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Our object was to provide chemists with theoretical procedures that could serve as practical adjuncts to experiment in studies of chemical problems, in particular studies of reactions and reaction mechanisms. We succeeded for the elements which have sp valence shells and main group elements where d AOs serve only as polarization functions, but attempts to extend this approach to elements with spd valence shells all failed. We had no experience of ab initio programming so we wrote a general program from scratch. Full scale parametrization for the "organic" elements (CHON) is now in progress. Computer programs were written for treating biradicals in procedures for correlation between the unpaired electrons. Proportionality factors were found by matching the singlet-triplet separation in carbene and singlet-triplet separations were then calculated for large numbers of other carbenes. AM1 parameters were optimized for aluminum, sulfur, germanium, tin, and mercury. We developed a new version of the DEWARPI procedure in which geometries are found by minimizing the total energy. We developed a new version of the AMPAC program at QCPE (AMPAC2.1) for a very effective method for finding transition states.

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PUBLICATIONS:

1. "AM1 Parameters for Phosphorus"; M.J.S. Dewar and C. Jie, *J. Mol. Struct. THEOCHEM* **1989**, *187*, 1.
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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Our object was to provide chemists with theoretical procedures that could serve as practical adjuncts to experiment in studies of chemical problems, in particular studies of reactions and reaction mechanisms. We succeeded for the elements which have sp valence shells and main group elements where d AOs serve only as polarization functions, but attempts to extend this approach to elements with spd valence shells all failed. We had no experience of ab initio programming so we wrote a general program from scratch. Full scale parametrization for the "organic" elements (CHON) is now in progress. Computer programs were written for treating biradicals in procedures for correlation between the unpaired electrons. Proportionality factors were found by matching the singlet-triplet separation in carbene and singlet-triplet separations were then calculated for large numbers of other carbenes. AM1 parameters were optimized for aluminum, sulfur, germanium tin, and mercury. We developed a new version of the DEWARPI procedure in which geometries are found by minimizing the total energy. We developed a new version of the AMPAC program at QCPE (AMPAC2.1) for a very effective method for finding transition states.

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for the period 11/01/88 - 4/30/91

Michael J.S. Dewar and Marye Anne Fox, Principal Investigators

Introduction

This project was conducted solely under Professor M.J.S. Dewar's supevision from 1/1/88-9/1/89. During the period from 9/1/89-9/1/90, Professor Dewar was commuting between his existing group in Austin and his new group at the University of Florida. During that time, Professor Dewar acted as PI on the grant as Professor Fox began to become involved in student supervision for the work. On 9/1/90 Professor Dewar resigned from the University of Texas and Professor Fox assumed full responsibility for those aspects of the project being conducted in Austin, primarily finishing exploratory work and assisting Professor Dewar's students in writing their work for publication and for their dissertation defenses. An effort was also made for archival storage of the programs developed. Work during the last half of the grant period was somewhat disorganized due to the move of Professor Dewar to the University of Florida. Professor Fox remained at the University of Texas supervising the remainder of the students working on this research project. Nevertheless very good progress was made on the various projects supported by the grant, in particular in the preliminary work directed to the development of a new "fourth generation" semiempirical treatment. Since we have not yet decided on a name for it, it will be referred to here as "Procedure X". A summary of this, and other work carried out during the past grant period, follows.

Theoretical Procedures

A. Procedure X. One of the major objectives of the work on theoretical procedures for the last fifteen years has been the development of a satisfactory treatment for transition metals. Our current treatments (MINDO/3,[1] MNDO,[2] and AM1[3] have proved of major value to organic chemists, in industry as well as universities. According to a recent survey by Dr. John McKelvey, calculations using our procedures account for 40% of the money spent on chemical computing by chemical and pharmaceutical companies, as opposed to <1% on ab initio methods. Our own theoretical studies have led to many novel conclusions concerning the mechanisms of reactions in organic chemistry. Given this success in an area of chemistry where one would have thought fifteen years ago that little remained to be discovered, a comparable treatment of transition metals would unquestionably be of major value.

Our object has been to provide chemists (including ourselves) with theoretical procedures that can serve as practical adjuncts to experiment in studies of chemical problems, in particular studies of reactions and reaction mechanisms. Such a procedure must be applicable at reasonable cost to the (often large) molecules in which chemists are directly interested, using readily available computers. This goal was met by using a grossly simplified basic approximation (INDO or NDDO) and then upgrading its accuracy by introducing adjustable parameters. Allowance for electron correlation was made by empirical modification of the electron repulsion integrals, following Pariser and Parr.[4] A further saving of time was effected by using appropriate parametric functions[5] to estimate the repulsion integrals instead of evaluating them directly. As noted above, this approach has proved remarkably successful for the "organic" elements, which have sp valence shells, and also for main group elements where d AOs serve only as polarization functions and can be neglected in our treatments. However, our attempts to extend this approach to elements with spd valence shells have all failed. The formalism for the electron repulsion integrals becomes hopelessly cumberson if d AOs are introduced. We tried to overcome this difficulty by using a CNDO formalism for integrals involving d AOs while retaining the usual MNDO/AM1 formalism for ones involving only s and p AOs. This was indeed included as an option in the original MPOAC program which we submitted to QCPE, together with preliminary parameters for chromium. However, further study showed this approach to be unsatisfactory and all our attempts to it failed.

This difficulty could be overcome by calculating the repulsion integrals theoretically and then scaling them by some appropriate function of interatomic distance to allow for electron correlation.[4] If the ZDO approximation is retained, the only relevant integrals are two-center ones of the type (ii;kk). The corresponding corrected integrals $(ii;kk)_c$ would then be given by:

$$(ii;kk)_c = (ii;kk)F(R_{ik}) \qquad (1)$$

where F is a function of the internuclear distance (R_{ik}) between the two atoms. Since repulsion integrals involving d AOs can be calculated as easily as those involving only s and p AOs, such an approach could be applied to spd basis sets without difficulty. Indeed, Dr. James Ritchie (now at Los Alamos) tried this approach in Austin some time ago while working for his Ph.D. Unfortunately it soon became clear that the computing time required would be far too great, using the VAX 11-780 computer which I had just acquired. This is why we have tried so hard to develop a treatment based on the standard MNDO/AM1 formalism. However, just when it had become clear that this approach could not be implemented, my group acquired a half share in an Alliant FX-8 superminicomputer which benchmark tests showed to be 12-15 times faster than our VAX. We therefore returned to the approach indicated in Equation (1).

Since we had no experience of ab initio programming and since extensive exploration would clearly be needed to establish the best way to implement the new approach, we began by writing a general program from scratch. While this was a major undertaking and took much time, it has proved well worthwhile in the long run.

The first question we had to answer was the extent to which theoretical integrals would be used. Should the core-electron attractions and the core-core repulsions be calculated theoretically, as well as the electron-electron repulsions? Extensive trials showed this to be impracticable. The attractions and repulsions are very large and we were unable to keep them in balance, even when we included an additional parametric function in the core repulsion. We therefore reverted to the MNDO/AM1 formalism, all the attractions and repulsions being set essentially equal but with additional terms added to the core-core repulsions to allow for the net repulsions between pairs of atoms.

The next question concerned the type of function to use in Equation (1). Very extensive trials were needed to determine this. The situation was further confused by uncertainty concerning the parameric functions that appear in the MNDO/AM1 expressions for the one-electron resonance integrals (β) and the core repulsions. Eventually we decided that the expressions used for them in AM1 were as good as any so we retained them.

While these conclusions are quickly stated, reaching them took two years of concerted effort by several very able members of my group and an enormous amount of computing time. At this point our program was still in a somehwat primitive state and our exploratory calculations had been confined to simple hydrocarbons. Before embarking on the final parametrization, we had to optimize and debug the Procedure X program and insert it into our optimization program. This again was a massive undertaking which, together with preliminary parametrizations for the organic elements, was completed by the end of August when Professor Dewar finally left Austin. Full scale parametrization for the "organic" elements (CHON) is now in progress.

B. Treatment of Biradicals. Problems arise in treating biradicals in our procedures because the very strong correlation between the "unpaired" electrons is not adequately taken into account by the Pariser-Parr formalism. Use of an open shell HF treatment (e.g. UHF, or the "half electron" approximation) allows completely for the correlation between the "unpaired" electrons. However, in the corresponding versions of MNDO or AM1, an average (Pariser-Parr) correction for correlation is included for *all* pairs of electrons, including the two "unpaired" ones. The correlation energy for the latter is therefore overestimated by an uncertain and variable amount.

Walter Thiel, who developed MNDO while in Austin as a member of my research group, solved this problem in principle by parametrizing a version of MNDO in which CI was included throughout (MNDOC). This, however, has been little used because of the excessive computing time needed to optimize geometries, due in turn to the lack of analytical expressions for derivatives of the energy in CI versions of MNDO. Since analytical CI derivatives are now included in AMPAC, we had hoped that Thiel might be persuaded to develop a MNDOC-like version of AM1. Since he declined, we decided to do this ourselves. The necessary computer programs were written in Austin and parametrization began there. Unfortunately the student concerned had to interrupt this work to write his Ph.D. dissertation.

We have also tried a simpler approach to the problem, based on correcting the repulsion between the two "unpaired" electrons in a biradical. Intuitive arguments suggested that the correction should be roughly proportional to the extent to which the two contributing AOs (ϕ_i and ϕ_k) overlap. We therefore tried using a correction proportional to the "superoverlap" integral, σ_{iikk}:

$$\sigma_{iikk} = \Phi_i\Phi_i\Phi_k\Phi_k d\tau \tag{2}$$

The proportionality factor was found by matching the singlet triplet separation in carbene (CH_2) and singlet-triplet separations were then calculated for a large number of other carbenes. The ground state (singlet or triplet) was correctly predicted in all cases and the calculated separations agreed quite well with experiment when experimental data were available.

C. AM1 Parameters. AM1 parameters have been optimized for aluminum, sulfur, germanium, tin, and mercury.

D. Calculation of Geometries Using the DEWARPI Procedure. The earliest of our semi-empirical procedures was based onthe σ,π approximation, the contributions of the π electrons being calculated while those of the σ electrons were equated to sums of their bond energies and the energies needed to stretch or compress them to their final lengths. Geometries were estimated from an empirical relationship between π bond order and length. While this treatment proved remarkably successful, certain errors seemed to suggest that the method used to estimate geometries was unsatisfactory. We have now developed a new version of this "DEWARPI" procedure in which geometries are found by minimizing the total energy. In this form it gives astonishingly good results.

E. AMPAC2.1. This new version of the AMPAC program has proved a "best seller" at QCPE. Versions are now available for most of the more popular computers. Benchmark tests indicate that the CRAY version runs 20-30 times faster than Stewart's MOPAC 5.0. This is not surprising because Daniel Liotard virtually rewrote AMPAC while he was in Austin to make it easily vectorizable. AMPAC2.1 therefore runs much faster than MOPAC on any vector computer. However, it also runs faster on scalar computers as a result of Daniel's recoding. Other major advantages of AMPAC2.1 include analytical derivatives for calculations using CI versions of AM1 and a new and very effective method for finding transition states, both due again to Daniel.

CHEMICAL APPLICATIONS

Much of the work carried out during the grant period has been concerned with applications of our procedures to chemical problems. Studies of a number of reaction have led to significant contributions concerning their mechanisms.

A. Pericyclic Reactions. Our previous work, supported by AFOSR, led to very extensive revisions of ideas concerning the mechanisms of pericyclic reactions. Our calculations indicated that many "allowed" reactions to take place in a nonsynchronous manner, via biradical-like transition states (TS)(BR mechanism), instead of by synchronous (ARO mechanism) involving aromatic TSs as expected in terms of the Woodward-Hoffmann rules and Evans' Principle. The Cope rearrangement of 1,5-hexadiene provided the most striking example. This can take place via transition states with geometries analogous to the chair or boat conformations of cyclohexane and it had been generally assumed that both reactions take place by the ARO mechanism. We showed that the normal chair rearrangement in fact takes place by the BR mechanism, via a biradical-like TS, while the boat rearrangement takes place by the "normal" ARO path. Studies of a number of other Cope rearrangements showed not only that they followed one or another of the two mechanisms in a predictable manner but also that both mechanisms are viable in each case, often corresponding to distinct TSs. While the existence of multiple transition states for a reaction had been recognized as a theoretical possibility, no examples had been reported prior to our work. We have now found evidence that the same situation holds for a number of ene reactions and dipolar additions. However, the majority of Claisen rearrangements take place via unique transition states with sructures varying between the BR and ARO extremes. This is because the Claisen rearrangement is inherently strongly exothermic whereas the Cope rearrangement is inherently thermoneutral. The Claisen transition state is therefore an "early" one, preceding the bifurcation of the reaction path.

B. Benzidine Rearrangement. The benzidine rearrangement, the acid-catalyzed rearrangement of hydrazobenzene (**1**) to benzidine (**2**), has puzzled theoretical organic chemists ever since the first electronic mechanism was suggested for it by Robinson, sixty years ago. The problem is to explain how a CC bond can form between the *para* carbon atoms in **1**, given that they are initially very far apart, given that they cannot be brought together without generating severe steric interactions and angle strain, and given that the reaction takes place very rapidly in strong acids at room temperature. Since the reaction is now known to involve the diacid salt of **1**, one obvious possibility would be that **1** dissociates to a pair of aniline radical cations (**3**) which then recombine. The experimental evidence indicates, however, that the reaction is intramolecular. While alternative "classical" explanations have been suggested, invoking radical distortions during the reaction, it is difficult to see how these could be compatible with the ease with which the reaction takes place.

Nearly fifty years ago, Dewar suggested[6] that the monoacid salt of **1** may rearrange to a sandwich-like species (**4**) which he termed a π *complex*, in which the components ($PhNH_2$ and $PhNH^+$) are linked by a novel kind of multicenter dative bond (μ *bond*). This indeed represented the inception of π complex theory[7] whic now plays a major role in inorganic chemistry as well as providing the first, and probably still the best, general interpretation of the structures of nonclassical carbocations. While the benzidine rearrangement is now known to involve the diacid salt of **1**, this can easily be accommodated in terms of a corresponding π complex intermediate. Similar comments apply to recent experimental studies by Shine, et al which were claimed to refute the π complex mechanism but which can in fact be explained in terms of reversible formation of the π complex.

Over the years we have tried from time to time to test Dewar's interpretation of the benzidine rearrangement by numerical calculations. However, the procedures and computers available at that time proved inadequate. Since calculations of this kind have at last become feasible, we have tried again, this time with success.

Our results rule out the π complex mechanism, structures of this kind being predicted to have energies that are too positive. They also rule out all the other mechanisms so far suggested in which postulated distortions of the anilino moieties enabling the para carbon atoms to approach within bonding distance. However, we found, much to our surprise, a reaction path with a genuine transition state of quite low energy in which the two anilino moieties are still almost planar, the distance between the two *para* carbon atoms being still >5 A. The reason why the reaction takes place so easily has therefore nothing to do with formation fo a new CC bond. It is because the coulombic repulsions between the two anilino moieties decrease in forming the transition state, due to delocalization of the positive charges into the benzene rings. Once the transition state is passed, the system can collapse either to **5**, which is deprotonated to **2**, or to **6**, which could be deprotonated to o-benzidine (**7**). However, since **6** is much higher in energy than **5** and is separated from it by only a low barrier, only **2** is formed. The difference in energy between **5** and **6** can be attributed to the coulombic repulsions between the positively charged nitrogen atoms, these being closer together in **5** than in **6**.

While the mechanism of the benzidine rearrangement is not a matter of major importance, it represents a notable triumph for the AM1 procedure to have solved such a long standing problem in such an unexpected way.

C. E2 Elimination Reactions. We have completed a comprehensive study of E2 elimination reactions which led to some unexpected results. While our calculations reproduced the different regioselectivities observed in eliminations from alkyl halides and 'onium ions, as summarized embodied in the rules due to Saytzeff and Hoffman, the mechanisms differed from those generally accepted. Thus elimination from neutral species (halides) was predicted to involve E1 cb-like transition states while elimination from 'onium ions was predicted to involve E1-like transition states. It will be interesting to see whether the mechanisms of the reactions in solution are indeed different as a result of solvation.

D. Mechanism of Ozonolysis. Extensive calculations for the reactions of ethylene, and of 2-butene, with ozone support the Criegee mechanism and gave a seemingly better estimate of the heat of formation of the Criegee intermediate than a recent high level ab initio study. Our results suggest that the stereoselectivity often observed in the ozonolyses is probably due to steric effects of solvation.

E. Bond Strengths in Fluorocarbons. A minor problem of much potential practical significance was suggested to us by Dr. Hedberg. Does fluorination increase, or decrease, the strength of the central CC bond in biphenyl? The question is important in view of the potential use of perfluorinated polyphenyene derivatives as high temperature lubricants and the fact that qualitative arguments seemed to suggest that fluorination should weaken the central CC bond in biphenyl. However, our AM1 calculations indicate that the central CC bond is in fact much stronger in decafluorobiphenyl than it is in biphenyl itself. Since the AM1 value for the strength of this bond in biphenyl seems to be in reasonable agreement with experiment, the prediction is likely to be correct.

F. Calculation of Vibrational Frequencies. While AM1 seems to give good estimates of molecular vibration frequencies, no systematic tests have yet been published. We have now carried out AM1 calculations of vibration frequencies for a number of molecules that we had studied earlier, using MNDO. The AM1 errors are uniformly less than those from MNDO and the errors in thermodynamic properties (entropies and specific heats) calculated from them are also correspondingly smaller. Since the errors inthe vibration frequencies also tend to be systematic, they can be reduced by applying appropriate corrections. The errors in the correspondingly corrected AM1 values are again less than those inthe MNDO ones, being mostly <5% except for a few bending vibrations.

G. Enolization of Ketones. Extensive studies have been carried out for a α-deprotonation of ketones by methoxide ion. The relative rates of attack at different α-protons are usually correctly predicted and the errors can be attributed to steric effects, due to the greater size of methoxide ion in solution, due to solvation. The products from the reactions of the anions with methyl halides are correctly predicted.

H. Mode of Action of Esperamycin. AM1 calculations for a model of esperamycin confirm the suggested mechanism for its biological activity, involving cyclization of a 1,2-diynene system to a p-benyne.

I. Aldol Condensation. AM1 calculations for a number of aldol condensations have given results in good agreement with experiment.

J. Radical Cation from Tetramethylurea. ESR studies have indicated that the NMe_2 groups in the radical cation from $Me_2NCONMe_2$ are not equivalent, the unpaired electron being confined to one NMe_2 group. AM1 calculations for the radical cation indicate that one NMe_2 group is indeed orthogonal to the rest of the molecule.

K. Conversion of Phosphoenol Pyruvates to Phosphonylpyruvates. AM1 calculations for this reaction, which is of major importance in biochemisry, indicate that the gegenion plays a decisive role, the activation energy decreasing from 35 kcal/mol to zero.

L. Structures of Diboroxanes. While diboroxanes (R_2BOBR_2) are normally bent, it has been claimed on the basis of its IR spectrum that the central B-O-B group in divinylboric anhydride ($R = H_2C = CH\text{-}O\text{-}$) is linear, the isotopic (^{16} vs O^{18}) shifts for the symmetric (3 cm^{-1}) and antisymmetric (8 cm^{-1}) BOB stretching frequencies being very small. Our AM1 calculations indicate, however, that the anhydride is in fact bent, the corresponding species with BOB linear lying higher in energy by 13 kcal/mol. This difference is large enough to make it very unlikely that the molecule can in fact be linear. Furthermore, our calculations for the bent isotopic species indicate isotopic shifts for the symmetric and antisymmetric vibrations (4, 9 cm^{-1}, respectively) that agree very closely with the experiment. There can therefore be little doubt that the molecule is in fact bent. These results show the danger of arguments based on intuition and emphasize the value of AM1 calculations as an aid in interpreting experimental results.

M. Transannular Interactions in Medium-Sized Rings. AM1 calculations confirm the existence of transannular interactions between nitrogen and carbonyl in several cyclic aminoketones with medium-sized rings and indicate that the interactions are purely electrostatic.

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