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Letters to the Editor

Comments on a Comparison of AM1 with the Recently Developed PM3 Method

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A reparameterized version (PM3) of AM1 has recently been reported and the results for several hundred molecules compared with those from AM1 itself. The comparison implied that PM3 represents a significant improvement over the earlier treatment. The apparently poor performance of AM1 is, however, due to the inclusion of "AM1 results" for elements (Al, P, S) for which AM1 parameters were unavailable. If these are omitted, PM3 is seen to be only marginally better than AM1. Since this conclusion refers only to a specific set of stable molecules, it is not clear whether even this small improvement will apply to other species or studies of reactions. It is in any case insufficient to justify the confusion caused by the release of the new treatment.

Stewart¹ has recently described a new semiempirical treatment (PM3) which he implies is significantly better than AM1.² The mean unsigned PM3 (AM1) errors quoted in the abstract of his article, for compounds of elements in their normal valence states, were 7.8 (12.7) kcal/mol, and for compounds containing hypervalent atoms 13.6 (83.1) kcal/mol. Comparable differences are indicated by the plots in the figures while the tables indicate that the errors in AM1 heats of formation can amount to hundreds of kcal/mol.

The apparently poor performance of AM1 is, however, due to the inclusion of "AM1" results for elements (Al, P, S) for which AM1 parameters were not available. The "AM1" values were calculated using MNDO parameters in AM1, which leads to very bad results, especially for compounds of phosphorus and sulfur in their higher valence states where MNDO itself fails badly.³

We have also recently developed AM1 parameters for sulfur and aluminum. Articles describing them are being submitted for publication. We have used these, and our phosphorus parameters,⁴ to calculate AM1 heats of formation for most of the molecules containing phosphorus, sulfur, or aluminum, that were treated by Stewart.¹ Sulfur-iodine compounds are omitted because we found that the "experimental" values cited by Stewart were in fact theoretical estimates.⁵ No

thermochemical data for such compounds seem as yet to have been reported. We have included some additional organosulfur compounds which were listed in the compilation cited by Stewart which he omitted and for which we carried out PM3 calculations. Table I compares statistical analyses of the results from PM3 with the real AM1 results. While the AM1 errors in the heats of formation calculated for phosphorus compounds are somewhat greater than those from PM3, the reverse is true for aluminum while the errors for sulfur are almost the same.

The validity of such comparisons naturally depends on the molecules used in them. Since the errors in any procedure tend to be systematic, its apparent performance depends on whether or not the selected set of molecules contains examples where the systematic errors are large. During the development of AM1, we compiled a test set of organic (C, H, O, N) molecules which seemed to provide an effective overall indication of the performance of procedures of this kind. Table I compares the AM1 and PM3 errors for them, and also with inclusion of the molecules containing Al, P, and S. While the PM3 errors are a little smaller, the difference is far less than that implied by Stewart. It should also be remembered that while AM1 has been applied with success to a very wide range of chemical reactions and other chemical problems, PM3 remains virtually untested apart from the calculations reported by Stewart.

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Table I. Comparison of errors in AM1 and PM3 heats of formation.

Molecules containing:	Number of molecules	Mean unsigned Error (kcal/mol)		Standard deviation (kcal/mol)	
		AM1	PM3	AM1	PM3
C, H, O, N	134	5.4	4.4	7.2	6.3
Al	27	10.7	14.3	13.9	20.6
P	50	16.1	12.3	22.8	15.2
S	69	9.0	8.1	12.3	10.8
Sum of above	280	8.7	7.7	13.2	11.4

We have always followed the principle, that a new version of a treatment should be introduced only if it represents a major advance. Each of our treatments has made its predecessors virtually obsolete, except for the few specific areas where they happened to give systematically better results.⁶ In our opinion, PM3 does not meet this criterion. Now that it is available, it will of course be useful, if only in specific cases, e.g., compounds containing NO₂, where it gives results clearly superior to those from AM1. However, the effort put into optimizing PM3 could certainly have been spent more profitably in developing a new parametric treatment, based on a better approximation than the AM1 formalism. We ourselves are currently working on two approaches of this kind. It seems in any case most unlikely that any significantly better version of AM1 can be developed and it is to be hoped that there will be no more attempts in this direction.

Dr. Stewart's statements concerning parameterization in his preceding article⁷ also require comment. The main problem in developing treatments such as AM1 is not the actual determination of parameters but determining the best forms of the parametric functions and finding the best minimum on the parameter hypersurface.⁸ Our very extensive experience has indicated that the best minimum cannot be found reliably by simple minimization of the error function and indeed Dr. Stewart's attempts in Austin to optimize AM1 in this way failed. The parameterization of AM1² was carried out by Dr. Zoebisch, starting from first principles and using techniques, described in detail in her Ph.D. Dissertation⁹ and similar to those used in parametrizing MINDO/3¹⁰ and MNDO.¹¹ Dr. Stewart's final parameters were of no help to

her since they referred to a different minimum on the parameter hypersurface. Dr. Stewart naturally encountered no problems in his reparameterization of AM1 because he had AM1 as a starting point.

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6. Because of our policy, calculations by any of our procedures, carried out in different laboratories, have been directly comparable. This has allowed the accumulation of permanently useful results for many molecules. Indeed, an archive of our own MNDO and AM1 results for over 2000 molecules is available in computer-retrievable form from GGraph Software, PO Box 5641, Austin, TX 78763. We hope that others will also contribute to this project.
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