Ground States of Molecules. XXII.[1] Incorporation of Partial Configuration Interaction in MINDO/2 and Its Application to Bond Dissociation Energies and Sigmatropic Rearrangements[2]

Richard C. Bingham and Michael J. S. Dewar

Contribution from the Department of Chemistry,
The University of Texas at Austin, Austin, Texas 78712.
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Abstract: A modification of MINDO/2 (MINDO/CI) is described in which CI with the first doubly excited configuration is included throughout. The calculated heats of formation and geometries for normal molecules agree well with experiment as do also the calculated energies of pairs of radicals and the bond dissociation energies derived from them. Calculations using this procedure are reported for the 1,3 sigmatropic hydrogen shift in propene and the suprafacial and antarafacial 1,5 sigmatropic hydrogen shifts in *cis*-piperylene, the calculated activation energies being 49.2, 28.3 (obsd 35.4), and 37.0 kcal/mol, respectively. The effect of substituents on the suprafacial/antarafacial ratio is discussed in terms of PMO theory.

While the MINDO/2 method[3,4] has proved useful in a number of connections,[3–5] it suffered in its original form from a number of quite serious defects. While some can be, or have already been[6] corrected by changes in the parameters, two are probably inherent in the approximation itself. One of these, the failure to reproduce the dipole fields due to pairs of unshared electrons in hybrid AO's, has already been discussed.[3,4] Here we will be concerned with the second such failing, inability to reproduce the course of reactions where a molecule cleaves into a pair of radicals.

It is well known that a single-determinant MO approximation cannot reproduce bond dissociation processes because such a treatment overestimates the contribution of ionic structures. Thus H_2 is represented at all internuclear distances as a 1:1 hybrid of covalent ($H\cdot\ \cdot H$) and ionic (H^+H^-) states.[7] The bond dissociation energy calculated in this way is therefore too great by $^1/_2\gamma_{HH}$, γ_{HH} being the self-repulsion of two electrons in a hydrogen 1s AO, quite apart from any errors inherent in the orbital approximation. Similar difficulties occur in the analogous description of bond rupture in a polyatomic molecule to form two radicals. Here again the bond dissociation energy is overestimated.

The same kind of situation may also be expected to occur in a single molecule where two MO's are each singly occupied. This will happen whenever the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) become degenerate. Important examples of such degeneracy are provided by biradicals where the radical centers are widely separated (*e.g.*, $\cdot CH_2CH_2CH_2CH_2\cdot$), by the transition states for rotation about the double bonds in olefins and cumulenes (*e.g.*, the 90° twisted form of ethylene), and by the transition states in antiaromatic pericyclic reactions.[8] The use of single-determinant wave functions to describe reactions involving such structures as products or intermediates is therefore inherently suspect.[8c]

These difficulties arise through electron correlation. The repulsion between two electrons in the same AO $\phi_i(\gamma_{ii})$ or ϕ_j (γ_{ij}) is greater than that (γ_{ij}) between an electron in ϕ_i and one in ϕ_j. The difference between γ_{ij} and γ_{ii} or γ_{jj} will, of course, be greater the further apart the orbitals are in space. The errors due to use of a single-determinant wave function should therefore be much greater for pairs of radicals, or biradicals where the radical centers are widely separated, than for torsional or antiaromatic transition states (where the electrons occupy MO's covering the same set of atoms). The available evidence suggests[3,5] that MINDO/2 can, in fact, handle the two latter situations adequately whereas the errors in the former are of the order of 2 eV.

While the regions where MINDO/2 fails for this reason are thus limited, the situation is nevertheless unsatisfactory for two reasons. First, a number of important mechanistic problems are concerned with the choice between concerted one-step processes and two-step processes where "genuine" biradicals are involved. Secondly, the distinction between the situations where MINDO/2 succeeds, and those where it fails, is not clear-cut. When is a biradical a "genuine" biradical?

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(1) Part XXI: M. J. S. Dewar and H. I. Metiu, *Proc. Roy. Soc., Ser. A*, 173 (1972).

(2) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and by the Robert A. Welch Foundation through Grant F-126.

(3) (a) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); (b) N. Bodor, M. J. S. Dewar, E. Haselbach, and A. Harget, *ibid.*, **92**, 3854 (1970).

(4) For a review see M. J. S. Dewar, *Fortschr. Chem. Forsch.*, **23**, 1 (1971).

(5) (a) N. Bodor and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **92**, 4270 (1970); (b) A. Brown, M. J. S. Dewar, and W. W. Schoeller, *ibid.*, **92**, 5516 (1970); (c) M. J. S. Dewar, E. Haselbach, and M. Shanshal, *Angew. Chem.*, **82**, 774 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 738 (1970); (d) M. J. S. Dewar and W. W. Schoeller, *J. Amer. Chem. Soc.*, **93**, 1481 (1971); (e) M. J. S. Dewar, D. H. Lo, D. B. Patterson, N. Trinajstić, and G. E. Peterson, *Chem. Commun.*, 238 (1971); (f) M. J. S. Dewar and J. S. Wasson, *J. Amer. Chem. Soc.*, **93**, 3081 (1971); (g) M. J. S. Dewar, M. Kohn, and N. Trinajstić, *ibid.*, **93**, 3437 (1971); (h) M. J. S. Dewar and S. Kirschner, *ibid.*, **93**, 4290, 4291, 4292 (1971); (i) N. Bodor and M. J. S. Dewar, *ibid.*, **93**, 6685 (1971); (j) M. J. S. Dewar and M. C. Kohn, *ibid.*, **94**, 2699 (1972); (k) *ibid.*, **94**, 2704 (1972).

(6) (a) M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, **94**, 5296 (1972); (b) N. Bodor, M. J. S. Dewar, and D. H. Lo, *ibid.*, **94**, 5303 (1972).

(7) For a general account and references, see M. J. S. Dewar and J. Kelemen, *J. Chem. Educ.*, **48**, 494 (1971).

(8) (a) M. J. S. Dewar, *Angew. Chem.*, **83**, 859 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971); (b) L. Salem and C. Rowland, *Angew. Chem.*, **84**, 86 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972); (c) *cf.* A. R. Gregory and M. N. Paddon-Row, *Chem. Phys. Lett.*, **12**, 552 (1972).

Table I. Atomic Parameters[a]

	USS	UPP	g_{ss}	g_{pp}	g_{sp}	$g_{pp'}$	h_{sp}	$h_{pp'}$	F^0	E_A	ζ^b	I_s	I_p
H	--13.595		12.848						12.848	−13.595	1.0	−13.595	
C	−52.14	−40.88	12.23	11.08	11.47	9.84	2.43	0.62	10.833	−123.20	1.6083 (s) 1.5679 (p)	−21.34	−11.54

[a] Terms are defined in ref 6a, 9, and 11. [b] Slater orbital exponents are those of E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

It is well known[7] that this particular problem can be overcome by including configuration interaction (CI) and that the major contribution in this connection is by the lowest doubly excited configuration (corresponding to transfer of the pair of electrons in the HOMO to the LUMO).

To avoid any possible misunderstanding, it should perhaps be emphasized once more (see ref 5j) that the inclusion of CI in semiempirical treatments of the MINDO/2 type would as a rule be incorrect in principle. The objective in this kind of approach is to take electron correlation into account by adjusting the parameters in a semiempirical single-determinant SCF treatment, thus avoiding the need for CI. The results already obtained certainly suggest that this kind of approach can succeed for "normal" closed-shell molecules. They also, however, show that it cannot take care of the extreme correlation met in pairs of radicals or in biradicals where the radical centers are widely separated. The suggestion we are making here is that it may be possible to take this additional factor into account in MINDO/2, without any great increase in complexity, simply by including CI with the one crucial configuration. Here we report some preliminary studies of hydrocarbons using such a procedure, which may conveniently be termed MINDO/CI.

Theoretical Approach

The basic principles of MINDO/2 have been described in detail in earlier papers of this series.[3,9] The modifications needed to include the first doubly excited configuration are trivial, involving the solution of a 2 × 2 secular equation.[10]

The one-center parameters used here are derived according to the formulation of part XVII[6a] using the data of Oleari.[11] The one-center electron repulsion integrals (F^0) are chosen as an average of the 16 specific one-center interactions.

$$F_A{}^0 = {}^1/_{16}(g_{ss} + 6g_{sp} + 3\,g_{pp} + 6g_{pp'}) \qquad (1)$$

Table I summarizes the atomic parameters employed in the present calculations.

As before,[3a] the Ohno–Klopman approximation is used for the two-center repulsion integrals. The parameter expression for the core resonance integral ($\beta_{ij}{}^c$) also has the original[3a] form while the core repulsion functions between atoms m and n (CR_{mn}) of part XVIII[6b] have been adopted here. Thus

$$\beta_{ij} = B_{mn}S_{ij}(I_i + I_j) \qquad (2)$$

$$\mathrm{CR}_{mn} = Z_mZ_n\left[\gamma_{mn} + \left(\frac{e^2}{r_{mn}} - \gamma_{mn}\right)fe^{-r_{mn}}\right] \qquad (3)$$

where $f = e^{\alpha_{mn}}$ when $m = n$ (CC and HH), $f = \alpha_{mn}$ when $m \neq n$ (CH), Z_m and Z_n are the core charges on atoms m and n in units of the electronic charge (e), r_{mn} is the internuclear separation, γ_{mn} is the corresponding two-center repulsion integral, and S_{ij}, I_i, and I_j have their usual significance.[3a] The quantities B_{mn} and α_{mn} are parametric characteristics of the atom pair mn.

The parametrization followed a procedure analogous to that used earlier, the heats of formation and geometries of a set of standard hydrocarbons being fitted by a least-squares method.[3a] In the original treatment, one bond length in each molecule was fitted, the lengths of the other bonds, and the bond angles, being assumed. When we later began to calculate geometries by complete minimization of the energy with respect to the geometry, using the SIMPLEX procedure,[5b] the resulting heats of atomization were naturally uniformly too negative. We now fit the parameters by an iterative procedure. The first cycle follows the same pattern as before. The geometries of the standard molecules are then optimized by the SIMPLEX method. The parameters are now redetermined, using the SIMPLEX values for all bond lengths, bond angles, etc., in the molecule other than that involved in the parametrization. The cycle is repeated if necessary, until the geometry converges. We have also modified the original[3a] least-squares treatment in the parametrization procedure to cover bond angles as well as bond lengths.[12] A corresponding additional matrix and weighting factor appear in eq 18 of ref 3a, the modification being self-evident.

Table II summarizes the parameters found in this way.

Table II. Parameters for Hydrocarbons in MINDO/CI

Atom pair	B_{mn}	α_{mn}
HH	0.16590	2.59415
CH	0.25683	0.45273
CC	0.30151	1.82369

Results and Discussion

Table III compares calculated heats of formation and geometries both for the hydrocarbons used in the parametrization (marked with asterisks) and for a variety of other compounds. The quantity calculated is, of course, the heat of atomization, not of formation; for convenience the calculated heats of atomization have been converted to heats of formation (at 25°) by using the following values for the heats of atomization of graphite and H_2: C, 170.89 kcal/mol; H, 52.102 kcal/mol.

The calculated heats of formation are very similar to those given[4] by MINDO/2 and so are also in good gen-

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(9) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, 50, 1262, 1275 (1969).

(10) See R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience Publishers, New York, N. Y., 1959, p 474.

(11) L. Oleari, L. DiSipio, and G. DeMichelis, *Mol. Phys.*, 10, 97 (1966).

(12) A. Brown, unpublished results.

Table III. Comparison of MINDO/CI Calculated and Experimental Heats of Formation (ΔH_f) and Geometries of Hydrocarbons

	ΔH_f		Geometry		
Compound	Calcd	Exptl[a]	Bond or angle	Calcd	Exptl[b]
H_2*	−0.38	0.0	H—H	0.741	0.741
CH_4*	−19.06	−17.88	C—H	1.078	1.106[c]
HC≡CH*	57.92	54.19	C≡C	1.195	1.205
			C—H	1.054	1.059
$H_2C{=}CH_2$*	14.28	12.49	C—C	1.343	1.338
			C—H	1.085	1.086
			C—C—H	123.8	121.2
CH_3CH_3*	−20.82	−20.24	C—C	1.496	1.532[d]
			C—H	1.093	1.107[d]
			C—C—H	112.2	111.0[d]
$H_2C{=}CHCH_3$*	4.13	4.88	C=C[n]	1.350	1.336[e]
			C—C[n]	1.482	1.501[e]
			C—C—C[n]	125.9	124.3[e]
C_6H_6*	16.79	19.82	C—C	1.393	1.397
			C—H	1.098	1.087
$CH_3CH_2CH_3$	−25.99	−24.82	C—C	1.513	1.526[f]
			C—C—C	114.5	112.4[f]
anti-n-Butane	−28.22	−30.15	C—C—C	114.1	112.2
gauche-n-Butane	−27.93	−29.45	C—C—C	115.2	
Isobutane	−31.01	−32.15	C—C	1.520	1.525[g]
			C—C—C	111.1	111.2[g]
1-Butene	2.17	−0.03	C=C	1.352	
			=C—C	1.491	
			C—C	1.520	
trans-Butene	−6.72	−2.67	C=C	1.344	1.399
			C—C	1.479	1.520
			C—C—C	126.6	123.0
cis-Butene	−6.82	−1.67	C=C	1.350	
			C—C	1.480	
			C—C—C	128.0	
trans-Butadiene	34.15	26.33	C=C	1.337	1.341[h]
			C—C	1.449	1.463[h]
			C—C—C	124.1	123.3[h]
cis-1,3-Pentadiene	22.36	19.77	C=C[n]		
			C—C[n]		
Cyclopropane	−2.37	12.74	C—C	1.489	1.510[i]
			C—H	1.086	1.089[i]
			H—C—H	108.6	115.2[i]
Cyclobutane	−16.32	6.3	C—C	1.520	1.548[j]
Cyclobutene	11.53	37.5	C=C	1.351	1.342[k]
			=C—C	1.483	1.517[k]
			C—C	1.542	1.566[k]
Cyclohexane	−33.69	−29.43	C—C	1.511	1.528[l,m]
			C—H	1.100	1.104[l,m]
			C—C—C	115.3	111.6[l,m]
(e)-Methylcyclohexane	−37.82	−37.0	C—C_{endo}	1.515	1.528[m]
			C—C_{exo}	1.533	
(a)-Methylcyclohexane	−37.58	−35.1	C—C_{endo}	1.517	
			C—C_{exo}	1.529	

[a] "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953. [b] Unless otherwise noted, experimental structures are from "Table of Interatomic Distances," *Chem. Soc., Spec. Publ.*, **No. 11** (1958), and **No. 18** (1965). [c] L. S. Bartell, K. Kuchitsu, and R. J. deNeui, *J. Chem. Phys.*, **35,** 1211 (1961). [d] L. S. Bartell and H. K. Higginbotham, *ibid.*, **42,** 851 (1965). [e] D. R. Lide, Jr., and D. Christensen, *ibid.*, **35,** 1374 (1961). [f] D. R. Lide, Jr., *ibid.*, **33,** 1514 (1960). [g] D. R. Lide, Jr., *ibid.*, **33,** 1519 (1960). [h] Z. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1,** 463 (1967). [i] O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17,** 538 (1964). [j] A. de Meijere, *Acta Chem. Scand.*, **20,** 1093 (1965). [k] B. Bak, J. J. Led, L. Nygaard, J. Rastrup-Andersen, and G. O. Sorensen, *J. Mol. Struct.*, **3,** 369 (1969). [l] M. Davis and O. Hassel, *Acta Chem. Scand.*, **17** 1181 (1963). [m] H. J. Geise, H. R. Buys, and F. C. Mijlhoff, *J. Mol. Struct.*, **9,** 447 (1971). [n] See Figure 2.

eral agreement with experiment. As before, the strain energies of small rings are underestimated. One major advantage of the present procedure is that it correctly reproduces the heat of atomization of H_2. The value for this in the original version of MINDO/2 was far too large.

The agreement between the calculated and observed geometries is also very satisfactory. Here again the original version[3] of MINDO/2 is inferior, leading to CH bond lengths that are systematically too large by 0.1 Å. MINDO/CI reproduces CH bond lengths correctly, as also does a recent improved version[6b] of MINDO/2.

Inclusion of CI has not, therefore, had any detrimental effect on the calculations for normal molecules; indeed, it has if anything improved them.

Table IV shows calculations for a number of bond dissociation energies. These were found by calculating the energy of the molecule in question by MINDO/CI for various lengths of the appropriate bond, the other geometrical parameters being optimized by the SIMPLEX method at each point. A plot of energy *vs.* bond length

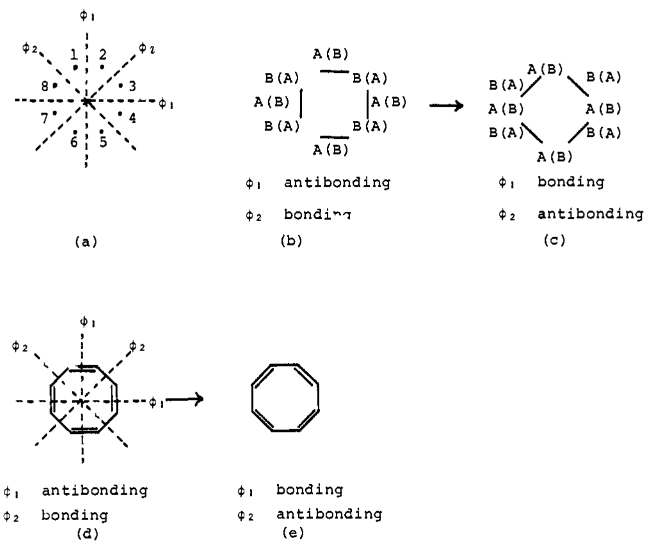

Figure 1. (a) Nodes in the HOMO and LUMO of a Hückel-type eight-membered ring; (b), (c) bonding/antibonding properties of these MO's in the reactant and product of a corresponding pericyclic reaction; (d), (e) bonding/antibonding properties of the two MO's in the interconversion of the two Kekulé structures for cyclooctatetraene.

Table IV. Comparison of Calculated and Experimental Bond Dissociation Energies (DH°)

Compound	DH°, kcal/mol Calcd	DH°, kcal/mol Exptl
H_2 (H—H)	104.5	104[a]
CH_4 (C—H)	103	104 ± 1[a,b]
CH_3CH_3 (C—H)	99.5	98 ± 1[a,b]
CH_3CH_3 (C—C)	78	88 ± 2[a]
$(CH_3)_3CH$ (C_2—H)	93	95 ± 1[a,b]
$CH_3CH_2CH_2CH_3$ (C_2—C_3)	71	82 ± 2[a]
$CH_2{=}CHCH_3$ (C_3—H)	100	85 ± 1,[a] 89 ± 1[b]
$H_2C{=}CH_2$ (C—H)	109	103 ± 2,[a] ≥108 ± 2[b]
$HC{\equiv}CH$ (C—H)	114	
C_6H_6 (C—H)	100	103 ± 2,[a] 112 ± 1[b]

[a] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965). [b] D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

increased monotonically, in agreement with experimental evidence that combination of atoms and/or radicals normally involves no activation. It will be seen that the bond dissociation energies for CH bonds are in very good agreement with experiment while those for CC bonds are systematically too small by 10 kcal/mol. This represents a major improvement over MINDO/2, and the remaining discrepancy might well be removed in our continuing efforts to improve the parameterization.

Calculations were also carried out for the trimethylene and tetramethylene biradicals (Table V). The calculated values are again too negative, the discrepancies being much the same as for the pair of radicals formed by cleavage of CC bonds (Table IV).

Table V. Heats of Formation of Biradicals

Biradical	Heat of formation, kcal/mol (at 25°) MINDO/CI	Obsd[a]
$\cdot CH_2CH_2CH_2\cdot$	51.0 (99.0)[b]	67
$\cdot CH_2CH_2CH_2CH_2\cdot$	51.4 (104.0)[b]	62

[a] Calculated from the heat of formation of the corresponding paraffin (C_3H_8, −24.8; C_4H_{10}, −30.2 kcal/mol[3a]) by adding twice the difference between the heats of formation[3a] of ethyl radical (25.7 kcal/mol) and ethane (−20.4 kcal/mol). Note that there is an arithmetical error in ref 3a in the calculation of ΔH_f for tetramethylene. [b] Calculated without configuration interaction.

1,5-Sigmatropic Hydrogen Migration. One of the problems studied by MINDO/2 was the mechanism of pericyclic reactions with special reference to the differences between the aromatic ("allowed") and antiaromatic ("forbidden") paths.[8] Calculations were carried out[5h] for the electrocyclic opening of cyclopropyl anion, cation, and radical, and for cyclobutene, with results that supported the interpretation of pericyclic reactions first put forward in 1937 by Evans.[13]

Now it is very easily shown that during the course of an antiaromatic pericyclic reaction the HOMO and LUMO must cross at some point, presumably at or near the transition state. This result follows from the topology of cyclic conjugated systems and is not dependent on symmetry. It can be demonstrated most simply in the case of even Hückel-type[8a] systems where an antiaromatic ring contains 4*n* atoms and 4*n* bonds. The HOMO and LUMO each contain *n* nodes which consequently intersect alternate bonds in the ring. Thus one of the MO's is bonding between atoms 1 and 2, 3 and 4, etc., and antibonding between atoms 2 and 3, 4 and 5, etc., while the other follows exactly the opposite pattern. Figure 1a–c illustrates this situation in the case of an eight-membered ring. Now a pericyclic reaction involves the conversion of a reactant in which there are bonds between atoms 1 and 2, 3 and 4, etc., but no bonds between atoms 2 and 3, 4 and 5, etc., to a product in which the bonds have switched to positions 23, 45, etc. A typical process of this kind would be bond exchange in cyclooctatetraene (Figure 1d,e). Obviously the MO with nodes between atoms 1 and 2, 3 and 4, etc., will be antibonding in the reactants and bonding in the products while the MO with nodes between atoms 2 and 3, 4 and 5, etc., will be bonding in the reactants and antibonding in the products, for in each case one set of bonding or antibonding interactions vanishes because the atoms are not bonded.[14] During the reaction the MO which was originally bonding becomes antibonding and the MO that was originally antibonding becomes bonding. At some point during the reaction the MO's must therefore cross.

In view of the analogy between transition states, where the HOMO and LUMO are degenerate, and biradicals, it is of some interest to see whether the use of MINDO/2 for the former is justified. In the work on electrocyclic reactions it was shown[5h] that the general conclusions remain unaffected if CI with the lowest doubly excited configuration is included. These calculations, however, referred to small ring compounds (where MINDO/2 gives rather poor extimates of heats of formation) and were carried out with the usual MINDO/2 parameters (derived for single-determinant wave functions). It therefore seemed of interest to check the treatment of antiaromatic reactions by studying a system where no small rings are involved, using MINDO/CI.

A good choice for this purpose seemed to be the 1,5

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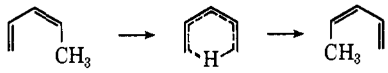
[13] M. G. Evans and E. Warhurst, *Trans. Faraday Soc.*, **34**, 614 (1938); M. G. Evans, *ibid.*, **35**, 824 (1939).

[14] The same situation arises in cyclooctatetraene due to the difference in β between C═C and C—C bonds. Here neither set of bonding and antibonding interactions vanishes, but one is much less than the other.

sigmatropic shift of hydrogen in *cis*-piperylene (**1** → **3**).



1 **2** **3**

The reaction can take place without significant strain either suprafacially or antarafacially, the suprafacial transition state being aromatic and the antarafacial one antiaromatic.[8a,15]

For comparison, calculations were also carried out for the 1,3 suprafacial hydrogen shift in propene which should, of course, also involve an antiaromatic transition state. Since the rearrangements are degenerate, it was assumed that the transition states are symmetrical, suprafacial and antarafacial transition states having C_s and C_2 symmetry, respectively. For the suprafacial rearrangements, this assumption follows directly from the analysis of narcissistic reactions presented by Salem, *et al.*,[16] apart from the unlikely possibility that the symmetrical structure might be a stable intermediate. We therefore felt it would be irresponsible to calculate complete reaction paths in the present case since the cost of the calculation would be out of all proportion to any possible gain, particularly at this stage of refinement of MINDO/CI.

Figure 2 shows the calculated geometries and heats of formation of the reactants and the two transition states. The corresponding activation energy for suprafacial rearrangement of **1** (28.3 kcal/mol) is in reasonable agreement with the experimental value (35.4 kcal/mol) of Roth and König.[17,18] The suprafacial path is of course favored, in accordance with the Woodward–Hoffmann rules[19] and Evans' principle.[8a,13]

The calculated difference in energy between the suprafacial and antarafacial transition states is 8.7 kcal/mol. When the calculations were repeated without CI, the activation energy for the aromatic ("allowed") reaction changed little (0.5 kcal/mol), but that of the antiaromatic ("forbidden") one increased by 6.0 kcal/mol. The antiaromatic transition state does therefore respond to CI in the same manner as a genuine biradical (Table V) though the change in energy is, as expected, much less. Dewar and Kirschner[5h] found similar decreases (*i.e.*, *ca.* 10 kcal/mol) in the difference in activation energy between the aromatic and antiaromatic paths for rearrangement of cyclopropyl or cyclobutene when CI with the lowest doubly excited configuration was included.

There are unfortunately no reliable estimates of the differences in activation energy between analogous aromatic and antiaromatic processes. Roth, *et al.*,[20] have deduced a lower limit (8 kcal/mol) in the case of the 1,5 sigmatropic hydrogen shift in optically active **4**. Here competition between suprafacial and antarafacial rearrangement would lead to racemization which was not observed, the product being entirely derived from the suprafacial process. This result is consistent with our MINDO/CI estimate, particularly since the effect of the alkyl groups in **4** is uncertain.

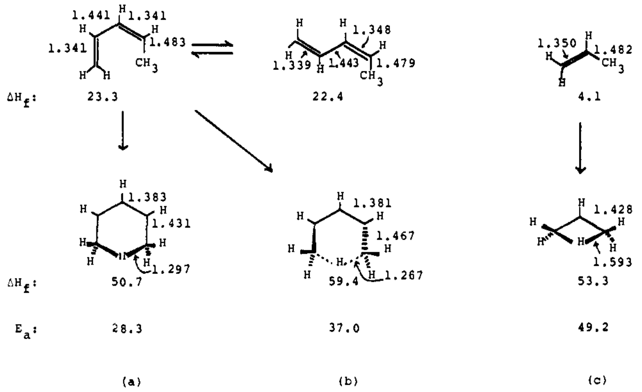
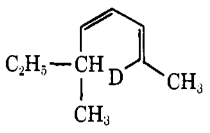


Figure 2. Calculated ground and transition state structures, heats of formation (ΔH_f, kcal/mol), and activation energies (E_a, kcal/mol): (a) 1,5-suprafacial shift in **1**; (b) 1,5-antarafacial shift in **1**; (c) 1,3-suprafacial shift in propene.



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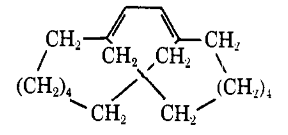

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Our calculations (Figure 2) predict a very high activation energy (49.2 kcal/mol) for the 1,3 allylic hydrogen shift in propene, the calculated differences between it and those for the aromatic suprafacial, and antiaromatic antarafacial, 1,5 shifts in **1** being 21.3 and 12.6 kcal/mol, respectively. No intramolecular 1,3 allylic hydrogen shifts have as yet been reported nor are they likely to be if our estimates are correct, for alternative radical chain processes should prove much more facile.

The antiaromatic ("forbidden") antarafacial 1,5 hydrogen shift should, however, be observable if our estimate of the difference between it and the suprafacial one is correct. It would be interesting in this connection to study compounds such as **5** where the suprafacial rearrangement is sterically inhibited. Examination of models shows that the geometry of **5** is particularly appropriate for 1,5 antarafacial hydrogen shifts.

Substituent Effects in 1,5 Sigmatropic Shifts. If the difference in activation energy between the suprafacial and antarafacial paths for rearrangement of **1** is as small as our calculations suggest, it might be possible to invert their relative stabilities, and so favor the antarafacial rearrangement, by suitable substitution. We have not tested this idea by direct calculation of the effects of substituents on the two transition states, but some interesting predictions can be obtained by using the PMO method.[21]

The suprafacial transition state (TS(S)) for rearrangement of **1** has a plane of symmetry (Figure 3a) while the antarafacial one (TS(A)) has a twofold axis of sym-

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(15) Preliminary studies of these processes had, in fact, been carried out by Dr. W. W. Schoeller, using the original[3b] version of MINDO/2. The results obtained were, however, unsatisfactory because of one of the main failings of this treatment, *i.e.*, the overestimation of the heat of atomization of hydrogen and consequent overestimation of attractions between pairs of nonbonded hydrogen atoms. This led to a spurious stabilization of the antarafacial transition state by interactions between the hydrogen atoms of the terminal methylene groups.

(16) L. Salem, J. Durup, G. Bergeron, D. Cazes, X. Chapuisat, and H. Kagan, *J. Amer. Chem. Soc.*, **92**, 4472 (1970).

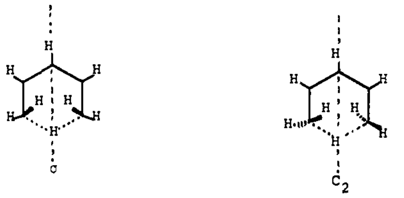
(17) W. R. Roth and J. König, *Justus Liebigs Ann. Chem.*, **699**, 24 (1966).

(18) For a review of 1,5 sigmatropic rearrangements, see H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

(19) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(20) W. R. Roth, J. König, and K. Stein, *Chem. Ber.*, **103**, 426 (1970).

(21) M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3341, 3345, 3350, 3353, 3355, 3357 (1952); "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.



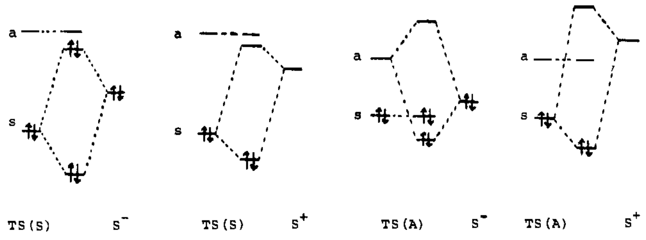
(a) (b)

Figure 3. (a) Plane of symmetry in the transition state for suprafacial rearrangement of **1**; (b) twofold axis of symmetry in the transition state for antarafacial rearrangement of **1**.

metry (Figure 3b). The MO's of TS(S) must therefore be either symmetric, or antisymmetric, for reflection in the plane of symmetry while those of TS(A) must be either symmetric, or antisymmetric, for rotation through 180° about the twofold axis of symmetry.

Both transition states can be derived[21] by combination of the pentadienate anion ($CH_2{=\!=}CH{=\!=}CH{=\!=}CH{=\!=}CH_2)^-$ with a proton. It is easily seen[21] that in the case of the suprafacial transition state TS(S), the resulting bonding MO (HOMO) is symmetric and the antibonding MO (LUMO) antisymmetric. In the case of the antarafacial transition state TS(A), both MO's would be nonbonding if the electronegativities of carbon and hydrogen were the same. Since hydrogen is more electronegative than carbon, the lower energy MO (*i.e.*, the HOMO) should be symmetric, being derived mainly from the hydrogen 1s AO, while the higher energy MO (LUMO) should be antisymmetric.

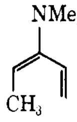
The relevant AO of C_3 in the pentadienate moiety is a 2p AO. This is symmetric for reflection in the plane of symmetry of Figure 3a, but antisymmetric for rotation about the twofold axis of Figure 3b. This AO can therefore contribute only to symmetric MO's of the suprafacial transition state TS(S) (in particular, the HOMO) and to antisymmetric MO's of the antarafacial one (TS(A)) (in particular, the LUMO). Electromeric substituents at this position will therefore interact only with the HOMO of the suprafacial transition state, not with the LUMO, while in the antarafacial transition state such substituents will interact only with the LUMO, not the HOMO. Since $-E$ (donor-type) substituents are characterized[21] by having a HOMO of high energy and $+E$ (acceptor-type) substituents by having a LUMO of low energy, the interactions between the relevant orbitals are as indicated in Figure 4.



(a) (b) (c) (d)

Figure 4. Effect of a $-E$ substituent (S^-) or a $+E$ substituent (S^+) on the HOMO and LUMO of the suprafacial (TS(S)) and antarafacial (TS(A)) transition states for 1,5 sigmatropic hydrogen shifts in **1**.

It will be seen that a $-E$ substituent should have little or no effect on TS(S) but a very large stabilizing effect on TS(A). A $+E$ substituent should stabilize both transition states, but the effect on TS(A) should be greater because the interacting MO's are closer together in energy. Thus any electromeric substituent at the 3 position should tend to favor the antiaromatic antarafacial 1,5 hydrogen shift in *cis*-piperylene, but the effect should be most pronounced with $-E$ substituents, particularly those with HOMO's of very high energy. Obvious targets in this connection would be derivatives of 3-dimethylamino-*cis*-1,3-pentadiene (**6**) and the enolate (**7**) of ethyl vinyl ketone.



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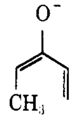

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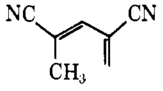

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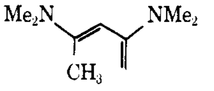

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Similar arguments can be shown to apply in the case of other symmetrical substitution patterns, *e.g.*, **8** and **9**, the antiaromatic transition state again being stabilized more than the aromatic one. Here again the effect should be most pronounced with $-E$ substituents (*i.e.*, **9**).