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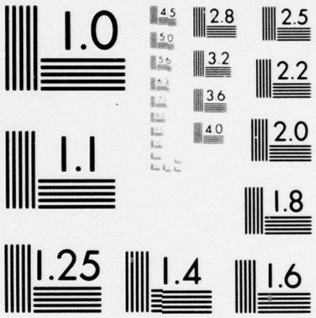

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⑩ MICHAEL J.S. DEWAR

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A new semiempirical method (MNDO), based on NDDO, has proved superior to MINDO/3 in nearly all respects. Parameters are available for H, Be, B, C, N, O, F, and (without 3d AOs) Si, P, S, and Cl. MINDO/3 and MNDO give good estimates of molecular vibration frequencies and isotopic shifts, and hence of entropies, specific heats, entropies of activation, and kinetic isotope effects. MNDO calculations were carried out for a number of normal and mesoionic oxazoles and imidazoles and for pentadienyl ions and their methyl derivatives.

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The most notable result during the grant period has been the development of a new semiempirical treatment, MNDO [143], based on the NDDO approximation, which has proved superior to MINDO/3 in almost every respect. In particular, no problems arose in its extension to heteroatoms. Also, since it involves parameters for atoms, not atom pairs, extension to a new element involves only a fixed number of new parameters. Parameters are available for CHON[144], F[162], B[146], Be[166], and (without as yet 3d AOs) for Si, P, S, and Cl.

A second important development has been the extension of MINDO/3 and MNDO to the calculation of molecular vibration frequencies [135,164] and isotopic shifts in vibration frequencies [148], and hence of entropies and specific heats [158], of entropies of activation [158], and of kinetic isotope effects [119]. The errors in vibration frequencies are no greater than those given by Pulay's ab initio methods which are limited to small molecules. In collaboration with Dr. Basil Swanson we have used MNDO force constants to estimate compliance constants and hence the mode of dissociation of molecules [160] and also to arrive at what are probably the best available potential surfaces for some simple molecules [165].

Programs have been written for the study of linear polymers, using MINDO/3 or MNDO in the tight binding approximation and leading to good estimates of the electronic band structure of polyethylene [103,151]. Methods have been developed for optimizing the geometries of polymers and for calculating their vibration frequencies; good results were obtained for polyethylene and polyethylene-d_4 [150].

MINDO/3 has been used with success to calculate polarizabilities [100] and hyperpolarizabilities [130]. In this way we were able for the first time to calculate the non-linear optical properties of a crystal ($LiOOCH \cdot H_2O$), with results in good agreement with experiment [131]. Calculations of this kind should be of practical value in laser technology for screening molecules of possible use as frequency multipliers, etc.

Other successful applications of MINDO/3 and MNDO have been to the calculation of ESCA chemical shifts [121], ionization potentials of radicals [107], nuclear quadrupole coupling constants [128], and energies of singlet and triplet excited states [3]. Calculations of nmr coupling constants were less satisfactory [140]. Other technical developments concerned the calculation of repulsion integrals in NDDO [159], analytical expressions for derivatives of the energy in NDDO [174], a simple and very effective extrapolation procedure for the bond order matrix in SCF calculations [175], and a theoretical treatment of the angular dependence of photoelectron crossections [109].

MNDO has been found to give remarkably good estimates of ionization energies using Koopman's theorem. All the ionizations appear almost invariably in the right order, even the well known "exceptions" like F_2 and N_2, and with reasonable numerical values [144,162]. Calculations of ionization energies, and vibration frequencies of the ions, for the first five polynes gave results in excellent agreement with their observed photoelectron spectra [154]. MNDO also gave good estimates of electron affinities, except in cases where the negative charge in the anion is localized on a single atom [167].

Calculations have been carried out for all the known boron hydrides and borohydride anions up to B_{14} [170], and carboranes up to $(B,C)_{12}$ [7]. The results were generally in very good agreement with experiment, though one or two highly symmetric species (e.g. B_5H_9) were calculated to have geometries of lower symmetry, due probably to a tendency of MNDO to underestimate the stabilities of multicenter bonds. Heats of formation were, however, quite well predicted, implying that the error is not large [146].

Calculation of the vibration frequencies of o-benzyne led to a reassignment of its observed in IR spectrum, removing an apparent discrepancy concerning its geometry [1].

Calculations for beryllium borohydride confirmed the suggestion that it is an equilibrium mixture of d_{2d} and d_{3d} isomers, the former predominating, and the calculated vibration frequencies agreed well with experiment [166]. Calculations for half-sandwich compounds of beryllium with cyclopentadienyl, indenyl, and fluorenyl anions seemed to account well for the properties of such species [5].

MINDO/3 has been found to be a "method of choice" for the study of carbocations. Results for a number of simple "classical" and "nonclassical" ions were in agreement with experiment and with calculations by very sophisticated _ab initio_ methods [110,134,155]. It had previously been argued on the basis of simpler and less accurate SCF treatments (STO-3G, 4-31G) that MINDO/3 overestimates the stabilities of "nonclassical" ions. Calculations for a number of larger ions, in particular 2-norbornyl, were in agreement with experiment but refuted Olah's claim to have proved the latter to be "nonclassical" [134].

The rearrangement of benzyl cation to tropylium was found (MINDO/3) to take place by the mechanism currently postulated but to involve a high activation barrier, apparently in agreement with recent mass spectral evidence [133]. A detailed study of the $C_7H_8^{+\cdot}$ surface was in complete agreement with the experimental results of McLafferty and confirmed his suggested mechanisms for hydrogen scrambling [137]. Calculations for derivatives of $C_7H_7^+$ were equally successful [142, 156]. Detailed calculations were also carried out for a series of reactions of gaseous cations involving formal loss of hydrogen as H_2 from two adjacent atoms. The results were in good agreement with experiment and showed that the eliminations take place by a mechanism which, while concerted, can be regarded as involving a 1,2 hydrogen migration followed by

α elimination, the two steps being fused into one [155].

The rearrangement of phenylcarbene to cycloheptatrienacarbene was found to follow the same course as that of benzyl cation to tropylium [153].

A detailed MINDO/3 study of the Cornforth rearrangements of 5-methoxyoxazole-4-carboxamide and its 2-vinyl derivative led to a mechanism in agreement with experiment and involving an unusual "nonclassical" intermediate [139].

A detailed study (MINDO/3) of the Cope rearrangement of 1,5-hexadiene led to a two-step mechanism involving a biradical-type intermediate, in agreement with experiment [141,145].

A detailed reexamination (MINDO/3) of the Diels-Alder reaction between ethylene and butadiene led to a mechanism which has not so far been considered, involving biradical-like intermediates, in which the rate-determining step is the closure of the second bond. Calculations of entropies of activation and kinetic isotope effects showed this mechanism to be entirely consistent with all the available experimental evidence, refuting current beliefs that the reaction has been "proved" to be synchronous [173].

MNDO studies of the hydroboration of a number of olefins and acetylenes indicated that these reactions take place by sterically controlled, unactivated, rearrangements of π complex intermediates [169].

A MINDO/3 study of addition of methyl radicals to a number of unsaturated hydrocarbons gave results in good agreement with experiment and explained an apparent anomaly shown by kinetic isotope effects [172].

A detailed MNDO study of the conversion of Dewar benzene to benzene indicated that this reaction, although "forbidden" is synchronous. The activation parameters were in good agreement with experiment [161]. A ($S_0 \rightarrow T_1$) crossing occurs after the transition state is passed, confirming the earlier MINDO/3 explanation of the low-yield chemiluminescence [105,124]. Trans-Dewar benzene was found to be a local minimum on the potential surface in spite of the enormous exothermicity of its "allowed" conversion to benzene [161]. The rearrangements of 1- and 2-aza-Dewar benzenes to pyridine follow a very similar course to that of the parent hydrocarbon [168].

A detailed study of the Norrish Type II reactions of singlet and triplet excited ($n \rightarrow \pi^*$) butyraldehyde gave results in good agreement with experiment and seem to have resolved a controversy concerning the possiblity of a direct conversion of the singlet species to product [171].

A MINDO/3 study of the di-π-methane rearrangement of triplet excited 1,5-pentadiene indicated it to have a very large activation energy, contrary to current ideas concerning photochemical mechanisms but in agreement with experiment [147].

The electrocyclic conversions of cyclobutene radical cation and radical anion to butadiene radical ions were predicted by MNDO to take place via unsymmetrical transition states with activation energies less than that for conversion of cyclobutene to butadiene [9].

A detailed study of the rearrangements of C_4H_7 radicals led to mechanisms in agreement with experiment [8].

A detailed study of pentadienyl anion and its methyl derivatives seems to have cleared up a number of longstanding problems concerning their geometries. A new definition of stabilization ("resonance") energy is suggested for odd conjugated systems (ions and radicals) [10].

Calculations for a number of S_N2 and carbonyl addition reactions has led to a new view of enzyme reactions [12].

Four reviews of our work have appeared during the grant period [108,122,147,163].

The additivity of bond energies was discussed in terms of the maximum overlap approximation and MINDO/3 [101].

Papers reporting studies of the electrocyclic conversion of cyclobutene to butadiene [103], the chemiluminescent thermolysis of dioxetanes [104] and predicted chemiluminescence in the electrocyclic conversions of cyclobutadiene dimers to cyclooctatetraene and of benzotricyclooctene to benzocyclooctatriene [106], have appeared, as have the papers [111,112, 113, 114, 115] describing MINDO/3 and its applications to C,H,O,N,F,Si,S,P,Cl.

The electrocyclic conversion of bicyclobutane to butadiene is predicted by MINDO/3 not to be concerted, taking place via a stable intermediate biradicaloid [116]. The "allowed" and "forbidden" paths differ by only 2 kcal/mole in activation energy, in agreement with experiment [116].

The electrocyclic conversion of benzvalene to benzene is "allowed", although it corresponds stereochemically to the "forbidden" mode of conversion of bicyclobutane to butadiene [117].

The ground state of cyclobutadiene is a rectangular singlet. If, as has been claimed, cyclobutadiene has a square geometry in matrices at low temperatures, this must be the metastable triplet [118,152].

A simple relation exists between valence angles and hybridization indices in AX_2Y_2 molecules [120].

A study of the thermal isomerizations of bicyclo [2,1,0] pentene, and of its 1- and 2-methyl derivatives, to cyclopentadienes, showed that these reactions are normal, synchronous electrocyclic processes although "forbidden" [124], in contradiction to alternative suggestions (later proved experimentally to be incorrect).

A detailed MINDO/3 study of the reactions of singlet $(^1\Delta g)O_2$ with olefins predicted the first product in each case to be a peroxirane [125,126,136].

MINDO/3 calculations for CH_2, O_2 and NH_2^+ gave results as good as, or better than, those from very sophisticated ab initio procedures [127].

MINDO/3 seems to give a good account of the rearrangement of vinylcyclopropane to cyclopentene and of cyclopropylallene to methylenecyclopentene.

The decomposition of ozone was studied by MNDO [138].

MINDO/3 has been used to study the properties of a variety of normal and mesoionic derivatives of oxazole and imidazole [132].

MNDO calculations for the bisdehydropyridines (pyridynes) led to predictions of interesting differences between them and their benzene analogs [149].

A detailed MINDO/3 study of the retroene conversion of vinylacetic acid ($H_2C{=}CHCH_2COOH$) to propene + CO_2 gave results (heats of reaction and activation, entropy of activation, D and C^{13} kinetic isotope effects) in good agreement with experiment [157]. The reaction is a synchronous pericyclic process.

A detailed MNDO study of borohydride reduction [169] in conjunction with similar calculations for hydroboration [176], accounted very nicely for the difference between these two formally "forbidden" reactions, the latter involving a cruci-conjugated transition state which is analogous to that in a linear (not cyclic) conjugated molecule.

A MNDO study of the potential surface relating the 2-fluorethyl cation and the ethylene fluoronium π complex showed it to have rather unique features [2].

A detailed MNDO study of the fluorinated pyridines explained some puzzling results from electron diffraction studies [4].

MNDO calculations for a number of chlorine=containing molecules are being reported [6].

Omissions in a recent paper by Halgren et al are being remedied [11].

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MANUSCRIPTS SUBMITTED FOR PUBLICATION

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1. Journal of Mol. Struct. "MNDO Study of Transient Species, The IR Spectrum of Benzyne" - Dewar, Ford, Rzepa.

2. Journal of Mol. Struct. "Detailed Potential Energy Surfaces from MNDO Semiempirical Molecular Orbital Theory. 2-Fluoroethyl and Ethylene Fluoronium Ions" - Dewar, Ford.

3. JCS Faraday II (Chem. Society) "A MINDO/3 Comparison of the Generalized SCF Coupling Operator and "Half-electron Methods for Calculating the Energies and Geometries of Open Shell Systems" - Dewar and Olivella.

4. Chem. Phys. "Structures and Properties of Fluorinated Pyridines; etc." - Dewar, Yamaguchi, Doraiswamy, S. D. Sharma, Suck.

5. Inorg. Chem. "Ground States of Molecules. 52. A MNDO Study of the Coordination of Beryllium Indenyl and Fluorenyl Complexes. - Dewar, Rzepa.

6. J.A.C.S. "Ground States of Molecules. 53. MNDO Calculations for Molecules Containing Chlorine. - Dewar, Rzepa.

7. Inorg. Chem. "Ground States of Molecules. 54. MNDO Study of Carboranes". Dewar, McKee.

8. J.A.C.S. "Ground States of Molecules 55. MINDO/3 Study of Rearrangements of C_4H_7 Radicals". Dewar, Olivella.

9. J.A.C.S. "A MNDO Study of the Electrocyclic Ring Opening of Cyclobutene Radical Cation and Radical Anion". Dewar, Rzepa.

10. J.A.C.S. "A MNDO Study of the Structure and Stabilities of some Substituted Pentadienyl Anions". Dewar, Fox, Nelson.

11. J.A.C.S. "An Addendum to a Recent Paper by Halgren, Lipscomb, and Their Coworkers Concerning the Relative Accuracies of Several Current MO Methods". Dewar, Ford.

12. NATURE. "Consequences of an Apparent Analogy Between Enzyme-Catalyzed Reactions and Reactions in the Gas Phase" - Dewar