2CN^-	19.3[a]	30.8[a]	378.7	372.1	6.6	15.4	3.9	10.5
CH_3CH_2CN	CH_3CHCN^-	13.0[a]	17.9	372.1	373.7	−1.6	12.3	0.7	0.9
$(CH_3)_2CHCN$	$(CH_3)_2CCN^-$	8.5	7.5	366.2	373.8	−7.6	5.6	2.9	−4.7
		48.8	56.1	374.5	374.1	0.4	43.5	5.3	5.7
CH_3OCH_2CN	CH_3OCHCN^-	−17.1	−16.0	368.3	371.4	−3.1	−13.0[g]	−4.1	−7.2
$C_6H_5CH_2CN$	$C_6H_5CHCN^-$	46.7	26.9	347.4	353.3	−5.9	44.5[g]	2.2	−3.7
		38.0	43.8	373.0	371.6	1.4	36.0[g]	2.0	3.4
CH_3OCH_3	$CH_3OCH_2^-$	−53.2[a]	−8.6	411.8	407.0	4.8	−44.0	−9.2	−4.4
CH_3CHO	CH_2CHO^-	−41.6[a]	−37.2	371.6	366.4	5.2	−39.7	−1.9	3.3

Table V (Continued)

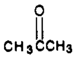
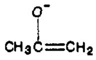
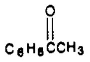
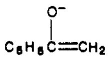
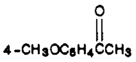
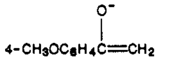
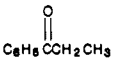
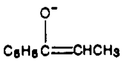
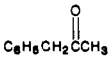
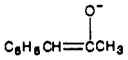
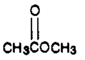
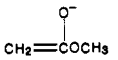
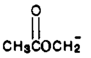
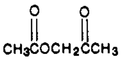
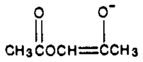
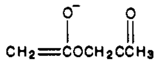
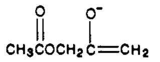
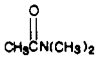
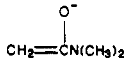
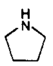
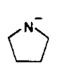
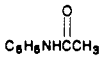
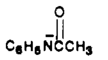
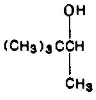
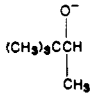
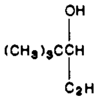
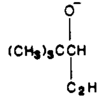
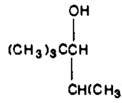
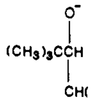
		calcd ΔH_f		deprotonation enthalpy			exptl	error in calcd ΔH_f	
HB	B^-	HB	B^-	calcd	exptl[b]	error	$\Delta H_f(HB)$[c]	HB	B^-
	CH_3CO^-		-14.1	394.7					
CH_3CH_2CHO	CH_3CHCHO^-	-48.0[a]	-49.9	365.3	365.7	-0.4	-44.4	-3.6	-4.0
 $CH_3\overset{O}{\overset{\|}{C}}CH_3$	 $CH_3\overset{O^-}{\overset{\|}{C}}{=}CH_2$	-49.2[a]	-43.6	372.8	368.8	4.0	-51.9	2.7	6.7
 $C_6H_5\overset{O}{\overset{\|}{C}}CH_3$	 $C_6H_5\overset{O^-}{\overset{\|}{C}}{=}CH_2$	-15.0	-15.9	366.3	363.2	3.1	-20.7	5.7	8.8
 $4\text{-}CH_3OC_6H_4\overset{O}{\overset{\|}{C}}CH_3$	 $4\text{-}CH_3OC_6H_4\overset{O^-}{\overset{\|}{C}}{=}CH_2$	-52.7	-55.3	364.6	362.8	1.8	-59.8	7.1	8.9
 $C_6H_5\overset{O}{\overset{\|}{C}}CH_2CH_3$	 $C_6H_5\overset{O^-}{\overset{\|}{C}}{=}CHCH_3$	-20.8	-26.5	361.5	362.4	-0.9	-26.0	5.2	4.3
 $C_6H_5CH_2\overset{O}{\overset{\|}{C}}CH_3$	 $C_6H_5CH{=}\overset{O^-}{\overset{\|}{C}}CH_3$	-20.3	-41.0	346.5	352.5	-6.0	-24.1	3.8	-2.2
 $CH_3\overset{O}{\overset{\|}{C}}OCH_3$	 $CH_2{=}\overset{O^-}{\overset{\|}{C}}OCH_3$	-96.4[a]	-94.2	369.4	371.0	-1.6	-98.4	2.0	0.4
	 $CH_3\overset{O}{\overset{\|}{C}}OCH_2^-$		-63.3	400.3					
 $CH_3\overset{O}{\overset{\|}{C}}OCH_2\overset{O}{\overset{\|}{C}}CH_3$	 $CH_3\overset{O}{\overset{\|}{C}}OCH{=}\overset{O^-}{\overset{\|}{C}}CH_3$	-131.1	-141.8	356.5	350.3[j]	6.2	-137.9[k]	6.8	13.0
	 $CH_2{=}\overset{O^-}{\overset{\|}{C}}OCH_2\overset{O}{\overset{\|}{C}}CH_3$		-138.7	359.6					
	 $CH_3\overset{O}{\overset{\|}{C}}OCH_2\overset{O^-}{\overset{\|}{C}}{=}CH_2$		-133.6	364.7					
 $CH_3\overset{O}{\overset{\|}{C}}N(CH_3)_2$	 $CH_2{=}\overset{O^-}{\overset{\|}{C}}N(CH_3)_2$	-33.6	-33.3	367.5	373.5	-6.0	-55.6[h]	22.0	16.0
CH_3NO_2	$CH_2{=}NO_2^-$	-9.9[a]	-29.2[a]	347.9	358.7 357.6	-10.8 -9.7	-17.8	7.9	-2.9
$CH_3CH_2NO_2$	$CH_3CH{=}NO_2^-$	-16.8	-39.0	345.0	358.1	-13.1	-24.5	7.7	-5.4
$(CH_3)_2CHNO_2$	$(CH_3)_2C{=}NO_2^-$	-21.5	-46.0	342.7	358.2	-15.5	-33.2	11.7	-3.8
$(CH_3)_3CCH_2NO_2$	$(CH_3)_3CCH{=}NO_2^-$	-30.7	-53.0	344.9	357.3	-12.4	-45.2[g]	14.5	2.1
				Nitrogen Acids					
NH_3	H_2N^-	-7.3[a]	52.5	427.0	403.6	23.4	-11.0[m]	3.7	27.1
CH_3NH_2	CH_3NH^-	-7.4[a]	33.1[a]	407.7	403.2	4.5	-5.5	-1.9	2.6
	$^-CH_2NH_2$		40.3	414.9					
$CH_3CH_2NH_2$	$CH_3CH_2NH^-$	-15.1[a]	27.4	409.7	399.4	10.3	-11.3	-3.8	6.5
$C_6H_5NH_2$	$C_6H_5NH^-$	20.7[a]	19.4	365.9	367.1	-1.2	20.8	-0.1	-1.3
$3\text{-}CH_3C_6H_4NH_2$	$3\text{-}CH_3C_6H_4NH^-$	13.0	12.1	366.3	367.5	-1.2	12.9[g]	0.1	-1.1
$4\text{-}CH_3C_6H_4NH_2$	$4\text{-}CH_3C_6H_4NH^-$	12.9	10.9	365.2	368.2	-3.0	12.9[g]	0.0	-3.0
$4\text{-}CH_3OC_6H_4NH_2$	$4\text{-}CH_3OC_6H_4NH^-$	-16.6	-21.2	362.6	368.0	-5.4	-16.5[g]	-0.1	-5.5
$(CH_3)_2NH$	$(CH_3)_2N^-$	-5.6[a]	22.4[a]	395.2	396.4	-1.2	-4.4	-1.2	-2.4
		39.9[a]	28.1[a]	355.4	360.8	-5.4	25.9	14.0	8.6
 $C_6H_5NH\overset{O}{\overset{\|}{C}}CH_3$	 $C_6H_5\bar{N}\overset{O}{\overset{\|}{C}}CH_3$	-15.0	-34.6	347.6	352.7	-5.1	-30.8	15.8	10.7
				Oxygen Acids					
H_2O	HO^-	-59.2[a]	-14.1[a]	412.3	390.8	21.5	-57.8[m]	-1.4	20.1
CH_3OH	CH_3O^-	-57.0[a]	-38.8[a]	385.4	379.2, 381.4[d]	6.2, 4.0	-48.2	-8.8	-2.6, -4.8
CH_3CH_2OH	$CH_3CH_2O^-$	-62.7[a]	-45.8[a]	384.1	376.1, 378.3[d]	8.0, 5.8	-56.2	-6.5	1.5, -0.7
$CH_3(CH_2)_2OH$	$CH_3(CH_2)_2O^-$	-70.6[a]	-53.7	384.1	374.7, 376.9[d]	9.4, 7.2	-61.0	-9.6	-0.2, +2.4
$(CH_3)_2CHOH$	$(CH_3)_2CHO^-$	-67.7[a]	-50.7	384.2	374.1, 376.3[d]	10.1, 7.9	-65.2	-2.5	7.6, 5.4
$(CH_3)_2CHCH_2OH$	$(CH_3)_2CHCH_2O^-$	-74.0	-59.5	381.7	373.4, 375.6[d]	8.3, 6.1	-67.9	-6.1	2.2, 0.0
$(CH_3)_3COH$	$(CH_3)_3CO^-$	-71.6[a]	-54.2	384.6	373.3, 375.5[d]	11.3, 9.1	-74.7	3.1	14.4, 12.2
$(CH_3)_3CCH_2OH$	$(CH_3)_3CCH_2O^-$	-76.5	-63.5	380.2	371.8, 374.0[d]	8.4, 6.2	-76.1[g]	-0.4	8.0, 5.8
 $(CH_3)_3C\underset{\underset{CH_3}{\mid}}{\overset{\overset{OH}{\mid}}{C}}H$	 $(CH_3)_3C\underset{\underset{CH_3}{\mid}}{\overset{\overset{O^-}{\mid}}{C}}H$	-79.7	-66.1	380.8	370.7	10.1	-83.8[g]	4.1	14.2
 $(CH_3)_3C\underset{\underset{C_2H_5}{\mid}}{\overset{\overset{OH}{\mid}}{C}}H$	 $(CH_3)_3C\underset{\underset{C_2H_5}{\mid}}{\overset{\overset{O^-}{\mid}}{C}}H$	-86.1	-73.2	380.1	369.6	10.5	-88.7[g]	2.6	13.1

Table V (Continued)

HB	B^-	calcd ΔH_f HB	calcd ΔH_f B^-	deprotonation enthalpy calcd	deprotonation enthalpy exptl[b]	deprotonation enthalpy error	exptl $\Delta H_f(HB)$[c]	error in calcd ΔH_f HB	error in calcd ΔH_f B^-
 $(CH_3)_3CCH(OH)CH(CH_3)_2$	 $(CH_3)_3CCH(O^-)CH(CH_3)_2$	-88.6	-76.4	379.4	368.5	10.9	-93.6[g]	5.0	15.9
$((CH_3)_3C)_2CHOH$	$((CH_3)_3C)_2CHO^-$	-86.3	-75.3	378.2	367.3	10.9	-99.1[g]	12.8	23.7
$CH_3O(CH_2)_2OH$	$CH_3O(CH_2)_2O^-$	-103.5	-92.2	378.5	372.5	6.0	-87.4[g]	-16.1	-10.1
$C_6H_5CH_2OH$	$C_6H_5CH_2O^-$	-31.2	-21.7	376.7	369.6	7.1	-24.0	-7.2	-0.1
	$C_6H_5C^-HOH$		-29.5	368.9					
C_6H_5OH	$C_6H_5O^-$	-22.2[a]	-41.0[a]	348.4	349.8	-1.4	-23.0	0.8	-0.6
4-$CH_3C_6H_4OH$	4-$CH_3C_6H_4O^-$	-29.8	-49.2	347.8	350.9	-3.1	-30.0	0.2	-2.9
HCO_2H	HCO_2^-	-97.4[a]	-110.0[a]	354.6	345.2	9.4	-90.5	-6.9	2.5
CH_3CO_2H	$CH_3CO_2^-$	-103.0[a]	-116.0[a]	354.2	348.5	5.7	-103.4	0.4	6.1
$CH_3CH_2CO_2H$	$CH_3CH_2CO_2^-$	-108.0[a]	-122.3	352.9	347.3	5.6	-108.4	0.4	6.0
$C_6H_5CO_2H$	$C_6H_5CO_2^-$	-68.0[a]	-86.9	348.3	338.3	10.0	-70.3	2.3	12.3
$CH_3CH{=}NOH$	$CH_3CH{=}NO^-$	-8.4	-22.8	352.8	366.2	-13.4	-4.7[l]	-3.7	-17.1
$(CH_3)_2C{=}NOH$	$(CH_3)_2C{=}NO^-$	-15.3	-31.3	351.2	366.7	-15.5	-13.0[g]	-2.3	-17.8
$(CH_3)_3CCH{=}NOH$	$(CH_3)_3CCH{=}NO^-$	-21.9	-37.4	351.7	364.6	-12.9	-23.2[g]	1.3	-11.6
$C_6H_5CH{=}NOH$	$C_6H_5CH{=}NO^-$	24.4	-5.5	337.3	355.1	-17.8	25.8[g]	-1.4	-19.2

[a] Reference 5. [b] Unless otherwise noted, experimental DPEs are from ref 52. [c] Unless otherwise noted, experimental heats of formation are from ref 38. [d] Reference 54. [e] Reference 40. [f] Calculated for the formation of propyne upon protonation. [g] Estimated in ref 52. [h] Reference 36a and references therein. [i] Reference 15. [j] Reference 1b. See text. [k] Estimated by group additivity method, ref 53. Value for C-$(H)_2(CO)(O)$ approximated as that for C-$(H)_2(O)(C)$. [l] Reference 52 and references therein. [m] Reference 39.

Table VI. Comparison of ab Initio and AM1 Deprotonation Enthalpies[9] (kcal/mol)

molecule	4-31+G//4-31+G DPE[a]	4-31+G//4-31+G error[b]	MP2/4-31+G//4-31+G DPE[a]	MP2/4-31+G//4-31+G error[b]	AM1 error[c]
C_2H_6	439.1	18.1	432.0	11.0	-1.9
C_2H_4	423.8	17.8	417.9	11.9	12.5
CH_2CHCH_3	405.5	14.8	399.1	8.4	-2.5
CH_3CN	386.1	14.0	383.4	11.3	6.6
CH_3CHO	374.5	8.1	369.2	2.8	5.2
CH_3NH_2	422.6	19.4	410.7	7.5	4.5
CH_3OH	393.1	12.8[d]	381.4	1.1[d]	5.1[d]
CH_3CH_2OH	391.7	14.5[d]	378.7	1.5[d]	6.9[d]
HCOOH	346.9	1.7	337.3	-7.9	9.4
Av Unsigned Error		13.5		7.0	6.0

[a] Reference 7. [b] Errors are calculated by using experimental values from Table V. [c] From Table V. [d] Based on the average of the two experimental values quoted in Table V.

$CH_2C{\equiv}CH$, C_{2v}). While the negative charge in the allenyl or propynyl anion is concentrated largely on a single carbon atom, in propargyl it is dispersed over an allylic system.

Experiment[43] indicates that the propynyl anion is lower in energy than the allenyl anion by 3 kcal/mol while ab initio calculations[8w,44,45] imply the allenyl anion is lower than propargyl by 7-9 kcal/mol. Thus the difference between the propargyl and propynyl anions is ca. 11 kcal/mol. By using the experimental[42] value for the heat of formation for the latter, we arrive at an estimate (68 kcal/mol) for that of propargyl anion, in good agreement with AM1 (64.5 kcal/mol). This supports the interpretation given above of the errors for allenyl and propynyl.

A similar situation is expected in the case of propene and its derivatives. While allyl anion is correctly predicted to be the most stable isomer, the difference between it and 1- or 2-propenyl anion is probably overestimated by AM1. The relative order of stability predicted by AM1 agrees with that given by MNDO[11] and by the ab initio calculations of Boerth and Streitwieser,[8mm] except that the E and Z isomers of 1-propenyl anion are predicted by AM1 to have essentially identical energies. AM1 also reproduces the effects of substituents at the central carbon atom, attributed by Bartmess and Burnham to be primarily polar in nature.[46]

The errors in the DPEs calculated for the nitro alkanes are also relatively large. These, however, are due primarily to errors in the heats of formation calculated for the neutral acids[5] rather than in those for their conjugate bases.

In all but one case AM1 overestimates the stabilizing effect of a methyl or phenyl substituent at the anionic center in a carbanion, the exception being the 2-nitro-2-propyl anion. The effect is most significant when the parent anion is primary, the error being approximately -8 kcal/mol for methyl substitution and -10 kcal/mol for phenyl substitution.[47]

The experimental evidence[48] and ab initio[7] calculations agree with the AM1 prediction that the α-hydrogens of carbonyl compounds are more acidic than the acyl hydrogen. The difference between the corresponding DPEs in acetaldehyde is calculated by AM1 to be 23 kcal/mol, in reasonable agreement with the value (29 kcal/mol) derived from 4-31 + G//4-31 + G and MP2/4-31 + G//4-31 + G calculations.[7] Additionally, AM1 predicts the lowest DPE in acetonyl acetate to be that for the methene hydrogens, in agreement with an earlier assignment.[1b] However, due to uncertainty concerning the change in entropy accompanying the loss of a methene hydrogen, neither the deprotonation site nor the experimental value of the DPE is firmly established.[49]

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(39) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Juttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Supplementary 2.

(40) The allenyl anion is not a stationary point on the AM1 surface. The AM1 ΔH_f value was calculated by fixing the ∠C-C-H value at the value optimized in ref 8w and forcing C_s symmetry. The same method was used in ref 11 to calculate the MNDO ΔH_f value (Olivella, S., personal communication).

(41) While ion cyclotron resonance data point to initial formation of acetylenic and propargylic (or allenic) anions, equilibration leads to the dominance of acetylenic anions at long times,[42] implying the propynyl anion is the most stable of the three. Likewise the allenyl anion has been found to be more stable than propargyl anion both experimentally[43] and by ab initio calculations.[8w,44,45]

(42) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046.

(43) Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 2969.

(44) Bushby, R. J.; Patterson, A. S.; Ferber, G. J.; Duke, A. J.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 2* **1978**, 807.

(45) Wilmshurst, J. K.; Dykstra, C. E. *J. Am. Chem. Soc.* **1980**, *102*, 4668. The "allenyl"-like structure optimized in this study had ∠C-C-C = 175.9°.

(46) Bartmess, J. E.; Burnham, R. D. *J. Org. Chem.* **1984**, *49*, 1382.

(47) Direct methyl and phenyl substitution on HO^-, H_2N^-, and HCC^- is not included in calculating these averages due to the excessive errors in the calculated ΔH_f values for these anions.

(48) Bartmess, J. E.; Caldwell, G.; Rozenboom, M. D. *J. Am. Chem. Soc.* **1983**, *105*, 340.

(49) Bartmess, J. E., personal communication.

(2) Nitrogen Acids. The average unsigned error in the DPEs calculated for the nitrogen acids listed in Table V is 6.1 kcal/mol. If NH_3 is eliminated for the reasons indicated above, the error is reduced to 4.1 kcal/mol and that for the heats of formation of the anions to 4.6 kcal/mol. These values again compare favorably with the corresponding error (4.1 kcal/mol) in the heats of formation of the neutral acids.

The relative acidities of methylamine and ethylamine are predicted incorrectly by AM1. This error is due to two systematic errors discussed above in detail, one being the error accompanying methyl substitution at an anionic site while the other involves increasing alkyl chain length. The prediction that methylamine behaves as a nitrogen acid rather than a carbon acid coincides with chemical intuition and with the ab initio results of Lohr and Ponas.[8d]

The acidities of *p*-methyl- and *p*-methoxyaniline are predicted incorrectly relative to aniline. These errors can again be attributed to the overestimation of the stabilizing effects of methyl groups attached to negatively charged carbon atoms.

(3) Oxygen Acids. For the oxygen acids listed in Table I, the average unsigned error in the DPEs is 9.4 kcal/mol.[16] The error in the case of H_2O has already been discussed. The errors for oximes are also significantly larger than those for the other compounds (see below). Excluding water and the oximes from the statistical analysis, the average unsigned error for the remaining 19 DPEs falls to 7.6 kcal/mol[16] and that in the heats of formation of the conjugate bases to 7.4 kcal/mol.[16] These are larger than the corresponding errors for the carbon acids or nitrogen acids, and they are also larger than the average unsigned error (5.0 kcal/mol) in the heats of formation of the parent acids. Since the errors associated with compounds containing oxygen are, in general, larger than those for hydrocarbons or nitrogen-containing compounds[5] and since the charge on oxygen in an oxygen-containing anion is usually large, it is not surprising that the AM1 errors for such species are larger than usual.

The large errors in the DPEs of oximes are due to overestimation of the stability of the conjugate bases. Given the tendency of AM1 to overestimate the stabilization associated with phenyl and methyl substitution on the anionic center (see above), the pattern of errors in the heats of formation of the variously substituted oximes is consistent with significant charge buildup on the methene carbon (i.e., errors in heat of formation are large and negative with methyl and phenyl substitution on the methene carbon but decrease significantly with *tert*-butyl substitution). Analysis of atomic charges in acetaldoxime indicates that 0.40 of the formal charge of the anion is on the methene carbon, with the methyl group absorbing another 0.13. Additionally, the coefficient of the methene carbon p-orbital in the HOMO increases from 0.57 in the neutral acid to 0.75 in the anion. These results point to an overestimation of charge delocalization by AM1 through a conjugated system terminated by a methyl or phenyl group, similar to the effect noted with the anilines.

While the decrease in the DPEs of aliphatic alcohols with increasing size of the alkyl group is reproduced qualitatively by AM1, the calculated difference (7.2 kcal/mol) between the highest DPE (CH_3OH) and the lowest DPE ($t\text{-}Bu_2CHOH$) is less than that observed (11.9–14.1 kcal/mol). Moreover, the order of decreasing DPEs is not in agreement with experiment. While the scatter in the errors of the calculated heats of formation of the neutral alcohols may be partly responsible, the major problem seems to lie in the increase in the errors with size of the alkyl groups. Thus AM1 does not fully reproduce the charge-induced dipole stabilization of the anions to which the trend in gas-phase acidities in alcohols has been attributed.[50,51]

The benzylic hydrogens are calculated to be more acidic than the hydroxyl hydrogen in benzyl alcohol. Applying a 10-kcal/mol correction to the heat of formation of the carbon anion to compensate for the overestimation by AM1 of the added stability due to phenyl substitution at an anionic center, the hydroxyl hydrogen becomes the more acidic, as is observed.[42]

(4) Comparison with Ab Initio Results. Table VI lists ab initio DPEs, without (4-31+G//4-31+G) and with (MP2/4-31+G//4-31+G) allowance for electron correlation by second-order Møller–Plesset (MP) perturbation theory,[7] for nine of the compounds included in Table I. Five other molecules included in both studies (CH_4, NH_3, H_2O, HCN, HCCH) have not been included in Table VI since it has already been recognized that AM1 cannot describe the corresponding conjugate bases adequately.

The basis set in the ab initio study includes diffuse AOs, known[7] to be essential for the proper description of anions. While a few ab initio values are better than the corresponding AM1 ones, the overall average error is less for AM1.

Conclusions

With a few exceptions, AM1 seems to be an effective method for studying processes involving deprotonation or protonation of neutral molecules. The errors in the calculated DPEs and PAs, as well as in the calculated heats of formation of deprotonated and protonated species, are comparable with those in the calculated heats of formation of the neutral precursors. Intramolecular hydrogen bonding in protonated bifunctional bases is also effectively reproduced.

The main problems encountered with AM1 involve small anions, in which the charge is largely concentrated on one atom and anions formed by the deprotonation of oximes. Systematic errors accompany introduction of methyl or phenyl substituents at anionic centers. Systematic errors also arise in the extension of alkyl chains by addition of methene groups and in substitution of amine and hydroxyl groups for methyl groups bonded to secondary or tertiary carbons in neutral molecules. The errors involved in the deprotonation of alcohols and protonation of amines are not, however, totally systematic. As a result, the relative DPEs of alcohols and PAs of amines are not accurately reproduced by AM1.

The comparisons in Tables IV and VI suggest that AM1 performs as well here as do quite high level ab initio procedures.[55] The fact that the comparisons refer only to a few simple cases is due simply to the dearth of relevant ab initio data. Calculations at this level, if carried out with full geometry optimization, become very expensive for larger molecules. Since the accuracy achieved by AM1 is sufficient for the results to be chemically useful and since it can be used to study reactions of quite large molecules

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(50) Taft, R. W. In *Progress in Physical Organic Chemistry*; Taft, R. W., Ed.; Wiley: New York, 1983; Vol. 14, pp 276–283.

(51) Recent experimental evidence has indicated alkyl group size—acidity relationships are also present in the neutral alcohol molecules. (Chauvel, J. P., Jr.; True, N. S. *Chem. Phys.* **1985**, *95*, 435.) This calls into question the relative importance of charge-induced dipole stabilization of anions in determining the relative acidities of alcohols.

(52) Bartmess, J. E., intended for publication in *J. Phys. Chem. Ref. Data*.

(53) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; Chapter 2.

(54) These values are based on a proposed change to the anchor point at the methanol end of the acidity scale. (Moylan, C. R.; Brauman, J. I. *J. Phys. Chem.* **1984**, *88*, 3175.) Moylan et al. suggest the discrepancy is the result of difficulties in studying reactions of HF, the previous anchor point. Bartmess has indicated[52] the discrepancy may be due to the temperature correction problem in ICR work.[1b,36a]

(55) Wiberg[56] and Ibrahim and Schleyer,[57] have shown that good estimates of heats of formation of organic molecules can be obtained from ab initio total energies (6-31G* basis set) by applying empirical corrections based on group additivity relationships or their equivalent. A similar scheme could probably be developed for calculating PAs and DPEs. Such an approach could not, however, be used to study reactions for the same reason that molecular mechanics cannot be used in this connection, i.e., the fact that empirical corrections cannot be derived for the variable partially bonded groups present in transition states.

Koppel et al.[8qqq] have recently carried out linear regressions on ab initio PAs and DPEs calculated by using various basis sets (STO-3G, 3-21G, 4-31G, 6-31G*, 3-21+G, 4-31+G) and with the 6-31G** basis set using fourth-order Møller–Plesset perturbation theory. This procedure leads to a much better fit with experiment. However, even with these corrections, the results become markedly superior to our uncorrected ones only at or above the 6-31G* level. The computing time required restricts such procedures to reactions of very small molecules.

(56) Wiberg, K. B. *J. Comput. Chem* **1984**, *5*, 197.

(57) Ibrahim, M. R.; Schleyer, P. v. R. *J. Comput. Chem* **1985**, *6*, 157.

at moderate cost, AM1 should prove useful as an aid in interpretating proton transfer in chemistry and biochemistry.

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Ab Initio Calculations of the Singlet–Triplet Energy Separation in 3,4-Dimethylenefuran and Related Diradicals

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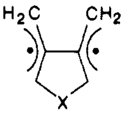
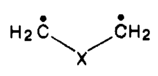
Abstract: Ab initio π CI calculations predict a singlet ground state for the title diradical (**2**). In order to determine the effect of the oxygen in **2** on the singlet–triplet splitting, additional calculations on the diradicals in which this heteroatom was replaced by a methylene (**1**) or by an amino group (**3**) have been performed, and the singlet–triplet splitting in carbonyl ylide (**5**) has also been computed. The results of these calculations show that the π nonbonding electrons on oxygen have but a mildly perturbative effect on the size of the singlet–triplet splitting in **2**.

Violations of Hund's rule[1] have been predicted to be possible for diradicals in which the two nonbonding MOs are confined to disjoint sets of atoms.[2,3] Berson and co-workers have obtained experimental evidence that indicates a singlet ground state for 3,4-dimethylenefuran (**2**)[4]—a diradical which, if viewed as a derivative of planar tetramethyleneethane,[2,3,5] is disjoint. In this paper we report the results of ab initio calculations on **2**. In agreement with Berson's experimental results and with a previous semiempirical study,[6] our calculations indicate a singlet ground state for **2**.



1: X = CH_2
2: X = O
3: X = NH



4: X = CH_2
5: X = O
6: X = NH

In order to determine the effect of the oxygen in **2** on the singlet–triplet splitting, calculations on the diradicals in which this heteroatom was replaced by a methylene (**1**) or by an amino group (**3**) have been performed, and the singlet–triplet splitting in carbonyl ylide **5** has also been computed. The results of these calculations show that the π nonbonding electrons on oxygen have but a mildly perturbative effect on the size of the singlet–triplet splitting in **2**.

The geometries of **1–3** were optimized by unrestricted Hartree–Fock (UHF) calculations[7] on the lowest triplet state of each diradical, using the STO-3G basis set.[8] Previous work has shown that triplet UHF optimizations should give reasonable geometries for these diradicals.[9,10] The optimized geometries are available as supplementary material.

In order to calculate the singlet–triplet energy splittings in **1–3**, CI calculations[11] were performed at the optimized geometries, using the Dunning [9s,5p] → [3s,2p] split-valence (SV) basis set.[12] Two types of CI calculations were performed for the lowest singlet and triplet state of each diradical. The first included all excitations through quadruples (SDTQ CI) within a conceptual minimal basis set of 7 π MOs for **2** and **3** and 8 π MOs for **1**.[13] The second involved multi-reference SD CI, using the entire π orbital basis set. Included in the reference space were all those configurations with SDTQ CI coefficients larger than 0.12 and most of the configurations with coefficients greater than 0.10. Comparable configurations were included in the reference space for the singlet and triplet states to ensure that the configuration selection did not bias the computed energy differences. The results of our CI calculations are contained in Table I.

In **1** the in-phase combination of the allylic nonbonding MOs ($3b_1$) and the out-of-phase combination ($2a_2$) are nearly degenerate in energy.[14] This is reflected in the fact that the two dominant configurations, $|...2a_2^2\rangle$ and $|...3b_1^2\rangle$, in the CI wave functions for

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[1] Hund, F. *Z. Phys.* **1925**, *33*, 345.

[2] Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

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[4] Stone, K. J.; Greenberg, M.; Goodman, J. L.; Peters, K. S.; Berson, J. A. *J. Am. Chem. Soc.*, in press.

[5] (a) Dowd, P. *J. Am. Chem. Soc.* **1970**, *92*, 1066. (b) Roth, W. R.; Erker, G. *Agnew. Chem., Int. Ed. Engl.* **1973**, *12*, 503. (c) Roth, W. R.; Scholz, B. P. *Chem. Ber.* **1982**, *115*, 1197 and references therein.

[6] Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2273.

[7] These calculations were performed with Gaussian 82: Binkley, J. S.; Frisch, M.; Raghavachari, Fluder, E.; Seeger, R.; Pople, J. A.

[8] Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. The bond lengths for **2** that were found with this basis set were all within 0.02 Å of those optimized with the 3-21G basis set (Lahti, P. Ph.D. Thesis, Yale University, 1985).

[9] Borden, W. T.; Davidson, E. R.; Feller, D. *Tetrahedron* **1982**, *38*, 737.

[10] Du, P.; Hrovat, D.; Borden, W. T.; Lahti, P.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 5072.

[11] CI calculations were perfomed with MELD, developed at the University of Washington by E. R. Davidson and co-workers.

[12] Dunning, T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 2.

[13] For these CI calculations two reference configurations were used for the $^1A_1$ states. The triplet RHF MOs and singlet TCSCF MOs were transformed to K orbitals (Feller, D.; Davidson, E. R. *J. Chem. Phys.* **1981**, *74*, 3977), which were used, respectively, for the CI calculations on $^3B_2$ and $^1A_1$. Test computations on **1** showed that K orbitals from a TCSCF calculation on $^1A_1$ gave the same singlet and triplet CI energies as the K orbitals from an RHF calculation on $^3B_2$, but for **2**, **3**, and **5** the TCSCF derived K orbitals gave lower $^1A_1$ CI energies than did the K orbitals from the triplet RHF calculations.

[14] The orbital energies of $2a_2$ and $3b_1$ from an RHF calculation on $^3B_2$ differ by 5 kcal/mol, with $2a_2$ lower in energy.

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