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Comparison of Computational Methods Applied to Oxazole, Thiazole, and Other Heterocyclic Compounds

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A variety of computational methods, including the semiempirical techniques AM1, PM3, and MNDO, and the thermochemical basis sets of Benson and Stine, was used to calculate and compare heats of formation ($\Delta H_f°$) data for optimized geometries of a variety of aromatic and nonaromatic heterocycles. Detailed analyses, including 6-31G* and MP2/6-31G* *ab initio* calculations, were performed for the oxazole and thiazole heterocycles. The results indicate a scatter among the methods sensitive to the nature of the heterocycle. This was in particular evident in the oxazole molecule, where AM1 gave a singularly high value of $\Delta H_f°$ consistent with longer calculated bond lengths, particularly about the oxygen atom. Aromatic stabilization energy appears to be addressed differently among the employed methods. Implications of this contrast applied to calculation of macromolecular systems containing heterocyclic units are discussed.

INTRODUCTION

Organic heterocycles are becoming increasingly important in materials chemistry. Several promising conducting polymers, nonlinear optical polymers, biomaterials, and high-strength polymers contain heterocyclic moieties. In the field of high-strength polymers, oxazole and thiazole heterocycles are incorporated into two advanced high-strength polymer fibers (Fig. 1).[1-4] These materials exhibit extremely high mechanical strength in the direction of the polymer backbone due to the overall rod-like fiber orientation.

There is a great deal of interest in determining the relationship between computationally derived parameters (such as the heat of formation) with ultimate strength and elastic modulus properties of these polymeric materials. In this context, we performed comparative quantum chemical calculations on the *cis*-PBO structure using the three most commonly employed semiempirical methods (MNDO,[5] AM1,[6] and PM3).[7,8] The RHF[9] optimized geometries using MOPAC 6.0[10] gave, in order of increasing $\Delta H_f°$, the results shown in Figure 2. To isolate this comparison to the fused aromatic system (eliminating the effect of interplane angle, $\propto$, and the paraphenylene unit), these calculations were repeated for the *cis*-benzo-bisoxazole structure (see Fig. 3). The magnitude of $\Delta\Delta H_f°$s were comparable to those seen in the polymer system, indicating neither $\propto$ nor the paraphenylene unit to be a major contributor to the observed differences.

This persistently large contrast in heat of formation results led us to suspect a significant difference in these computational methods applied to the oxazole heterocycle. We thus concentrated our further efforts on the oxazole and the related thiazole heterocycles to determine which method is most appropriate for studying these polymers. (The application of these calculations to polymeric systems will be addressed in a subsequent article.)

RESULTS AND DISCUSSION

Heat of Formation Calculations

Heats of formation data were computed for the oxazole heterocycle using MOPAC 6.0 and an eigenvector following routine for geometry optimization.[11] The thiazole heterocycle, (the next homologue in the chalcogen family) was also examined due to the importance of thiazole based high-ordered polymers.[12] The results are summarized below in descending order of agreement to experiment. Because experimental data for thiazole are unavailable, results obtained here are reported in the same order as that for oxazole.

	$\Delta H_f°$ (kcal/mol)	
	Oxazole	Thiazole
Exp =	-3.70 ± 0.12	Unknown
PM3 =	-1.48	40.28
MNDO =	-8.24	33.18
AM1 =	12.46	38.63

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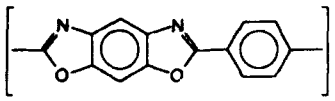
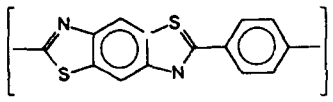


cis poly paraphenylene benzo-bisoxazole (cis-PBO)



trans poly paraphenylene benzo-bisthiazole (trans-PBZT)

Figure 1. Structures of *cis*-poly paraphenylene benzobisoxazole (*cis*-PBO) and *trans* poly paraphenylene benzobisthiazole (trans PBZT).

AM1 predicts a much higher heat of formation for oxazole than any other method. This startling contrast raised the question of how these results would compare with those predicted by *ab initio* methods. This contrast also supported our suspicion that the oxazole heterocycle was a major source of discrepancy between the semiempirical methods in the PBO polymer because increasing $\Delta H_f°$ followed the same sequence for both structures: MNDO < PM3 < AM1. For thiazole, the range of $\Delta H_f°$ values is about half that of oxazole. This implies that the parametric basis sets for sulfur cause less variation in the $\Delta H_f°$ results. This is of note because sulfur was only recently incorporated into the AM1 model (1990).[13]

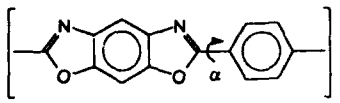
Geometries for the oxazole and thiazole heterocycles were optimized using the 6-31G* basis set[14] at both the RHF and MP2 (Moller–Plesset second-order perturbation theory)[15] levels as implemented in the Gaussian 90 program.[16]* The resulting molecular energies were coupled with experimental $\Delta H_f°$s in the isodesmic reaction schemes shown in Table I to obtain 6-31G*//6-31G* and MP2/6-31G*//MP2/6-31G* $\Delta H_f°$s for oxazole and thiazole. The calculation employed for oxazole and the *ab initio* $\Delta H_f°$ results are shown below.

$$\Delta H_{r\,xn(\text{isodesmic})}° = \Delta H_f°(\text{oxazole}) + \Delta H_f°(\text{cyclopentadiene}) - \Delta H_f°(\text{pyrrole}) - \Delta H_f°(\text{furan})$$

$$\Delta H_f°(\text{oxazole}) = \Delta H_{r\,xn(\text{isodesmic})}° - \Delta H_f°(\text{cyclopentadiene}) + \Delta H_f°(\text{pyrrole}) + \Delta H_f°(\text{furan})$$

Oxazole		Thiazole	
Method	$\Delta H_f°$ (kcal/mol)	Method	$\Delta H_f°$ (kcal/mol)
Exp	−3.70	Exp	Unknown
MP2/6-31G*	−4.13	MP2/6-31G*	35.54
6-31G*	−9.25	6-31G*	32.24

*Performed on CRAY XMP 2/16.



	α (degrees)	$\Delta H_f°$ (kcal/mol)	$\Delta\Delta H_f°$ (kcal/mol)		
MNDO	79.26	13.99	PM3-MNDO	AM1-PM3	AM1-MNDO
PM3	3.24	37.98	23.99	39.38	63.37
AM1	22.17	77.36			

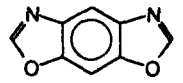
Figure 2. Interplane angle and $\Delta H_f°$ calculations/comparisons using semiempirical methods applied to *cis*-PBO.

As anticipated, the more rigorous *ab initio* treatment (MP2/6-31G*) gave the closer to $\Delta H_f°$ value for oxazole. (For thiazole, such a comparison is not possible because an experimental value for thiazole is not known.) For the oxazole heterocycle, the PM3 method gives significantly better agreement with experimental and the MP2/6-31G* results than AM1. The MNDO results were intermediate between the two *ab initio* values for both oxazole and thiazole and was much closer to the experimental value than AM1 for oxazole. For thiazole, AM1 gives a better agreement with both *ab initio* values than PM3. Here, however, the magnitude of deviation of the AM1 and PM3 methods from MP2/6-31G* is more comparable than for oxazole.

Molecular Structural Analysis

To understand the origin of this range of results in heats of formation, a detailed structural comparison was carried out for the oxazole and thiazole heterocycles using the atom numbering scheme shown in Figure 4. The results are tabulated in Tables II–V. Experimental values were obtained from microwave spectral analysis of the gas-phase molecules. Due to the complete planarity of these molecules, no dihedral angle data is presented. A compilation of percent error data is shown in Tables VI and VII.

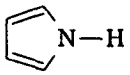
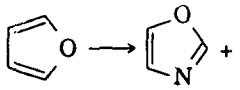
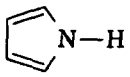
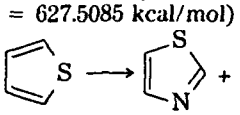
Atomic charge densities obtained from Mulliken population analyses were also compared between the predictive methods for oxazole and thiazole (Tables VIII and IX, respectively).[17] For both compounds, the MNDO method gives charges consistently much closer to *ab initio* results than PM3 or AM1. Also, the MNDO method places greater negative charge density on the N heterocyclic atom than does PM3 or AM1. For oxazole, greater positive charge density is observed for the hydrogens using



	$\Delta H_f°$ (kcal/mol)	$\Delta\Delta H_f°$ (kcal/mol)		
MNDO	-11.19	PM3-MNDO	AM1-PM3	AM1-MNDO
PM3	7.61	18.80	33.31	52.11
AM1	40.92			

Figure 3. Semiempirical $\Delta H_f°$ calculations/comparisons applied to *cis*-benzo-bisoxazole.

Table I. *Ab initio* calculations.

Ab initio method					ΔH_{rxn}° (isodesmic)
Isodesmic equation 1					
		Optimization energies (au) (1 au = 627.5085 kcal/mol)			
					
6-31G*[22]	−208.80785	−228.62521	−244.63297	−192.79172	8.37×10^{-3} au (5.25 kcal/mol)
MP2/6-31G*[15,23]	−209.50418	−229.33278	−245.37077	−193.44967	16.52×10^{-3} au (10.37 kcal/mol)
Exp ΔH_f°(kcal/mol)	25.9	−8.3	−3.70	32.1	
Isodesmic equation 2					
		Optimization energies (au) (1 au = 627.5085 kcal/mol)			
					
6-31G*	−208.80785	−551.29035	−567.28889	−192.79172	17.59×10^{-3} au (11.04 kcal/mol)
MP2/6-31G*	−209.50418	−551.95597	−567.98762	−193.44967	22.86×10^{-3} au (14.34 kcal/mol)
Exp ΔH_f°(kcal/mol)	25.9	27.6	Unknown	32.1	

Calculations were performed on a CRAY XMP 2/16.

PM3 and AM1 vs. MNDO. The magnitude of the charges cannot be easily compared between the semiempirical and *ab initio* treatment because each uses a different set of orbitals. However, the general superior agreement of the MNDO method with *ab initio* methods is of statistical interest. Differences in the signs of charge density, however, can reveal a genuine contrast between semiempirical and *ab initio* treatment. It is interesting to note that of the three semiempirical methods only the MNDO method assigns a positive charge density to C2 in oxazole, as found in the *ab initio* methods. For thiazole, the signs of charge density are consistent for all methods for each atom in the structure. This could, to some degree, account for the lower deviation in ΔH_f° results observed for thiazole vs. oxazole.

The MNDO method was consistently much closer to the *ab initio* results for bond lengths than PM3 or AM1. In terms of percent error from experimental value, the MNDO method had a somewhat lower error on average. Almost all bond lengths (with the exception of the C(5), 0 bond with MNDO, 6-31G*, and MP2/6-31G*) were predicted by all methods to be longer to varying degrees than that found experimentally. This was in particular so for the AM1 method, which predicted much longer bond lengths to oxygen than that observed experimentally. These longer bond distances are consistent with the significantly greater ΔH_f° obtained for the oxazole ring using the AM1 method. Although the AM1 method incorporates an additional set of parameters in the form of Gaussian core–core interaction to correct for excessive long-range repulsion in the original MNDO core–core repulsion term,[6] the MNDO method gives a lower ΔH_f° and shorter bond length values for oxazole. Indeed, bond lengths appear to be a fairly sensitive function of relative ΔH_f° values. In Table VI, signed percent errors for bond lengths are arranged in descending order, paralleling the descending order for the ΔH_f° values.

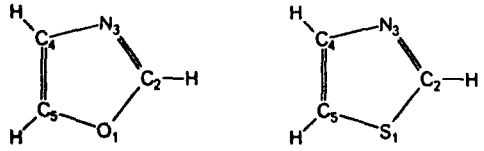
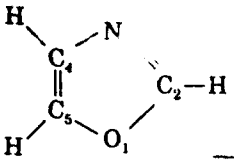


Figure 4. Structures and atom number assignments for oxazole and thiazole.

All methods, other than AM1, have a fairly consistent magnitude of signed error, although the ΔH_f° varies over a 7.78-kcal/mol range excluding the AM1 value. This magnitude of error (approximately 9.5–11% total) appears to have no direct influence on agreement of ΔH_f° with experimental (the closest method to experimental, MP2/6-31G*, has a 9.64% error). For AM1, however, a significantly higher signed error is observed with a much higher ΔH_f° result. The longer bond lengths of the AM1 method appear to be a major structural manifestation of the higher ΔH_f° result. Any possible stabilization due to aromaticity does not appear to be as effectively addressed in the AM1 method. Bond angle errors ap-

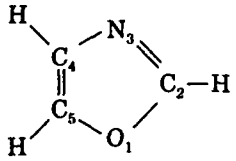
Table II. Comparison of bond lengths by method, Angstroms (% deviation from experimental): Oxazole.



Bond	MNDO	AM1	PM3	6-31G*	MP2/6-31G*	Exp[24] Uncert. <0.002 Å
O, C(2)	1.3642	1.4025	1.3717	1.3640	1.3640	1.3574
	(0.50)	(3.32)	(1.05)	(0.49)	(0.49)	
C(2), N	1.3368	1.3276	1.3257	1.3369	1.3374	1.2915
	(3.51)	(2.79)	(2.65)	(3.52)	(3.56)	
N, C(4)	1.3996	1.4053	1.4160	1.3991	1.3998	1.3954
	(0.30)	(0.71)	(1.48)	(0.27)	(0.31)	
C(4), C(5)	1.3905	1.3873	1.3683	1.3906	1.3911	1.3525
	(2.81)	(2.57)	(1.17)	(2.82)	(2.86)	
C(5), O	1.3678	1.3962	1.3809	1.3678	1.3674	1.3696
	(−0.13)	(1.94)	(0.83)	(−0.13)	(−0.16)	
C(2), H(2)	1.0862	1.0902	1.0900	1.0858	1.0861	1.0750
	(1.04)	(1.41)	(1.40)	(1.01)	(1.04)	
C(4), H(4)	1.0811	1.0896	1.0897	1.0812	1.0814	1.0751
	(0.56)	(1.35)	(1.35)	(0.56)	(0.59)	
C(5), H(5)	1.0817	1.0834	1.0855	1.0818	1.0819	1.0732
	(0.80)	(0.96)	(1.14)	(0.80)	(0.81)	

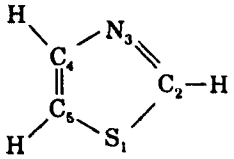
pear to be less systematic. Indeed, the PM3 angle error is the highest of all methods used, although it came in second only to MP2/6-31G* method for accuracy of ΔH_f°. Consistently, for the interior ring angles PM3 gives the highest or lowest predicted angle and in alternating fashion [for the C(4), C(5), 0 angle, all predictions were within a narrow margin of the experimental value]. All methods predicted

Table III. Comparison of bond angles by method, degrees (% deviation from experimental): Oxazole.



Angle	MNDO	AM1	PM3	6-31G*	MP2/6-31G*	Exp[24]
O, C(2), N	112.40	112.42	110.06	112.46	112.43	114.99
	(−2.25)	(−2.23)	(−4.29)	(−2.20)	(−2.22)	
C(2), N, C(4)	105.29	105.83	107.90	105.27	105.20	103.92
	(1.32)	(1.84)	(3.83)	(1.30)	(1.24)	
N, C(4), C(5)	108.21	109.08	106.48	108.22	108.29	109.04
	(−0.76)	(0.03)	(−2.34)	(−0.76)	(−0.68)	
C(4), C(5), O	107.73	107.62	108.58	107.75	107.65	108.14
	(−0.38)	(−0.48)	(0.40)	(−0.36)	(−0.45)	
C(5), O, C(2)	106.36	105.05	106.97	106.31	106.42	103.91
	(2.36)	(1.10)	(2.95)	(2.31)	(2.41)	
O, C(2), H(2)	119.37	116.11	119.01	119.42	119.37	117.09
	(1.95)	(−0.83)	(1.64)	(1.99)	(1.95)	
N, C(2), H(2)	128.22	131.46	130.92	128.12	128.20	127.92
	(0.23)	(2.77)	(2.35)	(0.16)	(0.22)	
N, C(4), H(4)	121.45	120.99	121.77	121.49	121.41	121.89
	(−0.36)	(−0.74)	(−0.10)	(−0.33)	(−0.39)	
C(5), C(4), H(4)	130.34	129.93	131.75	130.30	130.29	129.07
	(0.98)	(0.67)	(2.08)	(0.95)	(0.95)	
C(4), C(5), H(5)	134.12	136.95	135.61	134.12	134.17	135.00
	(−0.65)	(1.45)	(0.45)	(−0.66)	(−0.61)	
O, C(5), H(5)	118.15	115.42	115.57	118.13	118.17	116.86
	(1.10)	(−1.23)	(−1.10)	(1.09)	(1.12)	

Table IV. Comparison of bond lengths by method, Angstroms (% deviation from experimental): Thiazole.

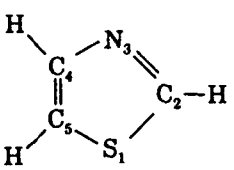


Bond	Method					
	MNDO	AM1	PM3	6-31G*	MP2/6-31G*	Exp[25]
S, C(2)	1.6856	1.7109	1.7482	1.6860	1.6874	1.7239
	(−2.22)	(−0.76)	(1.41)	(−2.20)	(−2.12)	±0.0009
C(2), N	1.3240	1.3284	1.3236	1.3236	1.3232	1.3042
	(1.52)	(1.86)	(1.49)	(1.49)	(1.45)	±0.0011
N, C(4)	1.4034	1.3877	1.4090	1.4035	1.4024	1.3721
	(2.28)	(1.14)	(2.69)	(2.29)	(2.21)	±0.0002
C(4), C(5)	1.3788	1.3880	1.3679	1.3788	1.3795	1.3670
	(0.87)	(1.53)	(0.06)	(0.86)	(0.91)	±0.0004
C(5), S	1.6739	1.6761	1.7284	1.6746	1.6742	1.7130
	(−2.29)	(−2.16)	(0.90)	(−2.24)	(−2.27)	±0.0003
C(2), H(2)	1.0861	1.0931	1.0909	1.0858	1.0860	1.0767
	(0.87)	(1.52)	(1.31)	(0.84)	(0.86)	±0.0018
C(4), H(4)	1.0859	1.0958	1.0919	1.0862	1.0860	1.0798
	(0.56)	(1.48)	(1.12)	(0.60)	(0.57)	±0.0001
C(5), H(5)	1.0794	1.0869	1.0887	1.0795	1.0792	1.0765
	(0.27)	(0.97)	(1.13)	(0.28)	(0.25)	±0.0002

bond angles for the heteroatoms, O, and N, to be slightly greater than that determined experimentally.

Critical computational method analysis for the thiazole heterocycle is hampered by the lack of an experimentally determined ΔH_f° in the literature. However, a close practical estimation of an experimental ΔH_f° for thiazole can be obtained by combining the experimental ΔH_f° for 4-methyl thiazole[18]

Table V. Comparison of bond angles by method, degrees (% deviation from experimental): Thiazole.



Angle	Method					
	MNDO	AM1	PM3	6-31G*	MP2/6-31G*	Exp[25]
S, C(2), N	115.07	114.98	114.16	115.00	114.98	115.18
	(−0.10)	(−0.18)	(−0.77)	(−0.15)	(−0.17)	±0.01
C(2), N, C(4)	109.46	109.20	111.55	109.49	109.48	110.12
	(−0.60)	(−0.84)	(1.30)	(−0.57)	(−0.58)	±0.02
N, C(4), C(5)	113.86	114.92	113.38	113.85	113.99	115.81
	(−1.69)	(−0.77)	(−2.10)	(−1.69)	(−1.57)	±0.01
C(4), C(5), S	110.39	110.22	111.85	110.39	110.26	109.57
	(0.75)	(0.59)	(2.08)	(0.75)	(0.63)	±0.01
C(5), S, C(2)	91.22	90.69	89.06	91.27	91.34	89.33
	(2.12)	(1.52)	(−0.30)	(2.17)	(2.24)	±0.03
S, C(2), H(2)	122.14	123.23	124.26	122.13	122.19	121.26
	(0.73)	(1.62)	(2.47)	(0.72)	(0.77)	±0.5
N, C(2), H(2)	122.79	121.79	121.58	122.87	122.87	123.56
	(−0.62)	(−1.43)	(−1.60)	(−0.56)	(−0.56)	±0.5
N, C(4), H(4)	118.42	118.66	118.93	118.40	118.29	119.35
	(−0.78)	(−0.58)	(−0.35)	(−0.80)	(−0.89)	±0.01
C(5), C(4), H(4)	127.72	126.42	127.69	127.75	128.73	124.84
	(2.31)	(1.26)	(2.28)	(2.33)	(3.11)	±0.01
C(4), C(5), H(5)	127.77	125.58	125.45	127.60	127.87	129.03
	(−0.97)	(−2.67)	(−2.78)	(−1.11)	(−0.90)	±0.03
S, C(5), H(5)	121.83	124.20	122.71	122.01	121.87	121.40
	(0.36)	(2.31)	(1.08)	(0.51)	(0.39)	±0.03

Table VI. Compilation of percent error: Oxazole.

Method	Bond lengths				Bond angles				ΔH_f°
	Unsigned	Average[a]	Signed	Average[a]	Unsigned	Average[b]	Signed	Average[b]	(kcal/mol)
AM1	15.06	1.88	15.06	1.88	13.36	1.21	2.34	0.21	12.46
PM3	11.06	1.38	11.06	1.38	21.54	1.96	5.87	0.53	−1.47
MP2/6-31G*	9.80	1.23	9.64	1.21	12.24	1.11	3.54	0.32	−4.13
MNDO	9.65	1.21	9.51	1.19	12.34	1.12	3.54	0.32	−8.24
6-31G*	9.60	1.20	9.47	1.18	12.09	1.10	3.49	0.32	−9.25

[a]Averaged over all eight bond distances, Table II.
[b]Averaged over all 11 angles, Table III.

and the enthalpic additivity value for the methyl substituent from Benson's method[19]:

$$\Delta H_f^\circ(\text{thiazole}) = \Delta H_f^\circ(\text{4-methylthiazole}) - \Delta H_f^\circ(\text{methyl})$$
$$= 26.7 - (-10.08)\ (\text{kcal/mol})$$
$$= 36.78\ (\text{kcal/mol})$$

In Table VII, signed percent errors for bond lengths are again arranged in descending order and compared with ΔH_f° values.

The spread of ΔH_f° values for thiazole (8.04 kcal/mol) is considerably less than that of oxazole (21.71 kcal/mol). An examination of compiled percent errors for the bond length structural parameter (Table VII) shows a comparable unsigned percent for all methods. PM3, however, has the greatest *signed* error of all methods (identical to its unsigned error), indicating that, for thiazole, the PM3 method calculates too long a bond length of *all* bonds in the molecule. Consistent with oxazole, where AM1 predicted the longest bond lengths and the highest ΔH_f°, so here does PM3 calculate the highest ΔH_f°. Again, bond angle errors are less systematic and do not appear to have any significant effect on ΔH_f° values.

The thiazole vs. oxazole comparison points to AM1's anomalous behavior for the oxazole heterocycle to be directly related to the oxygen atom—the only structural variant in this contrast. Indeed, if the average signed percent error for the 0, C(2) and C(5), 0 bond lengths is determined for each method AM1 gives the greatest positive error by a substantial margin: AM1 (2.63%), PM3 (0.94%), MNDO (0.19%), 6-31G* (0.18%), and MP2/6-31G* (0.17%). PM3's treatment of the sulfur atom presumably accounts for its high value of ΔH_f° for thiazole, but here the contrast between the methods is of much less magnitude than for oxazole. The effect of sulfur parameterization differences appears to be much less.

A structural comparison between the semiempirical methods focused on bond length was also applied to the larger fused ring aromatic system, *cis*-benzo-bisoxazole. The data is presented in Table X. Lengthening of the C(1), O(2) and C(11), 0(10) bonds with AM1 vs. MNDO or PM3 was comparable to that seen in the oxazole system. In the fused benzene ring system, there is a comparable elongation of the C—C bonds common to the oxazole system: C(3), C(4) and C(7), C(8) for MNDO (0.046 Å) and AM1 (0.055 Å). PM3's bond elongation is less (0.033 Å). However, the large difference between the MNDO and AM1 ΔH_f° values (Fig. 3) despite this comparable phenyl bond elongation indicates this structural factor not to be important in accounting for the $\Delta\Delta H_f^\circ$s.

An identical structural comparison was performed for the *cis*-PB0 repeat unit. Completely analogous bond length comparisons were seen in the fused aromatic portion of this structure. For the paraphenylene system, essentially identical (and equivalent around the ring) bond lengths were observed for all three methods. These comparisons underscore the prime structural manifestation of AM1's high ΔH_f° to be related to the oxygen atom. While the greater C, O bond lengths of AM1 may not in themselves generate the higher ΔH_f°, this bond

Table VII. Compilation of percent error: Thiazole.

Method	Bond lengths				Bond angles				ΔH_f°
	Unsigned	Average[a]	Signed	Average[a]	Unsigned	Average[b]	Signed	Average[b]	(kcal/mol)
PM3	10.11	1.26	10.11	1.26	17.11	1.56	1.31	0.12	40.28
AM1	11.41	1.43	5.59	0.70	13.77	1.25	0.84	0.08	38.63
6-31G*	10.79	1.35	1.92	0.24	11.35	1.03	1.59	0.14	32.24
MNDO	10.88	1.36	1.87	0.23	11.03	1.00	1.50	0.14	33.18
MP2/6-31G*	10.64	1.33	1.86	0.23	11.82	1.07	2.46	0.22	35.54

[a]Averaged over all eight bond distances, Table IV.
[b]Averaged over all 11 bond angles, Table V.

Table VIII. Atomic charge densities: Oxazole.

Atom	Method				
	MNDO	AM1	PM3	6-31G*	MP-2/6-31G*
O	−0.1375	−0.1278	−0.0946	−0.1369	−0.1373
C(2)	0.0690	−0.0538	−0.0177	0.0687	0.0686
N	−0.2248	−0.1423	−0.1291	−0.2246	−0.2242
C(4)	−0.0666	−0.1745	−0.1524	−0.0665	−0.0671
C(5)	−0.0479	−0.1203	−0.0884	−0.0484	−0.0479
H(2)	0.1566	0.2249	0.1715	0.1565	0.1566
H(4)	0.1187	0.1907	0.1523	0.1187	0.1186
H(5)	0.1325	0.2031	0.1582	0.1325	0.1327

lengthening can be described as a discernible structural effect of AM1's parameterization of oxygen when applied to an aromatic system.

From Figures 2 and 3, it can be seen that $\Delta\Delta H_f^\circ$s between semiempirical methods for the *cis*-PBO repeat unit and the *cis*-benzo-bisoxazole system are of comparable magnitude. (The slightly greater $\Delta\Delta H_f^\circ$ for *cis*-PBO can be related to minor influences of polymer vs. monomer geometry optimizations, interplane angle ($\propto$), and the paraphenylene unit.) Clearly, however, the fused aromatic structure accounts for most of the $\Delta\Delta H_f^\circ$s observed.

These $\Delta\Delta H_f^\circ$s from Figure 3 are considerably greater than those observed for the oxazole structure (PM3-MNDO = 7.77 kcal/mol, AM1-PM3 = 13.94 kcal/mol). However, the PM3-MNDO $\Delta\Delta H_f^\circ$ for the *cis* benzo-bisoxazole system can be largely accounted for by structural constituents of the fused aromatic system as follows:

Structural contribution (PM3 vs. MNDO)	kcal/mol
Two oxazole units (7.77 × 2) =	15.54
One benzene ring (PM3-MNDO ΔH_f°) = (Table XI)	1.20
	16.74

This value is close to the PM3-MNDO $\Delta\Delta H_f^\circ$ observed for the *cis* benzo-bisoxazole system (18.80 kcal/mol).

The AM1-PM3 $\Delta\Delta H_f^\circ$ is more difficult to address. A calculation in the manner just shown gives the following:

Structural contribution (AM1 vs. PM3)	kcal/mol
Two oxazole units (13.94 × 2) =	27.88
One benzene ring (AM1-PM3 ΔH_f°) = (Table XI)	−0.50
	27.38

This does not as completely account for the AM1-PM3 $\Delta\Delta H_f^\circ$ observed for *cis*-benzo-bisoxazole, 33.32 kcal/mol. The greater $\Delta\Delta H_f^\circ$ discrepancy could be due to the compounding effect of AM1's relative minimization of aromatic stabilization energy applied to a larger aromatic structure.

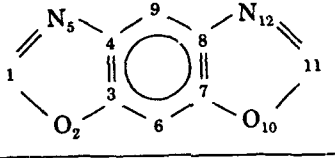
Comparison with Thermochemical Data Bases

The oxazole heterocycle appears to be a structure maximizing the predictive differences of semiempirical and *ab initio* methods. This raises a question of how these semiempirical methods contrast with each other and experimental heats of formation for a range of heterocyclic compounds. The question of aromatic stabilization of oxazole obviously being addressed very differently by the AM1 method prompted a compilation of results for two classes of heterocyclic compounds: aromatic and nonaromatic.

Table IX. Atomic charge densities: Thiazole.

Atom	Method				
	MNDO	AM1	PM3	6-31G*	MP-2/6-31G*
S	0.3071	0.4838	0.2808	0.3073	0.3063
C(2)	−0.1423	−0.3456	−0.2361	−0.1420	−0.1414
N	−0.1948	−0.1020	−0.0594	−0.1949	−0.1946
C(4)	−0.0170	−0.1385	−0.1068	−0.0173	−0.0177
C(5)	−0.2981	−0.4529	−0.3320	−0.2984	−0.2979
H(2)	0.1224	0.1914	0.1551	0.1225	0.1226
H(4)	0.1104	0.1824	0.1431	0.1104	0.1102
H(5)	0.1123	0.1814	0.1554	0.1124	0.1126

Table X. Comparison of bond lengths for semiempirical methods: *cis*-Benzo-Bisoxazole.

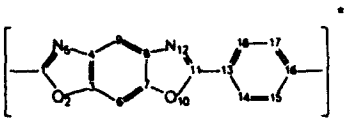


	Bond lengths (Å)														
	Hetero bonds								Phenyl C—C bonds						ΔH_f°
Method	C1—O2	O2—C3	C4—N5	N5—C1	C7—O10	O10—C11	C11—N12	N12—C8	C3—C6	C6—C7	C7—C8	C8—C9	C9—C4	C4—C3	(kcal/mol)
MNDO	1.3756	1.3687	1.4101	1.3271	1.3697	1.3753	1.3272	1.4078	1.4034	1.4059	1.4524	1.4073	1.4044	1.4508	−11.19
PM3	1.3867	1.3912	1.4310	1.3182	1.3916	1.3861	1.3180	1.4271	1.3899	1.3917	1.4266	1.3928	1.3915	1.4239	7.61
AM1	1.4196	1.3950	1.4195	1.3188	1.3956	1.4184	1.3185	1.4193	1.3879	1.3878	1.4500	1.3971	1.3969	1.4448	40.92

Table XI. Comparison of ΔH_f° for aromatic heterocycles (deviation from experimental).

Name	Exp	MNDO		AM1		PM3		Benson		Stine/Kramer		Order of agreement[a] (best to worst)
Benzene	19.8[b]	21.3	(1.5)	22.0	(2.2)	22.5	(2.7)	19.8	(0)	19.6	(0.2)	B S M A P
Pyridine	34.6[b]	28.8	(−5.8)	32.0	(−2.6)	30.4	(−4.2)	33.2	(1.4)[c]	32.1	(−2.5)	B S A P M
Pyrazine	46.9[b]	37.8	(−9.1)	44.2	(−2.7)	39.3	(−7.6)	55.8	(8.9)	44.6	(−2.3)	S A P B M
Pyrimidine	47.0[b]	35.0	(−12.0)	43.9	(−3.1)	38.0	(−9.0)	55.8	(8.8)	46.8	(−0.2)	S A B P M
Pyridazine	66.5[b]	43.6	(−22.9)	55.3	(−11.2)	56.0	(−10.5)	67.2	(0.7)	64.7	(−1.8)	B S P A M
Pyrrole	25.9[b]	32.5	(6.6)	39.9	(14.0)	27.1	(1.2)	29.5	(3.6)	28.8	(2.9)	P S B M A
Dibenzopyrrole	50.1[d]	54.3	(4.2)	67.9	(17.8)	55.1	(5.0)	51.6	(1.5)	50.5	(0.4)	S B M P A
Furan	−8.3[b]	−8.6	(−0.3)	3.0	(11.3)	−4.0	(4.3)	−8.3	(0.0)[c]	−2.2	(6.1)	B M P S A
Dibenzofuran	19.9[d]	14.4	(−5.5)	36.3	(16.4)	25.5	(5.6)	13.3	(−6.6)	17.8	(−2.1)	S M P B A
Thiophene	27.6[b]	26.5	(−1.1)	36.7	(9.1)	30.7	(3.1)	27.9	(−0.3)[c]			B M P A
Dibenzothiophene	49.0[d]	44.5	(−4.5)	55.6	(6.6)	57.7	(8.7)	58.6	(9.6)			M A P B
Oxazole	−3.7[d]	−8.2	(−4.5)	12.5	(16.2)	−1.5	(2.2)	6.5	(10.2)	−3.6	(0.1)	S P M B A
Isoxazole	18.8[d]	19.2	(0.4)	42.9	(24.1)	35.1	(16.3)	14.1	(−4.7)	21.2	(2.4)	M S B P A
Thiazole	36.8[e]	33.38	(−3.5)	38.6	(1.8)	40.4	(3.6)	42.5	(5.7)			A M P B
4-Methylthiazole	26.7[d]	22.2	(−4.5)	31.1	(4.4)	30.5	(3.8)	39.5	(12.8)			P A M B
Dimethylfurazan	25.6[d]	21.0	(4.6)	68.8	(43.2)	55.3	(29.7)	17.8	(−7.8)	25.6	(0.0)	S M B P A
1,2,3-Benzoxadiazole	71.9[d]	37.9	(−34.0)	81.9	(10.0)	67.5	(−4.4)	38.8	(−33.1)	87.0	(15.1)	P A S B M
[^{1}H]Tetrazole	79.9[b]	53.8	(−26.1)	109.6	(29.7)	86.3	(6.4)	97.4	(17.5)	90.5	(10.6)	P S B M A
Average unsigned error		8.68		13.21		7.34		7.50		3.34		
Average signed error		−6.65		10.91		3.14		1.65		2.06		

[a]M, MNDO; B, Benson; A, AM1; S, Stine/Kramer; P, PM3.
[b]Obtained from ref. 8.
[c]Obtained from ref. 26.
[d]Obtained from ref. 21.
[e]Derived from ΔH_f° for 4-methylthiazole (ref. 18). This compound is therefore not included in comparative study.



Atom #	Notation	Computation (kcal/mol)	Total (kcal/mol)
1,11	C(N2,C1,O1)	2 x -2.96	-5.92
2,10	O(C1,C1)	2 x 12.42	24.85
5,12	N(C2,C1)	2 x -16.94	-33.88
4,8	C(N1,C5,C5)	2 x 20.74	41.48
3,7	C(O1,C5,C5)	2 x -16.28	-32.56
6,9,14,15,17,18	C(C5,C5,H1)	6 x 3.27	19.62
13,16	C(C1,C5,C5)	2 x 5.41	10.82
Strain Corrections			
1,3,4,11	Cd5(2,1)	4 x 0.62	2.46
2,10	O5(1,1)	2 x 0.95	1.90
5,12	N5(2,1)	2 x -3.85	-7.70
7,8	C5(1,1)	2 x 1.19	2.38
			23.45

*Kekule structure used to assign strain corrections for fused aromatic structure.

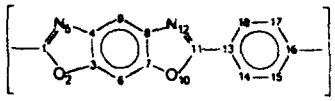
Figure 5. Stine/Kramer $\Delta H_f°$ calculation for *cis*-PBO.

Two thermochemical data bases developed by Benson and Stine/Kramer were also employed to determine heats of formation in this comparative study.[20] The recently developed Stine/Kramer method (1989) employs constituent $\Delta H_f°$ values for all possible atomic bonding schemes of compounds containing any combination of C, H, N, and/or O. These values were obtained empirically by least-squares analysis of gas-phase data of 1129 molecules. This approach differs from earlier thermochemical data bases (i.e., Benson's)[19] in that it (1) is structured toward energetic molecules and (2) uses fewer parameters that span a larger range of organic molecules.

Calculations using the Stine/Kramer and Benson methods to determine $\Delta H_f°$ values involve summation of constituent values for specific bonding environments of each atom in the molecule of interest, plus strain/interaction energy correction terms. A different notation scheme is used in the Stine/Kramer method to avoid confusion.

A detailed accounting for the Stine/Kramer $\Delta H_f°$ calculation for the *cis*-PBO and oxazole structures using the notation of ref. 20 is presented in Figures 5 and 6, respectively. The uncertainty associated with the Stine/Kramer method is ±5–6 kcal/mol.[20]

For the Benson calculations, several best matches had to be derived from similar bonding environments



Atom #	Notation	Computation (kcal/mol)	Total (kcal/mol)
1,11	C_d-(O)(C)	10.3 x 2	20.6
2,10*	O-(C_d)(C_B)	-27.05 x 2	-54.1
5,12	N_I-(C_B)	16.7 x 2	33.4
4,8	C_B-(N)	-0.5 x 2	-1.0
3,7	C_B-(O)	-0.9 x 2	-1.8
13,16	C_B-(C_d)	5.68 x 2	11.36
6,9,14,15,17,18	C_B-(H)	3.30 x 6	19.8
Ring Strain Correction			
**		-5.8 x 2	-11.6
			16.66

* O-(C_d)(C_B) is an average of O-$(C_d)_2$ = -33.0 and O-$(C_B)_2$ = -21.1

** Closest value from table to parallel oxazole ring system.

Both of these are sources of error of approximately ± 5 kcal/mol.

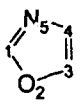
Figure 7. Benson $\Delta H_f°$ calculation for *cis*-PBO.

listed in the tables. This procedure introduces more error than that inherent in the tabular data itself, which overall is approximately ±1 kcal/mol.[19] Benson calculations for the *cis*-PBO and oxazole structures are presented in Figures 7 and 8, respectively.

In Table XI, the proposed *experimental* $\Delta H_f°$ for thiazole is based on that for 4-methylthiazole with a methyl group correction from the Benson method. However, the full Benson calculation for thiazole is shown in Figure 9 and is used for the Benson entry in Table XI.

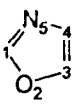
The Stine/Kramer method gives a $\Delta H_f°$ of 23.45 kcal/mol for the *cis*-PBO system, roughly intermediate between that of MNDO and PM3 from Figure 2, while Benson, $\Delta H_f°$ = 16.66 kcal/mol, agrees closely with MNDO. The AM1 result is still singularly high.

Further calculations on the structurally related monomers to the *cis*-PBO system gave the results shown in Figure 10 (in order of increasing $\Delta H_f°$). Again, the Benson method agrees with MNDO. The Stine/Kramer method is intermediate between Benson and PM3, and AM1 is considerably higher. For



Atom #	Notation	kcal/mol
1	C(N2,O1,H1)	0.34
2	O(C1,C1)	12.42
3	C(C2,O1,H1)	-17.27
4	C(N1,C2,H1)	18.92
5	N(C2,C1)	-16.94
Strain Corrections		
1,3,4	3 x Cd5(2,1)	1.85
2	O5(1,1)	0.95
5	N5(2,1)	-3.85
		-3.58

Figure 6. Stine/Kramer $\Delta H_f°$ calculation for oxazole.



Atom #	Notation	Computation (kcal/mol)	Total (kcal/mol)
1,3	C_d-(O)(H)	8.6 x 2	17.2
2	O-$(C_d)_2$	-33.0	-33.0
4	C_d-(N_I)(H)	6.78	6.78
5	N_I-(C)	21.3	21.3
Ring Strain Correction			
		-5.8	-5.8
			6.48

Figure 8. Benson $\Delta H_f°$ calculation for oxazole.

Atom #	Notation	Computation (kcal/mol)	Total (kcal/mol)
1,3	C_d-(S)(H)	8.56 x 2	17.12
2	S-(C_d)$_2$	-4.54	-4.54
4	C-(N_I)(H)	6.78	6.78
5	N-(C)	21.3	21.3
Ring Strain Correction			
		1.7	1.7
			42.36

Figure 9. Benson $\Delta H_f°$ calculation for thiazole.

the simple oxazole heterocycle, a large contrast is again noted using these methods. The Stine/Kramer value of $\Delta H_f° = -3.58$ kcal/mol provides the best agreement with the experimental value—actually within the experimental error. This allows us to give the final ordering of the oxazole $\Delta H_f°$ accuracy for the seven methods shown below:

$$\text{Experimental} = -3.70 \pm 0.12 \text{ kcal/mol}$$

$$\text{Stine/Kramer} = -3.58 \text{ kcal/mol}$$

$$\text{MP2/6-31G*} = -4.13 \text{ kcal/mol}$$

$$\text{PM3} = -1.48 \text{ kcal/mol}$$

$$\text{MNDO} = -8.24 \text{ kcal/mol}$$

$$\text{6-31G*} = -9.25 \text{ kcal/mol}$$

$$\text{Benson} = 6.48 \text{ kcal/mol}$$

$$\text{AM1} = 12.46 \text{ kcal/mol}$$

Here, Benson contrasts sharply with MNDO. For this heterocyclic compound, PM3 is the best of the semiempirical methods based upon its agreement with the experimental value.

To assess the general utility of these techniques in treating heterocyclic compounds, the MNDO, PM3, AM1, Stine/Kramer, and Benson methods were used to calculate $\Delta H_f°$ for optimized geometries of a series of aromatic and nonaromatic heterocycles. (The Stine/Kramer and Benson geometries are inherent in the additivity tables employed.) For the semiempirical methods, compiled data were drawn from the article by Stewart.[8] Compounds not included in that compilation were calculated using

MNDO =	11.45 kcal/mol	MNDO =	3.64 kcal/mol
Benson =	12.58 kcal/mol	Benson =	4.59 kcal/mol
Stine =	21.00 kcal/mol	Stine =	19.28 kcal/mol
PM3 =	33.47 kcal/mol	PM3 =	23.90 kcal/mol
AM1 =	68.00 kcal/mol	AM1 =	60.27 kcal/mol

Figure 10. $\Delta H_f°$ calculations for monomer systems.

MOPAC 6.0.[10] (The Stine/Kramer method is not applicable to compounds containing sulfur.) These results were compared with experimental $\Delta H_f°$ values in the gaseous phase[21] and are shown on Tables XI and XII for aromatic and nonaromatic compounds, respectively. Because a true experimental $\Delta H_f°$ for thiazole is not known, this compound was excluded from this final comparative study. (In Table XI, benzene is included as a contrast with homocyclic systems.)

To maintain as much simplicity as possible in these comparisons, structural features beyond that of the heterocycle unit (i.e., functional groups or alkyl appendages) have in general not been included. Exceptions to this are the dibenzo derivatives of pyrrole, furan, and thiophene, the benzo derivative of oxadiazole, and methyl substitution of the thiazole and furazan rings. The dibenzo derivatives were used because of their availability for all three N, O, and S heterocycles and so provided a convenient comparison to a larger structural system. The other modified structures were used because these were the simplest compounds of their class with reported $\Delta H_f°$ data in the gaseous state.

The degree of agreement between the five methods and experimental values shows considerable diversity. However, several general trends or patterns are evident:

1. For most aromatic compounds (with the exception of thiophene, dibenzothiophene, furan, and pyridine), the Stine/Kramer or PM3 methods place first or second in agreement with experimental values. The Benson and Stine/Kramer methods collectively work best for the simple monoheteroatomic saturated heterocycles. PM3, overall, is the best semiempirical method for this class of compounds.
2. For most of the N-containing six-membered aromatic ring compounds, AM1 gives the best semiempirical result. However, for pyridazine (adjacent N atoms) and for most five-membered aromatic heterocycles of one nitrogen and/or one oxygen AM1 gives the poorest agreement, usually by a substantial positive error.
3. While MNDO does most poorly for the N-containing six-membered aromatic compounds, it is the best semiempirical method for several key five-membered aromatic heterocyclics: furan, thiophene, isoxazole, and their dibenzo derivatives.
4. PM3 gives the best semiempirical results for oxazole, 4-methylthiazole, and pyrrole.
5. For compounds having three or more heteroatoms in connectivity, there is a wide scatter among the methods.
6. The Stine/Kramer method compares quite favorably with the three semiempirical methods in its agreement with experimental $\Delta H_f°$ values. For aromatic compounds, the Stine/Kramer method

Table XII. Comparison of ΔH_f° for nonaromatic heterocycles (deviation from experimental).

Name	Exp	MNDO	AM1	PM3	Benson	Stine/Kramer	Order of agreement[a] (best to worst)
Piperidine	−11.3[b]	−19.0 (−7.7)	−19.0 (−7.7)	−16.5 (−5.2)	−11.6 (−0.3)	−11.4 (−0.1)	S B P M A
Tetrahydropyran	−53.4[c]	−62.0 (−8.6)	−67.4 (−14.0)	−57.4 (−4.0)	−53.5 (−0.1)[d]	−53.2 (0.2)	B S P M A
Tetrahydrothiopyran	−15.2[b]	−28.0 (−12.8)	−23.9 (−8.7)	−15.7 (−0.5)	−14.6 (0.6)		P B A M
Pyrrolidine	−0.8[c]	−15.8 (−15.0)	−10.4 (−9.6)	−12.0 (−11.2)	−0.9 (−0.1)	−6.5 (−5.7)	B S A P M
Tetrahydrofuran	−44.0[c]	−59.3 (−15.3)	−58.4 (−14.4)	−51.3 (−7.3)	−44.0 (0.0)[d]	−33.4 (10.6)	B P S A M
Tetrahydrothiophene	−8.1[c]	−24.1 (−16.0)	−16.0 (−7.9)	−10.4 (−2.3)	−8.0 (0.1)		B P A M
Oxetane	−19.3[c]	−37.2 (−17.9)	−25.6 (−6.3)	−26.7 (−7.5)	−19.3 (0.0)[d]	−23.9 (−4.6)	B S A P M
Thietane	14.6[c]	−5.1 (−19.7)	8.0 (−6.6)	7.5 (−7.1)	14.6 (0.0)[d]		B A P M
Ethyleneimine	30.2[c]	25.1 (−5.1)	33.1 (2.9)	31.6 (1.4)	29.9 (−0.3)	30.4 (0.2)	S B P A M
Oxirane	−12.6[c]	−15.5 (−2.9)	−9.0 (3.6)	−8.1 (4.5)	−13.1 (−0.5)[d]	−11.3 (1.3)	B S M A P
Thiirane	19.7[c]	18.8 (−0.9)	32.3 (12.6)	28.8 (9.1)	19.9 (0.2)[d]		B M P A
2-Methyl-2-oxazoline	−31.2[b]	−39.6 (−8.4)	−22.9 (8.3)	−32.1 (−0.9)	−13.7 (17.5)	−27.7 (3.5)	P S A M B
Average unsigned error		10.85	8.55	5.08	1.64	3.28	
Average signed error		−10.85	−3.98	−2.58	1.43	0.68	

[a]M, MNDO; B, Benson; A, AM1; S, Stine/Kramer; P, PM3.
[b]Obtained from ref. 21.
[c]Obtained from ref. 8.
[d]Obtained from ref. 26.

Table XIII. Frequency of closest agreement with experimental $\Delta H_f°$.

Compound class	Method				
	Stine/Kramer	Benson	MNDO	AM1	PM3
Aromatics	6	5	2 (8)	0 (3)	4 (6)
Overall average error (unsigned; from Table IX)	3.34	7.50	8.68	13.21	7.34
Nonaromatics	2	8	0 (2)	0 (3)	2 (7)
Overall average error (unsigned; from Table X)	3.28	1.64	10.85	8.55	5.08

gives the greatest agreement. For nonaromatics, Benson gives the best results.

Table XIII summarizes these results giving the number of times each method's computed $\Delta H_f°$ was closest to the experimental value and its overall unsigned error. The same comparison for only the semiempirical techniques (MNDO, AM1, PM3) appears in parentheses.

In comparing average errors for all methods, clearly Stine/Kramer is superior for aromatic compounds. It shows the lowest overall error in terms of absolute magnitude. For the aromatic compounds, Stine/Kramer is followed by PM3, Benson, MNDO, and AM1 in terms of average unsigned error. For the nonaromatics, Benson is followed by Stine/Kramer, PM3, AM1, and MNDO.

Among the semiempirical techniques, it appears the PM3 and MNDO methods best address aromatic systems. AM1 is the best method only for specific N-containing six-membered ring compounds. This is a surprising result because the MNDO method is the oldest of these semiempirical methods and has the most limited basis set of empirical parameters. However, for nonaromatic compounds a dramatic reversal of MNDO's performance is noted. Here, it gives the worst agreement with experiment, consistently with negative error. For this compound class, PM3 gives best agreement of the three semiempirical methods. For both classes of compounds, AM1 gives the poorest overall agreement with experimental data.

From this comparison of aromatic vs. nonaromatic heterocyclics, it appears that the MNDO parameterization incorporates as effectively as PM3 the inherent aromatic stabilization in the predicted $\Delta H_f°$ values. With the exception of the six-membered N-containing aromatic heterocyclics, where AM1 gave an average error of −4.25 kcal (vs. −7.83 for PM3, −12.45 for MNDO, and −1.70 for Stine/Kramer), the AM1 method consistently gave a large positive error for the $\Delta H_f°$ value for aromatic compounds. Aromatic stabilization energy appears to be less adequately addressed by the AM1 method for five-membered heterocyclics in general. The consistently longer bond lengths in the AM1-optimized geometry appears to underscore the excessive importance AM1 places on repulsive atomic interactions. This factor would tend to negate any stabilization (lowering of bond lengths and $\Delta H_f°$) due to aromaticity.

CONCLUSION

We conclude that the Stine/Kramer and Benson methods give the best overall agreement with experimental $\Delta H_f°$s where applied to aromatic and nonaromatic heterocyclic compounds, respectively. The empirically derived constituent basis set of the Stine/Kramer method focuses on applicability to energetic compounds. Approximately 30% of energetic compounds could be classified as aromatic. (Unfortunately, the Stine/Kramer model is limited by its not considering hypervalent compounds and only those containing C, H, N, and O.) Ring strain energy, represented in the study here by the three- and four-membered nonaromatic heterocyclics, is best addressed by the Benson method.

The PM3 method, parameterized from 763 compounds (106 of which are hypervalent), comes closest to the Stine/Kramer and Benson methods of the three semiempirical models. Its scope is broader than Stine/Kramer and for this reason it provides an effective complement to the Stine/Kramer method for heterocyclic compounds. It is remarkable how well MNDO does for aromatic heterocyclics, considering only 34 molecules were used to develop the C—H—N—O set and up to a few tens of molecules for the other elements.

The Stine/Kramer and Benson methods are not applicable to the nonequilibrium energy calculations used for derivation of polymer elastic force constants or moduli values. This study implies that each semiempirical method is best suited to specific polymer structures assuming two points are valid: (1) The heterocyclic structural component mostly accounts for variation in calculated polymer properties and (2) the relative accuracies of semiempirical methods at highly strained, nonequilibrium geometries parallels that seen for the ground-state equilibrium geometry. From this perspective, the *cis*-PBO structure and others like it having fused-ring five-membered heterocyclics are best treated overall by the PM3 method. On the other hand, N-containing

six-membered heterocyclics (for example, the quinoxaline polymers) are best treated by AM1. Even MNDO may provide a comparably accurate treatment of furan, thiophene, and isoxozole-based polymers. Overall, PM3 performs best of the semiempirical methods, but there is a wide scatter sensitive to the nature of the heterocycle. Such a diversity of results obtained by the methods employed here for a fundamental property such as heat of formation implies the danger of an even more exaggerated scatter for predicted properties of a macromolecular array (i.e., polymers). Of particular concern in the polymer area is the effect of this method diversity on prediction of ultimate physical property terms such as elastic moduli. An extremely useful future predictive tool for a polymer/material chemist would involve a table of force constants for specific polymer structural units. This table could then be applied to any conceivable polymeric structure to predict its ultimate strength properties. However, for this capability to be realized inconsistencies in the semiempirical methods applied to heterocyclic compounds need to be resolved. Considering the central importance of aromatic heterocyclic compounds in burgeoning new areas of materials chemistry (for example, conducting polymers, NLO materials, and high-strength fibers), a more rigorous inclusion of this class of compounds into parameterization of semiempirical methods is obviously needed. From this, a single semiempirical method best suited to all aromatic heterocyclic systems may become available. This would provide a unified basis for prediction of the physical and chemical properties of this important class of compounds. It is important that the implications of this semiempirical method contrast, focused here in terms of the heterocyclic unit, be applied to ultimate polymer properties such as elastic moduli. These studies are currently being done and will be reported in a subsequent article.

References

1. D.R. Ulrich, *Polymer*, **28**, 533 (1987).
2. E.J. Roche, T. Takahashi, and E.L. Thomas, *ACS Symposium Series*, **141**, 303 (1980).
3. J.A. Odell, A. Keller, E.D.T. Atkins, and M.J. Metes, *J. Mater. Sci.*, **116**, 3309 (1981).
4. W. W. Adams and R.K. Eby, *MRS Bull.*, **12**(8), 22 (1987).
5. M.J.S. Dewar, *J. Phys. Chem.*, **89**, 2145 (1985).
6. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, and J.J.P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
7. J.J.P. Stewart, *J. Comp. Chem.*, **10**, 209 (1989).
8. J.J.P. Stewart, *J. Comp. Chem.*, **10**, 221 (1989).
9. C.C.J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).
10. J.J.P. Stewart, FJSRL TR-90-0004, November 1990.
11. J. Baker, *J. Comp. Chem.*, **7**, 385 (1986).
12. R.G. Spain and L.G. Picklesimer, *Text. Res. J.*, **36**(7), 619 (1966).
13. M.J.S. Dewar and Y.C. Yuan, *Inorg. Chem.*, **29**(19), 3881 (1990).
14. J.A. Pople and D.L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970.
15. C. Moller and M.S. Plesset, *Phys. Rev.*, **46**, 618 (1934).
16. M.J. Frische, M. Head-Gordon, G.W. Trucks, J.B. Foresman, H.B. Schlegel, K. Raghavachari, M.A. Robb, J.S. Binkley, C. Gonzalez, D.J. Defrees, D.J. Fox, R.A. Whiteside, R. Seeger, C.F. Melius, J. Baker, R.L. Martin, L.R. Kahn, J.J.P. Stewart, S. Topiol, and J.A. Pople, Gaussian 90, Gaussian, Inc., Pittsburgh, PA, 1990.
17. A. Szabo and N.S. Ostlund, *Modern Quantum Chemistry*, McGraw-Hill, New York, 1989, p. 151.
18. M. Mansson and S. Sunner, *Acta Chem. Scand.*, **20**, 845 (1966).
19. S. Benson, *Thermochemical Kinetics*, John Wiley and Sons, New York, 1976.
20. J.R. Stine and J.F. Kramer, Estimation of heats of formation and the development of chemical databases useful for energetic materials, *Proceedings of the 26th JANNAF Combustion Meeting*, 1989.
21. J.B. Pedley, R.D. Naylor, and S.P. Kirby, *Thermochemical Data of Organic Compounds*, 2nd ed., Chapman and Hall, London, 1986.
22. P.C. Hariharan and J.A. Pople, *Chem. Phys. Lett.*, **66**, 217 (1972).
23. J.S. Binkley and J.A. Pople, *Int. J. Quantum Chem.*, **9**, 229 (1975).
24. A. Kunar, J. Sheridan, and O.L. Stiefvater, *Z. Naturforsch*, **33a**, 145 (1978).
25. L. Nygaard, E. Asmussen, J.H. Hg, R.C. Maheshwari, C.H. Neilsen, I.B. Petersen, J. Rastrup-Andersen and G.O. Sorensen, *J. Mol. Struct.*, **8**, 225 (1971).
26. S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Haugen, H.E. O'Neal, A.S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

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