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Heats of formation of organic molecules calculated by density functional theory. III—Amines

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ABSTRACT: Two group increment schemes that convert HF/6–31G(d) and B3LYP/6–31G(d) calculated energies of aliphatic amines to estimates of heats of formation have been developed. For the set of 25 compounds used to develop the methods, root mean square errors for both methods were found to be 0.47 kcal mol^{-1} (1 kcal = 4.184 kJ). Calculations on an additional eight compounds are reported. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: heat of formation; density functional theory; aliphatic amines; bond equivalents; group equivalents; group increment scheme

INTRODUCTION

Heats of formation are fundamental thermochemical quantities, and as such can be helpful in understanding a wide variety of phenomena. Not surprisingly, there is a substantial amount of literature reporting experimental determinations of heats of formation, and many of these data are also available from an excellent NIST resource.[1] Despite this, one still encounters situations where the appropriate data are not available. Obtaining new, high-quality experimental determinations of heats is a time-consuming and demanding undertaking. For many chemists without experience in obtaining thermochemical data, this means either employing the services of a specialist with the appropriate equipment and expertise to do the determination, or attempting a less accurate determination themselves, or doing without the needed datum.

Alternatively, there are a variety of computational techniques for calculating heats of formation. These range from simple, empirical group additivity schemes such as Benson's tables,[2] to semiempirical MO methods,[3] to molecular mechanics methods,[4] to highly sophisticated compound *ab initio* methods.[5] The utility of any of these methods to chemists who are seeking missing data will depend on the nature of the compound in which they are interested, the accuracy of the method, the chemists expertise in computational chemistry and the computing equipment available to them. The simplest methods, such as Benson's tables, require a little thought and only a pencil and paper to apply. However, this method is not very flexible since even minor structural changes (e.g. *gauche* interactions in a carbon chain) require special parameters. Therefore, one must restrict oneself to compounds without any unusual structural features. Using schemes in which part or all of the energy of the molecule is explicitly calculated can enhance the flexibility of computational methods. Semiempirical MO methods use this approach but have proved to be considerably less accurate than experimental measurements. Molecular mechanics methods use their strength at calculating steric energies to increase flexibility, and a sophisticated bond and group additivity scheme to yield calculated heats of formation that are fairly accurate. Since the molecular mechanics method is fairly fast, the technique can be applied to large molecules. Most *ab initio* methods for the calculation of heats of formation are not truly *ab initio*, since they often use experimental heats of atomization or heats of formation for simple model compounds as part of the calculation. Some of the most popular *ab initio* methods, the G1, G2 and G3 methods,[5] have been fully automated within the Gaussian 98 program and are easy to use even for the non-expert. However, the computer resources necessary are substantial even for small molecules. For example, a G2 calculation requires all of the following calculations: geometry optimization and frequency calculations at the HF/6–31G(d) level, geometry optimization at the

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MP2(full)/6–31G(d) level and single-point calculations on the MP2 geometry at the following levels: MP4/6–311+G(d,p), MP4/6–311G(2df,p), MP2/6–311+G(3df,2p) and QCISD(T)/6–311G(d,p). With present-day computer technology such calculations are only possible on small molecules. For non-computational chemists who are unlikely to have state-of-the-art computers, this scheme is even more restrictive.

Our interest in obtaining heats of formation from *ab initio* calculations springs from the fact that we are the developers of molecular mechanics programs that attempt to calculate accurately molecular properties, and those include heats of formation. Since the molecular mechanics programs are parameterized to fit experimental data, we need a large amount of good data, and sometimes we find that they are not available. In addition, we sometimes find data that we cannot reproduce satisfactorily. In such a situation we must decide whether the parameterization, the molecular mechanics method or the experimental data is at fault. Hence, like many others, we needed a quick but accurate method of calculating the required data.

When Wiberg,[6] and Ibrahim and Schleyer[7] independently demonstrated that reasonably accurate heats of formation could be obtained from HF/6–31G(d) calculations and group or atom equivalents, we seized on this as the basis for a method that would be able to obtain the data we needed in a computationally efficient way. Our experience with molecular mechanics told us that a more elaborate group equivalent scheme than those used by Wiberg and Schleyer was needed to obtain more accurate results. We then set out to develop such a scheme, and eventually determined the equivalents necessary for converting HF/6–31G(d) energies to heats of formation for alkanes,[8] amines,[8] alcohols,[9] ethers,[9] aldehydes,[10] ketones,[10] carboxylic acids,[11] esters,[11] thiaalkanes,[12] radicals[13] and alkenes.[14] After a decade of experience we have now decided that the basic methods we used earlier can be improved in two important ways. First, in our original work the parameters for alkanes were determined from a limited set of experimental data. We have found that the limited data resulted in some small but significant systematic errors that could be corrected by simply using more data. The revised alkane parameters have been determined and published.[15] However, since most organic molecules contain saturated carbons, the parameters for the other functional groups also need to be updated since they depend upon the alkane parameters. In this paper, the appropriate parameters for amines are updated. Second, since our original work in the area, computer hardware and software have improved tremendously, allowing the average chemist to perform higher level calculations. B3LYP/6–31G(d) calculations (as implemented in G94[16] and G98[17]) have become routine. In this paper, we also report the equivalents necessary to convert B3LYP/6–31G(d) energies of amines to heats of formation.

COMPUTATIONAL METHODS

Our technique for calculating heats of formation has been described previously.[8–15] Briefly, it consists of calculating an energy using Hartree–Fock or density functional theory, and converting it to a heat of formation using bond and group equivalents and statistical mechanical terms. It can be summarized in the equation:

$$\Delta H_f = E + \sum_j a_j n_j + POP + TOR + T/R$$

where E is the HF/6–31G(d) or B3LYP/6–31G(d) (using the method in Gaussian 94[16] and 98[17]) energy calculated for the lowest energy conformer of the molecule, the a_j are the bond or group equivalents, the n_j are the counts of the bonds or groups and *POP*, *TOR* and *T*/*R* are statistical mechanical terms. *POP* is the excess energy in the heat of formation due to populating higher energy conformers. It is calculated as a Boltzmann population-weighted average of the relative energies of all conformations of the molecule. *TOR* is the excess energy due to populating low-energy rotational states involving rotation around single bonds. It is calculated by counting the number of single bonds in the molecule for which there is rather free rotation (excluding methyl groups) and multiplying by 0.001 594 hartree when using HF calculations, or 0.000 727 hartree when using B3LYP calculations.[15] *T*/*R* consists of the translational and rotational energy of the molecule (0.5*RT* per degree of freedom; 3*RT* for non-linear molecules) plus the energy (1*RT*) needed to convert an energy to an enthalpy. Actually, it might be pointed out that there are two methods being described here. The same equation is used for both, but for one HF energies are used and for the other B3LYP. The same procedure is used for both, and separate parameter sets are generated. The scheme can be applied to any consistent level of quantum mechanical calculations. For hydrocarbons, the calculated results are down to the level of accuracy of the experimental data already, so no higher level is necessary. With functionalized molecules, the situation is less clear.

To develop the scheme for calculating the heats of formation of amines, the structural elements that represent the group equivalents were selected, a list of molecules containing the appropriate structural elements and having accurately known experimental heats of formation was assembled, and the *E*, *POP*, *TOR*, and *T*/*R* terms were evaluated. In addition, the bond and group equivalents corresponding to the saturated alkyl portions of the amines were obtained from our previous work on alkanes.[15] Substituting these data into the equation yields a set of simultaneous equations (the number of which equals the number of molecules chosen) in which the only unknowns are the bond and group equivalents, a_j, for amines. These simultaneous equations were then solved by using the least-squares method.

Table 1. Aliphatic amines and the number of equivalents in each compound

Compound	CN	NH	NME	NISO	NSEC	NTER	NTBu
Ammonia	0	3	0	0	0	0	0
Methylamine	1	2	1	0	0	0	0
Dimethylamine	2	1	2	0	1	0	0
Trimethylamine	3	0	3	0	0	1	0
Ethylamine	1	2	0	0	0	0	0
Propylamine	1	2	0	0	0	0	0
n-Butylamine	1	2	0	0	0	0	0
tert-Butylamine	1	2	0	0	0	0	1
Piperidine	2	1	0	0	1	0	0
2-Methylpiperidine	2	1	0	1	1	0	0
Cyclopentylamine	1	2	0	1	0	0	0
Cyclohexylamine	1	2	0	1	0	0	0
Diethylamine	2	1	0	0	1	0	0
sec-Butylamine	1	2	0	1	0	0	0
Isobutylamine	1	2	0	0	0	0	0
Isopropylamine	1	2	0	1	0	0	0
Pyrrolidine	2	1	0	0	1	0	0
Triethylamine	3	0	0	0	0	1	0
Pyrrolizidine[a]	3	0	0	1	0	1	0
Dimethylpyrrolizidine[b]	3	0	0	3	0	1	0
Tetramethylpiperidine[c]	2	1	0	0	1	0	2
trans-Decahydroquinolidine	2	1	0	1	1	0	0
Dipropylamine	2	1	0	0	1	0	0
Tripropylamine	3	0	0	0	0	1	0
Disobutylamine	2	1	0	0	1	0	0

[a] 1-Azabicyclo[3.3.0]octane.
[b] *cis*-3,7a-*H*-*cis*-5,8-*H*-3,5-Dimethylpyrrolizidine.
[c] 2,2,6,6-Tetramethylpiperidine.

Experimental heats of formation for compounds in the gas phase at 298 K were taken for the collections of Cox and Pilcher,[18] Pedley *et al.*,[19] and a *NIST Chemistry Web Book* chapter by Afeefy *et al.*[1] Molecular orbital calculations were carried out using Gaussian 94, the 6–31G(d) basis set and, where appropriate, the B3LYP method. *POP* terms were evaluated using relative energies of conformers obtained from molecular mechanics.

RESULTS AND DISCUSSION

Seven bond and group equivalents were selected to fit the amines. These consist of, first, the bond equivalents for the CN and NH bonds. The NSEC and NTER group equivalents are then used for secondary and tertiary amines, respectively. Thus, the CN and NH bond equivalents are optimized for primary amines and no equivalent for the primary amines is required. In addition, equivalents for the type of carbon that bears the amino group are used. The NME, NISO and NTBU group equivalents are used when the carbon bearing the amino group is a methyl group, a secondary carbon or a tertiary carbon, respectively. (A group equivalent is not needed when the amino group is attached to a primary carbon, since the CN and NH equivalents will be optimized for this case.) In this work, 24 amines and ammonia were used to evaluate the equivalents. Complete listings of the compounds and the counts of the equivalents in each molecule are shown in Table 1. These compounds, their experimentally determined heats of formation, *POP* values and counts of the number of bonds requiring a *TOR* correction are shown in Table 2. The energies of the lowest energy conformation of these molecules at both the HF/6–31G(d) and B3LYP/6-31G(d) levels of theory are shown in Table 3.

Two *POP* terms each are listed for cyclopentylamine and pyrrolizidine. In each of these compounds, different conformers were found to be the most stable from the Hartree–Fock and the B3LYP methods. Normally, we calculate the *POP* terms using relative energies of conformers calculated using molecular mechanics. In these cases, separate *POP* terms were calculated using HF and B3LYP relative energies. In principle, the *POP* terms should always be calculated in this way. However, in practice there is usually only a minor (negligible) difference between the *POP* term calculated with molecular mechanics or the MO methods. In these cases, the two MO methods differ by 0.2 and 0.1 kcal mol^{-1} (1 kcal = 4.184 kJ) for cyclopentylamine and pyrrolizidine, respectively.

The data in Tables 1–3, along with the counts and values of our previously published alkane equivalents, allow one to obtain a least-squares fit for the values of the seven new equivalents needed to define aliphatic amine

Table 2. Heats of formation, *POP* and number of units of *TOR* for compounds used in determining the values of the equivalents

Compound	ΔH_f (kcal mol^{-1})	*POP* (hartree)	*TOR* (No. of units)
Ammonia	−10.98	0.00000	0
Methylamine	−5.50	0.00000	0
Dimethylamine	−4.43	0.00000	0
Trimethylamine	−5.67	0.00000	0
Ethylamine	−11.35	0.00005	1
Propylamine	−16.77	0.00038	2
n-Butylamine	−21.99	0.00094	3
tert-Butylamine	−28.80	0.00000	1
Piperidine	−11.76	0.00016	0
2-Methylpiperidine	−20.19	0.00025	0
Cyclopentylamine	−13.11	0.00047 (HF) 0.00021 (B3LYP)[a]	2
Cyclohexylamine	−25.07	0.00038	1
Diethylamine	−17.33	0.00075	2
sec-Butylamine	−25.07	0.00051	2
Isobutylamine	−23.59	0.00043	2
Isopropylamine	−20.02	0.00018	1
Pyrrolidine	−0.80	0.00022	1
Triethylamine	−22.06	0.00010	3
Pyrrolizidine	−0.93	0.00048 (HF) 0.00032 (B3LYP)[a]	2
Dimethylpyrrolizidine	−15.90	0.00035	2
Tetramethylpiperidine	−38.22	0.00026	0
trans-Decahydroquinolidine	−26.99	0.00026	0
Dipropylamine	−27.84	0.00082	4
Tripropylamine	−38.48	0.00036	6
Disobutylamine	−42.83	0.00092	4

[a] See text

Table 3. Electronic energies (hartee) of the lowest energy conformers of amines used in determining the values of the equivalents

Compound	HF/6–31G(d)	B3LYP/6–31G(d)
Ammonia	−56.18436	−56.54795
Methylamine	−95.20983	−95.85320
Dimethylamine	−134.23885	−135.16285
Trimethylamine	−173.26930	−174.47441
Ethylamine	−134.24773	−135.17073
Propylamine	−173.28248	−174.48459
n-Butylamine	−212.31708	−213.79821
tert-Butylamine	−212.32181	−213.80311
Piperidine	−250.18870	−251.90437
2-Methylpiperidine	−289.22681	−291.22205
Cyclopentylamine	−250.18635	−251.90043
Cyclohexylamine	−289.23035	−291.22429
Diethylamine	−212.31404	−213.79430
sec-Butylamine	−212.31937	−213.80075
Isobutylamine	−212.31733	−213.79818
Isopropylamine	−173.28567	−174.48727
Pyrrolidine	−211.14442	−212.58202
Triethylamine	−290.37244	−292.41613
Pyrrolizidine	−327.08472	−329.31564
Dimethylpyrrolizidine	−405.15925	−407.94977
Tetramethylpiperidine	−406.32432	−409.15967
trans-Decahydroquinolidine	−405.17222	−407.96005
Dipropylamine	−290.38334	−292.42333
Tripropylamine	−407.47638	−410.35706
Disobutylamine	−368.45284	−371.05204

Table 4. Values (hartree) of the equivalents for amines

Equivalent	HF/6–31G(d)	B3LYP/6–31G(d)
CN	27.630403	27.790293
NH	18.721013	18.842210
NSEC	−0.005396	−0.004978
NTER	−0.014561	−0.011133
NME	0.004105	0.002570
NISO	−0.003427	−0.002558
NTBu	−0.010249	−0.007853

structures. The values of the equivalents for both the HF and B3LYP methods are given in Table 4. The calculated heats of formation that one obtains by using the new increments are given in Table 5. The r.m.s. error for fitting the heats of formation of these amines using the HF and B3LYP methods was found to be the same, 0.47 kcal mol^{-1}. This is in contrast to our previous work on alkanes, where we found the B3LYP results to be of superior accuracy. (The r.m.s. errors from these two methods for the corresponding calculations on hydrocarbons were 0.71 and 0.36 kcal mol^{-1}, respectively.) The present result is probably due to the quality of the experimental data rather than to the relative merits of the two methods. We also carried out calculations using HF and B3LYP methods with the 6–31G(d) basis on carbon and hydrogen, but with the 6–311+G(d) basis set on nitrogen, and no improvement was found.

If our quantum calculations were exact, there would presumably be no need for the last five terms in Table 4. These terms lead to a stabilization of branched chains. This is a familiar effect, general for organic molecules. The cause of this effect is not entirely known, but apparently is due in part to electron correlation. In a branched chain such as neopentane, the electrons in the molecule are more influenced by one another than in an elongated chain such as *n*-pentane. In our calculations, the Hartree–Fock method does not reproduce electron correlation, and relatively large increments are needed here to account for that. (They may be accounting for additional things as well.) When we go to the density functional calculation, some electron correlation is included, and consequently the magnitude of this stabilization (the increment) is reduced. An examination of Table 4 shows this clearly. While these numbers are small in hartrees, and so small in a quantum sense, they have a large impact on the heats of formation, being in general on the order of several kcal mol^{-1}.

In addition to the 25 compounds used in fitting the equivalents, we performed calculations on an additional eight compounds for which we have trouble fitting the experimental data. These compounds and the number of equivalents in each are listed in Table 6, and Table 7 contains the data needed to calculate heats of formation for these compounds. Table 8 compares our calculated heats with experimental results and MM3 calculated heats.

Table 5. Calculated heats of formation (kcal mol^{-1}) and comparison with experimental values

Compound	Experimental	HF	Error	B3LYP	Error
Ammonia	−10.98	−10.98	0.00	−10.98	0.00
Methylamine	−5.50	−4.61	0.89	−4.74	0.76
Dimethylamine	−4.43	−3.85	0.58	−4.38	0.05
Trimethylamine	−5.67	−6.36	−0.68	−5.96	−0.29
Ethylamine	−11.35	−11.95	−0.60	−12.34	−0.98
Propylamine	−16.77	−17.13	−0.36	−17.51	−0.74
n-Butylamine	−21.99	−22.08	−0.09	−22.37	−0.38
tert-Butylamine	−28.80	−28.91	−0.11	−28.56	0.24
Piperidine	−11.76	−12.24	−0.48	−11.95	−0.19
2-Methylpiperidine	−20.19	−20.26	−0.07	−20.07	0.12
Cyclopentylamine	−13.11	−13.00	0.11	−12.74	0.38
Cyclohexylamine	−25.07	−24.96	0.11	−24.51	0.56
Diethylamine	−17.33	−17.73	−0.40	−16.91	0.42
sec-Butylamine	−25.07	−24.35	0.72	−24.64	0.43
Isobutylamine	−23.59	−24.44	−0.85	−24.16	−0.57
Isopropylamine	−20.02	−19.83	0.19	−19.72	0.30
Pyrrolidine	−0.80	−0.11	0.69	−0.97	−0.18
Triethylamine	−22.06	−21.76	0.29	−21.98	0.08
Pyrrolizidine	−0.93	−1.09	−0.16	−1.02	−0.10
Dimethylpyrrolizidine	−15.90	−16.25	−0.35	−16.59	−0.68
Tetramethylpiperidine	−38.22	−38.17	0.05	−38.34	−0.12
trans-Decahydroquinolidine	−26.99	−26.85	0.14	−26.63	0.36
Dipropylamine	−27.84	−28.34	−0.50	−28.42	−0.58
Tripropylamine	−38.48	−37.58	0.90	−37.50	0.98
Disobutylamine	−42.83	−42.85	−0.02	−42.70	0.12
R.m.s. Error			0.47		0.47

Table 6. Additional amines and the number of equivalents in each

Compound	CN	NH	NME	NISO	NSEC	NTER	NTBu
Disopropylamine	2	1	0	2	1	0	0
Quinuclidine	3	0	0	0	0	1	0
Butylmethylamine	2	1	1	0	1	0	0
3-Azabicyclo[3.2.2]nonane	2	1	0	0	1	0	0
Azacycloheptane	2	1	0	0	1	0	0
Butylisopropylamine	2	1	0	1	1	0	0
Dibutylamine	2	1	0	0	1	0	0
Butylisobutylamine	2	1	0	0	1	0	0

Table 7. *POP*, number of units of *TOR*, HF/6–31G(d) and B3LYP/6–31G(d) energies

Compound	*POP* (hartree)	*TOR* (No. of units)	HF (hartree)	B3LYP (hartree)
Disopropylamine	0.00035	2	−290.38368	−292.42547
Quinuclidine	0.00000	0	−327.07880	−329.31072
Butylmethylamine	0.00061	3	−251.34576	−253.10675
3-Azabicyclo[3.2.2]nonane	0.00026	0	−366.11498	−368.62483
Azacycloheptane	0.00031	1	−289.21264	−291.20873
Butylisopropylamine	0.00094	4	−329.41840	−331.73828
Dibutylamine	0.00128	6	−368.45258	−371.05059
Butylisobutylamine	0.00131	5	−368.45274	−371.05135

Table 8. Experimental and calculated heats of formation (kcal mol^{-1}) for additional amines

Compound	Exp.	HF	B3LYP	MM3
Disopropylamine	−32.58	−29.99	−30.89	−31.55
Quinuclidine	−1.03	1.56	1.20	−1.26
Butylmethylamine	−25.88	−21.32	−21.52	−21.11
3-Azabicyclo[3.2.2]nonane	−10.44	−13.39	−9.86	−6.83
Azacycloheptane	−10.80	−16.49	−12.63	−10.21
Butylisopropylamine	−39.44	−34.43	−34.81	−34.85
Dibutylamine	−37.43	−38.69	−38.58	−38.14
Butylisobutylamine	−41.80	−40.65	−40.52	−39.52

Disopropylamine is an interesting case. In our original paper using Hartree–Fock calculations to determine heats of formation of amines,[8] a heat of formation of −30.02 kcal mol^{-1} was found, which is in fair agreement with those reported here (−29.99 and −30.89 kcal mol^{-1} using the HF and B3LYP methods, respectively). As noted in the earlier paper, this value was in very poor agreement with the then accepted experimental value of −34.41 kcal mol^{-1}.[19,20] Since that time, the experimental heat of formation has been redetermined and found to be −32.58 kcal mol^{-1},[1,21] in better agreement with our calculated results but still more negative than our results. The MM3-calculated heat of formation of disopropylamine is −31.55 kcal mol^{-1}, which also suggests that the experimental result may still be too negative (Table 8).

For di-*n*-butylamine and *n*-butylisobutylamine, the experimental heats are consistently either more negative (*n*-butylisobutylamine) or more positive (di-*n*-butylamine) by roughly 1 kcal mol^{-1} than those calculated using the three methods (HF, B3LYP and MM3). Although the errors are relatively small, it might be appropriate to repeat the experimental work.

The consistency of the calculated heats of formation and the large disagreement with the experimental heats of methylbutylamine and butylisopropylamine suggest that the experimental numbers are very likely inaccurate. The experimental heat of formation for methylbutylamine (−25.88 kcal mol^{-1}) is more than 4 kcal mol^{-1} more negative than the calculated values (−21.32, −21.52 and −21.11 kcal mol^{-1} for the HF, B3LYP and MM3 methods, respectively). Similarly, the experimental heat of formation for butylisopropylamine (−39.44 kcal mol^{-1}) is more than 4 kcal mol^{-1} more negative than the calculated values (−34.43, −34.81 and −34.85 kcal mol^{-1} for

the HF, B3LYP and MM3 methods, respectively). The experimental heats of formation of methylbutylamine and butylisopropylamine clearly should be redetermined.

We also note that it is now becoming feasible to study outliers in our method of deriving heats of formation by employing the G2 method, which should yield results accurate to about 2 kcal mol^{-1} for small molecules.

The data in Table 8 suggest that there are large errors in either or both the experimental and/or calculated heats for quinuclidine, 3-azabicyclo[3.2.2]nonane and azacycloheptane. We are unwilling to speculate as to the source of the errors because of the inconsistency of the data.

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