wave or ordinary Fourier transform spectroscopy. This can be shown by analyzing the effect of the two proton pulses on the ABX system in terms of the Ernst formalism.[4,5]

(18) See Table V in D. M. Cheng and R. H. Sarma, *J. Am. Chem. Soc.*, **99**, 7333 (1977).

(19) Some modifications to the existing spin simulation programs would be required. For example, the nucleotides could be treated as seven-spin systems (one phosphorus and six protons) with the convention that all states with P_α are even numbered and those with P_β odd. All proton transitions between odd-numbered states could then be made negative. The iterative analysis should allow for the variation of only those coupling constants to which the local spectrum is sensitive.

Heat of Formation of the 2-Norbornyl Cation in the Gas Phase

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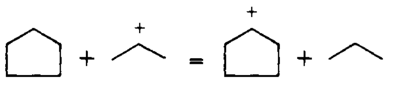
Received May 15, 1978

Abstract: Proton transfer equilibria BH^+ + 2-norbornene = B + 2-norbornyl$^+$ and their temperature dependence were measured with a high-pressure mass spectrometer. The entropy change obtained from a van't Hoff plot of the equilibrium constant indicates that there is no rearrangement on protonation, i.e., that the product from the reaction is the 2-norbornyl cation. The enthalpy change, when connected to a proton affinity ladder, leads to a heat of formation of the norbornyl cation which is in very good agreement with the earlier results by Field and by Beauchamp. Compared to other secondary cyclic ions like cyclopentyl, norbornyl is unusually stable.

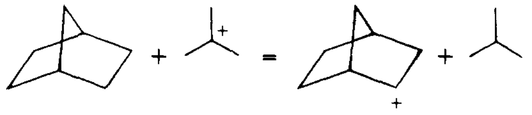
Introduction

Recently Solomon and Field[1] published several measurements of hydride ion transfer equilibria 1 measured with a pulsed high-pressure mass spectrometer. van't Hoff plots of K_1 lead to ΔH_1 and ΔS_1. In particular these authors deduced the energy changes for reactions 2, 3, and 4 (see Table I) which

$$R_1H + R_2^+ = R_1^+ + R_2H \quad (1)$$



(2)



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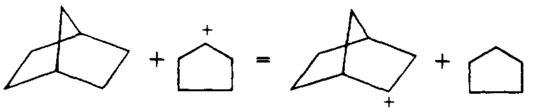
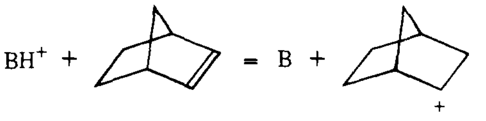


(4)

relate to the 2-norbornyl cation. The enthalpies for reactions 2 and 3 were obtained from van't Hoff plots of K_2 and K_3 while ΔH_4 was deduced from ΔH_2 and ΔH_3 and available thermochemical data. Since in mass spectrometric measurements only the mass, but not the structure, of the ion is identified, the assumption was made that the ionic product in reaction 3 is the most stable ion resulting from hydride abstraction without skeletal rearrangement, i.e., the 2-norbornyl cation. Reaction 4 shows that the norbornyl cation, which is nominally a secondary ion, is 11.4 kcal/mol more stable than the cyclopentyl cation.

Because of the importance of Solomon and Field's[1] results it is clearly desirable to obtain additional experimental data for the norbornyl cation. A second gas-phase route for production of the ion is the proton transfer reaction 5. This method was used in an early ion cyclotron resonance study by Kaplan,[2] which preceded Field's[1] work, and in a recent brief report by Beauchamp.[3] Kaplan's results[2] were not based on ion equilibria measurements but on the inferior[4] kinetic bracketing technique, which examines the direction in which a proton transfer reaction like (5) proceeds with different standard bases B. The proton affinities of B used by Kaplan were early values which were subsequently revised.



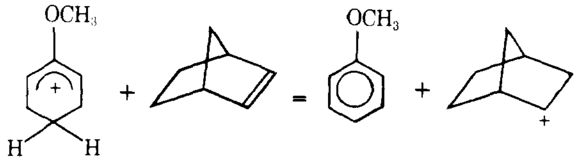
(5)

Beauchamp's[3] brief study gives results for equilibrium 5 with B = diethyl ether at room temperature. The known proton affinity of the ether with assumption of a small $\Delta S°_5$ leads[3] to a heat of formation of the 2-norbornyl cation which is in close agreement with Field's result.

The present work describes one more study of proton transfer equilibria 5. However, since the temperature dependence of K_5 was determined $\Delta S°_5$ could be evaluated. Knowledge of the magnitude of ΔS_5 is useful since a small entropy change can be taken as evidence that no extensive skeletal rearrangement has occurred, i.e., that the likely product of (5) is the 2-norbornyl cation.

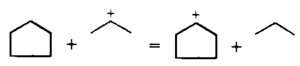
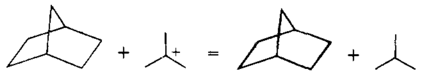
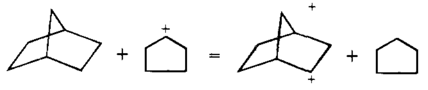
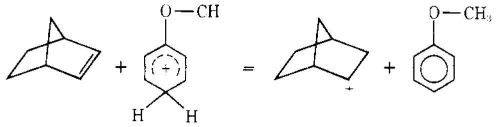
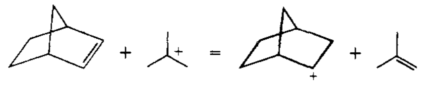
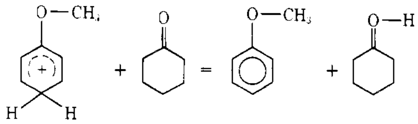
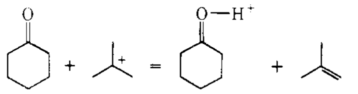
Results and Discussion

The temperature dependence of the equilibrium constant K_6 for proton transfer reaction 6 (see Table I) was determined in a number of runs with a pulsed electron beam high-pressure mass spectrometer (see Experimental Section). A van't Hoff plot of K_6 is shown in Figure 1. The invariance of K_6 with changing ratio of anisole and norbornene and total ion source pressure was tested at every temperature. Some of these results are also shown in Figure 1. The energy and entropy changes for reaction 6 are given in Table I. Anisole was selected as the



(6)

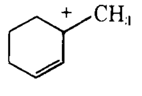
Table I. Summary of Thermochemical Data[a]

	ΔH[b]	ΔG[c]	ΔS
(2) 	−5.9[d]	−6.7 (300)[d]	+2.6[d]
(3) 	−1.5[d]	−2.3 (300)[d]	+2.8[d]
(4) 	−11.4[d]		
(6) 	−0.1	+1.5 (560 +0.78 (300)	−2.8
(7) 	−4.3[e] −4.8[f] ≤−6.1[g]		
ΔH_f(2-norbornyl$^+$) = 182.3[h] 181.8[k] 181.8[l]			
(8) 	~(−1.9)	−1.9 (560)	
(9) 	−6.1[m]	−7.4 (560)[m]	

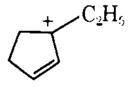
[a] All energies in kcal/mol, entropies in cal/deg. Rotational symmetry numbers used for ΔS estimates of proton transfer reactions: anisole, 1; anisole H$^+$, 1; isobutane, 2; *tert*-butyl$^+$, 6; Et$_2$OH$^+$, 1; Et$_2$O, 2; 2-norbornene, 1; 2-norbornyl$^+$, 1; cyclohexanone, 1; cyclohexanone H$^+$, 1. [b] Enthalpy changes near room temperature. [c] Figure in parentheses gives temperature in K. [d] Solomon and Field.[1] [e] Calculated from ΔH_6 = −0.1 kcal/mol (present work) and $\Delta G°$ (600) = −5.5 kcal/mol for reaction *tert*-butyl$^+$ + anisole = isobutene + anisole H$^+$ (see proton affinity ladder, Figure 1, ref 5). Using rotational symmetry numbers from footnote *a*, one evaluates ΔS and the corresponding ΔH = −4.2 kcal/mol which combined with ΔH_6 leads to ΔH_7 = −4.3 kcal/mol. [f] From Beauchamp's[3] result $\Delta G°$ (300) = −0.5 kcal/mol for reaction Et$_2$OH$^+$ + 2-norbornene = Et$_2$O + norbornyl$^+$. Evaluating ΔS with use of symmetry numbers from footnote *a*, one obtains ΔH = −0.9 kcal/mol. This combined with ΔH = −3.9 kcal/mol (McIver, Beauchamp, Taft[7]) for proton transfer from *tert*-butyl$^+$ to Et$_2$O leads to ΔH_7 = −4.8 kcal/mol. [g] $\Delta G°_8$ = −1.9 kcal/mol combined with $\Delta G°$ = 5.5 kcal/mol (see footnote *e*) leads to $\Delta G°_9$ (560) = −7.4 kcal/mol. Kaplan's result[2] $\Delta G° \leq 0$ for cyclohexanone H$^+$ + 2-norbornene = cyclohexanone + 2-norbornyl$^+$ leads to $\Delta G°_7$ (560) = −7.4 kcal/mol. Evaluating $\Delta S°_7$ with symmetry numbers from footnote *a* one obtains $\Delta H_7 \leq -6.1$ kcal/mol (Kaplan). [h] From present ΔH_7 = −4.3 kcal/mol and ΔH_f(2-norbornene) = 19.1 kcal/mol (Kozina[8]), ΔH_f(*tert*-butyl) = 163.5 kcal/mol (Beauchamp[10]) and ΔH_f(*i*-C$_4$H$_8$) = −4.04 kcal/mol (Rossini[9]). [k] From ΔH_7 = −4.8 kcal/mol (Beauchamp, see footnote *f*) and other values as in footnote *h*. [l] From ΔH_3 = −1.5 kcal/mol (Field[1]), ΔH_f(norbornane) = −12.4 kcal/mol (Boyd[8]); other values as in footnote *h*. [m] For evaluation of ΔG_9 see footnote *g*. ΔH_9 obtained from ΔG_9 by estimating ΔS_9 on basis of symmetry numbers in footnote *a*.

standard base B for several reasons. The proton affinity of anisole was determined recently as part of a free-energy ladder connecting to isobutene[5,6] and thus also the *tert*-butyl cation. Second, the temperature dependence of proton transfer reactions involving several substituted benzenes was determined recently[6] and it was found that the ΔS changes for these systems could be accurately calculated on basis of rotational symmetry number changes alone. Third, anisole is ring protonated,[6] and the resulting benzenium ion has strongly delocalized charge and therefore much lower tendency to form proton-held dimers (B)$_2$H$^+$ than oxygen (and nitrogen) bases like alcohols and ethers. The absence of such dimers permits the extension of the high-pressure mass spectrometry equilibrium measurements to lower temperatures.[5] Finally, as evident from the energy changes obtained for reaction 6 (Table I), the basicity of anisole is very close to that of norbornene so that the slightly endothermic, proton transfer (6) is very gentle, i.e., does not involve a large exothermicity, which might promote rearrangement of the norbornyl cation. The fact that protonated anisole is charge delocalized means also that the energy release on formation of the transition complex (anisole·H$^+$·norbornene) is also lower than would have been the case with a BH$^+$ in which most of the charge resides on the proton. This of course also reduces the energy contained in the complex and thus the likelihood for rearrangement.

The entropy change ΔS_6 = −2.8 cal/deg is quite small. Since there is no change in rotational symmetry numbers in reaction 6 the 2.8 cal/deg must be due to some other small changes. The important point is that a change of structure from the 2-norbornyl cation to ions with structures like I and II



I



II

(which could be expected to be of low energy of formation, see also Field[1]) will create near-free internal rotations of the methyl (structure I) and ethyl groups (structure II). Thus if reaction 6 led not to norbornyl but to ions like I or II, ΔS would have been not negative but positive and in the range 2–10 cal/deg.

The ΔH_6 obtained in the present work can be connected via a gas-phase basicity ladder[8] (see footnote *g*, Table I) to isobutene and *tert*-butyl$^+$. This provides ΔH_7 = −4.3 kcal/mol, which is very close to ΔH_7 = −4.8 kcal/mol obtained by

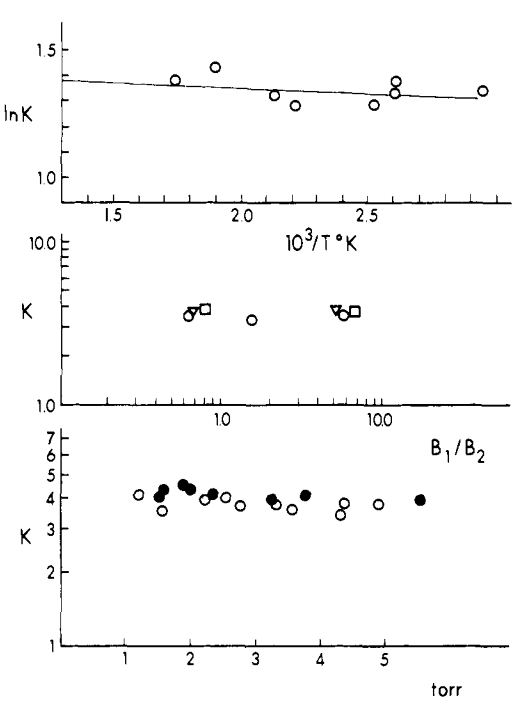
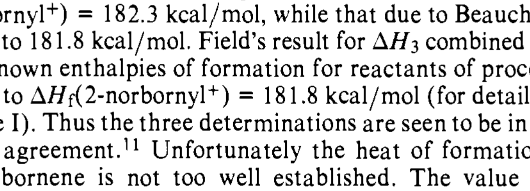


Figure 1. Top: van't Hoff plot of equilibrium constant K (Torr^{-1}) for reaction H^+(norbornene-2) + anisole = norbornene-2 + H^+ anisole. Middle: checks for independence of K with changes of partial pressures ratio B_1/B_2 = norbornene/anisole. ○, 395 K; ▽, 451 K; □, 419 K. Bottom: checks for independence of K with changes of total ion source pressure at constant B_1/B_2 ratio. Major gas: methane. ○, 383 K; ●, 525 K.

combining Beauchamp's[3] measurement to the McIver-Beauchamp-Taft[7] basicity ladder (see footnote *f*, Table I).

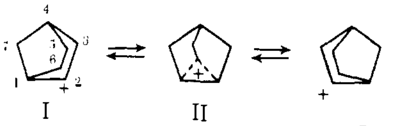
Also given in Table I is ΔG_8 measured in the present work for the proton transfer from anisole H^+ to cyclohexanone. Kaplan[2] reported fast proton transfer from cyclohexanone H^+ to 2-norbornene which indicates, provided that the reactant ions are thermalized, that the corresponding $\Delta G°$ for this reaction is zero or negative. Kaplan's result combined with the present $\Delta G°_8$ and a basicity ladder[5] leads to an upper limit for $\Delta H_7 \leq -6.1$ kcal/mol. This limit is in fair agreement with the $\Delta H_7 \approx -4.6$ kcal/mol from the present and Beauchamp's work. Kaplan's measurements might have been somewhat affected by the presence of excess internal energy in the ionic reactant.[4]

Enthalpies of formation for all reactants in reaction 7, except


(7)

the norbornyl cation, are available in the literature.[8-10] This permits the evaluation of the heat of formation of nonbornyl cation. The ΔH_7 from the present results leads to ΔH_f(2-norbornyl$^+$) = 182.3 kcal/mol, while that due to Beauchamp leads to 181.8 kcal/mol. Field's result for ΔH_3 combined with the known enthalpies of formation for reactants of process 3 leads to ΔH_f(2-norbornyl$^+$) = 181.8 kcal/mol (for details see Table I). Thus the three determinations are seen to be in very good agreement.[11] Unfortunately the heat of formation of 2-norbornene is not too well established. The value 19.1 kcal/mol due to Kozina[8] was used in the present calculation in preference to a value of 15.1 kcal/mol due to Hall,[8] since Kozina's value taken together with the established ΔH_f(norbornane) = −12.4 kcal/mol (Boyd[8]) is more consistent with the −33.1 kcal/mol enthalpy of hydrogenation of 2-norbornene determined by Turner[8] (albeit in solution of acetic acid) than the value due to Hall.[8] The absolute accuracy of the average ΔH_f(2-norbornyl$^+$) = 182 kcal/mol (Table I) is difficult to estimate, but one should count with an error around ±2 kcal/mol.

The gas-phase energetics in Table I show that the 2-norbornyl cation has special stability. Most convincing is the comparison of the exothermicities of reactions 2 and 4. The hydride ion transfer in reaction 2 involves cyclopentyl and the isopropyl cation and has an exothermicity of 5.9 kcal/mol. The change from isopropyl to cyclopentyl corresponds to a CH_2-CH_2 bridge insertion in positions α,α' to the secondary carbenium ion carbon. The change from cyclopentyl to 2-norbornyl, relating to reaction 4, involves again the insertion of a CH_2-CH_2 bridge into cyclopentyl in position α,β to the secondary carbenium ion carbon. Assuming that the stabilization in reaction 2 is due to the operation of the "usual" factors, i.e., increased polarizability and hyperconjugation, then the operation of the same factors in reaction 4 should lead to an exothermicity which is slightly lower than that of reaction 2. Since $\Delta H_4 = -11.4$ kcal/mol, some 6 kcal/mol additional exothermicity in reaction 4 must be assigned to special factors due to the specific structure of norbornyl cation. One possible explanation is to assume that the norbornyl cation does not have the classical structure I but the symmetric nonclassical structure II and that II confers special stability.[14] On principle,



(10)

I II III

the gas-phase energetics of the isodesmic reaction 4 and the geometries and relative energies of the norbornyl ions I and II could be provided by quantum mechanical calculations. Unfortunately, because norbornyl is a large molecule which also lacks simplifying symmetry, accurate ab initio calculations involving complete geometry optimization and electron correlation corrections would be prohibitively expensive. The most recent calculation by Allen[15] using limited geometry optimization and STO-3G and 4-31G basis sets predicted slightly higher energy for the nonclassical ion. The inclusion of electron correlation is expected[15] to favor the nonclassical ion placing its energy a few to several kilocalories per mole below the classical structure. Dewar's[16] recent, more completely geometry optimized but semiempirical MINDO/3 predicts a slightly higher energy for the nonclassical norbornyl cation.[17] Jorgensen,[18] using Dewar's classical norbornyl cation, has calculated a MINDO/3 predicted enthalpy change for reaction 4, ΔH_4(MINDO) = −4.2 kcal/mol. Comparing this with the experimental value $\Delta H_4 = -11.4$ kcal/mol (Table I), one sees that MINDO/3 underestimates the stabilities of the classical and nonclassical norbornyl cations.

Since more accurate calculations may become feasible in the near future, it is of interest to consider whether gas-phase energetics like those for reaction 4 and theoretical calculations are pertinent to solving the classical-nonclassical norbornyl ion controversy,[14] which involves solvolysis reactions in condensed media. Brown[19] has succinctly stated the problem on the basis of reaction 10 occurring in solution. The "classical" view[19] considers that the rearrangement between the classical isomers I and III proceeds via the nonclassical ion II, which is of higher energy and thus a transition state. Since the equilibration I to III is very rapid at low temperatures, the (nonclassical) intermediate II can be of higher energy by only a few kilocalories per mole.[19] In the nonclassical view, the ion II (in solution) is of lower energy than the classical ions I and III, and thus not a transition state but the stable ion. To relate reaction 10 to the gas phase one has to include the energy change due to the differential solvation of the cations. Jorgensen[18] has pointed out, and supported his argument with

MINDO/3 calculations, that the nonclassical ion, which should be more charge delocalized, will be probably less well solvated by the nucleophilic solvents commonly used. Since according to the "classical position" the difference between the energies of I and II in solution was small, inclusion of the differential solvation means that this difference in the gas phase should be even smaller. Thus the "classical position"[19] requires that the gas-phase energies of the classical and nonclassical structures should be very close, i.e., both structures lying within an energy plateau. On the other hand, the "nonclassical" position requires that the gas-phase energy of the nonclassical ion is lower (by a small or large amount) than the gas-phase energy of the classical ion. Since the gas-phase energies in Table I showed that the norbornyl cation is endowed with special (~6 kcal/mol) stability, the "classical position" with nearly isoenergetic ions suggests that the same stabilizing factors act on both ions. The significant participation of the C(1)-C(6) bond orbital to the LUMO of the classical norbornyl cation predicted by MINDO/3 (Jorgensen[18]), if real and occurring also in the nonclassical ion, might be such a factor. On the other hand, if reliable future theoretical calculations show that the nonclassical structure is significantly more stable, the special gas-phase stability found experimentally would be explained and the nonclassical position proven correct.

Experimental Section

The measurements were made with a high ion source pressure mass spectrometer used for proton transfer equilibria already described in earlier work.[5,6,20] The techniques used were also the same.[20] The two bases B_1 and B_2 were generally in the 0.5-50-mTorr range and CH_4 was used as a carrier gas at total pressures in the 1-4-Torr range.

Acknowledgment. The authors acknowledge some helpful correspondence with Professors H. C. Brown, M. J. S. Dewar, W. L. Jorgensen, and P. v. R. Schleyer.

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(3) R. H. Staley, R. D. Wieting, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 5964 (1977).

(4) The bracketing technique, apart from giving only the sign of the ΔG for the proton transfer, may also give erroneous results since the participating ions may be excited. This error is avoided in the equilibrium techniques since the ions observed at equilibrium should have suffered many excitation quenching collisions.

(5) P. Kebarle, *Annu. Rev. Phys. Chem.*, **28**, 445 (1977).

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(10) F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, to be published. (Some of the results of above paper were communicated to the present authors by Professor Beauchamp.)

(11) The reader should be alerted to the fact that $\Delta H_f(tert\text{-butyl}^+) = 163.5$ kcal/mol used in the above evaluations is a new value due to a new determination of the ionization potential of the *tert*-butyl radical by Houle and Beauchamp.[10] This value is considerably lower than the 169 kcal/mol widely used previously and based on work by Lossing.[12] The use of the old value leads to a $\Delta H_f(2\text{-norbornyl}^+) \approx 187.5$ kcal/mol. The ionization potential measurements of Houle and Beauchamp[10] also lower the IP of *sec*-propyl radical. Fortunately the lowering of the IP is essentially the same as that for *tert*-butyl so that the thermochemical evaluation of ΔH_4 from ΔH_2 and ΔH_3 is not affected. The old $\Delta H_f(t\text{-}C_4H_9^+) = 169$ kcal/mol was also used as primary standard in proton affinity ladders (see ref 5 and 7). That value connected to ladders[5,7] extending to ammonia led to $PA(NH_3) = 202.3$ kcal/mol. The new value of Beauchamp[10] connected to the same ladders[5,7] (and $\Delta H_f(H^+) = 367.1$ kcal/mol) leads to $PA(NH_3) \approx 207$ kcal/mol.[10]

(12) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

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(16) M. J. S. Dewar, R. C. Haddon, A. Komornicki, and H. Rzepa, *J. Am. Chem. Soc.*, **99**, 377 (1977).

(17) Since MINDO/3 is parameterized to fit experimental enthalpies of formation, electron correlation corrections are not applicable. Allen's[15] and Dewar's[16] calculations predict somewhat different geometries and significantly different net atomic changes for the norbornyl cation.

(18) W. L. Jorgensen and J. E. Munroe, *J. Am. Chem. Soc.*, **100**, 1511 (1978); *Tetrahedron Lett.*, 581 (1977).

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(20) Y. K. Lau, P. P. S. Saluja, P. Kebarle, and R. W. Alder, *J. Am. Chem. Soc.*, **100**, 7328 (1978).

Semiempirical Molecular Orbital Calculation of Atom-Pair Interactions in a Molecule

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Contribution from the Department of Chemistry, Miami University, Oxford, Ohio 45056. *Received January 9, 1978*

Abstract: A simple procedure is proposed to resolve the binding energy calculated from a semiempirical MO method into terms that are representative only of atom-pair interactions. These interactions are comparable to traditional bonded and nonbonded interactions. Practical calculations for a homologous series of compounds require parameter values to be determined for the series. The parameter values may be evaluated unambiguously from key compounds. Examples for the evaluation of parameter values are given for saturated hydrocarbons, amines, alcohols, and ethers using energy quantities obtained from a modified CNDO method. Preliminary calculations are made for benzene, ethylene, and acetylene. Applications of the proposed energy-partitioning technique yield quantum chemical estimates of "bond energies" that are comparable in magnitude to those discussed traditionally.

Introduction

A traditional chemist is interested in the binding energy of a molecule, which is defined as the difference between the total energy of the molecule and the sum of energies of the free atoms that constitute the molecule. On a crude level, the binding energy is simply taken as the sum of average bond energies, representing the interactions between the bonded atoms. To obtain more accurate estimates, the nonbonded

0002-7863/79/1501-1087$01.00/0