Theoretical Comparison of Tetrahedrane and Cyclobutadiene by *Ab Initio* Techniques

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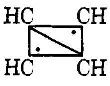
Abstract: The relative stability of the two C_4H_4 isomers tetrahedrane and cyclobutadiene is investigated by means of *ab initio* SCF MO and CI calculations. It is pointed out that the single determinantal wave function of the SCF method gives an intrinsically better representation of the tetrahedrane ground state, a classical closed-shell species, than that of cyclobutadiene, with its partially filled valence shell. Configuration interaction (CI) is introduced to increase the flexibility of the molecular wave functions employed, thereby removing the greater part of the bias toward tetrahedrane exhibited by the simple SCF treatment. The CI calculations thus find tetrahedrane to be considerably less stable (by 70 kcal/mole) than cyclobutadiene in its rectangular ground state; a stable minimum within the tetrahedral arrangement is indicated, however, for CC distances slightly smaller than the normal single-bond value. Tetrahedrane is found to have no such potential minima in any of its excited states and to be unstable with respect to dissociation into two acetylene molecules by from 70 to 100 kcal/mole.

The apparently unstable character of the cyclobutadiene (I) C_4H_4 species has led to the suggestion[2] that a tetrahedral isomer (II), differing from the former system by a nonplanar distortion, might possess greater stability. It was pointed out that such a tetrahedral structure (commonly known as tetrahedrane), with its six equivalent CC single bonds, would possess a closed-shell electronic configuration in contrast to cyclobutadiene, although its greater strain energy might well nullify this advantage. The molecule P_4, which has the same number of valence electrons as tetrahedrane, is well known to possess a tetrahedral geometry, but the failure to find similar stable structures for N_4 apparently indicates that such an arrangement is less probable for compounds consisting of first-row elements.


I


II

Experimental attempts[3] to isolate either tetrahedrane or its derivatives have thus far always proven to be unsuccessful. More recently semiempirical calculations by Baird and Dewar[4] have found this system to be approximately thermoneutral with the bicyclobutadiene biradical (III), from which it has been concluded that cyclobutadiene is substantially the more stable isomeric form.



III

Since *ab initio* calculations have not as yet been reported for tetrahedrane, it thus seems of interest to investigate what information can be gained from this approach relative to the stability of this system, particularly since the analogous study has already been carried out for cyclobutadiene.[5] Thus *ab initio* SCF and CI calculations have been undertaken for tetrahedrane to investigate its geometry and its stability relative not only to cyclobutadiene but also to two acetylene molecules.

SCF Calculations

The basis set employed for the tetrahedrane calculations is the same as that used previously for cyclobutadiene:[5] 120 single gaussians with 10 s- and 15 p-type on each carbon and 5 s functions on each hydrogen. These are arranged in fixed linear combinations so that the number of free SCF coefficients is reduced to 28. All electrons are explicitly taken into account, and no empirical parameters are assumed. A CH distance of 1.07 Å was chosen for the calculations, but a search within the tetrahedral arrangement was made to determine the optimum CC distance: values of 2.60, 2.80, 3.00, and 3.20 bohrs were considered (1 bohr = 0.52917 Å). The minimum SCF energy is thereupon found for CC = 1.560 Å, indicating the actual optimum CC distance to be somewhat smaller than the usual single-bond value since calculations at this level have systematically overestimated internuclear distances by at least 0.05 Å. The calculated stretching force constant for the expansion of tetrahedrane about equilibrium is 27.5 mdyn/Å; since all six CC bonds are varied simultaneously for the geometry changes considered, one calculates a value of 4.6 mdyn/Å for each individual stretching force constant, well within the range of values usually found for a CC single-bond stretch. At the very least these data indicate that C_4H_4 is bound *within* the tetrahedral nuclear configuration.

Total, kinetic, and orbital energies for the calculation nearest the theoretical equilibrium point (CC = 3.00 bohrs) are given in Table I; the symmetry notation is the same as that used in Cotton[6] for the T_d point group.

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(1) (a) University of Nebraska; (b) Justus Liebig-Universitaet.

(2) W. N. Lipscomb, *Tetrahedron Letters*, **18**, 20 (1959).

(3) (a) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, p 69; (b) S. Masamune and M. Kato, *J. Am. Chem. Soc.*, **87**, 4190 (1965); **88**, 610 (1966).

(4) N. C. Baird and M. J. S. Dewar, *ibid.*, **89**, 3966 (1967).

(5) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).

(6) F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, John Wiley and Sons, Inc., New York, N. Y., 1965.

Table I. Total Energy E_T, Kinetic Energy E_k, and Orbital Energies for the Ground State of Tetrahedrane (CC = 1.587 Å, CH = 1.07 Å)[a]

$1a_1$	−11.3739	$1e$	−0.3803
$1t_2$	−11.3730	$1t_1$	0.3024
$2a_1$	−1.2662	$4t_2$	0.3838
$2t_2$	−0.8359	E_T	−153.3710
$3a_1$	−0.7430	$-E_k/E_T$	0.9905
$3t_2$	−0.5637		

[a] Throughout this paper, unless otherwise specified, all energy values are given in hartree units (27.216 eV).

The minimum in total energy is 35 kcal/mole higher than the minimum SCF energy found for the cyclobutadiene ground state (rectangular singlet); such a direct comparison, however, is not reliable on theoretical grounds, as will be discussed in the following section. The ionization potentials calculated at equilibrium (*via* Koopmans' theorem) for tetrahedrane are compared with the analogous quantities obtained by Baird and Dewar in Table II. The minimum IP is roughly the same for both calculations while those at higher energy differ by as much as 5 eV; in all cases the *ab initio* results are higher than those obtained by the semiempirical technique.

Table II. First Ionization Potentials (in eV) of Tetrahedrane

	This work	B + D[a]
$1e$	10.35	9.58
$3t_2$	15.34	11.72
$3a_1$	20.22	14.90
$2t_2$	22.74	18.68

[a] N. C. Baird and M. J. S. Dewar, *J. Am. Chem. Soc.*, **89**, 3966 (1967).

Discussion

It is well known that the SCF method (or its limiting form Hartree–Fock theory) is generally inadequate for the prediction of heats of atomization (dissociation energies). The reason for this deficiency is the fact that the restricted form of electronic wave function employed in such treatments (single determinant) is usually more suitable for representing the combined molecule than the sum of its separated atoms. There is an interesting series of exceptions to this rule, however, exemplified by the systems[7] HeH^+ and NeH^+; in such cases, for which the separated species are each closed shell in nature, accurate potential curves and *per force* heats of atomization can be calculated using exclusively the single determinantal form of wave function. Generalization of this finding would lead one to expect accurate prediction of total energy differences by the SCF method for any case in which the systems being compared all possess closed-shell configurations. Consideration of the separation of benzene into three acetylene molecules tends to substantiate such a conclusion; experimental heats of combustion[8] find benzene to be more stable than three C_2H_2 molecules by 142.7 kcal/mole, while SCF calculations of the type discussed in this paper[5] obtain a corresponding value of 131.2 kcal/mole.

In a broader sense it can be stated that accurate differences in total energies can be calculated by *ab initio* methods only if the form of the wave function employed is equally satisfactory for the representation of both systems being compared. In the present context the important point is that even when the SCF method cannot achieve this necessary balance of treatment, the introduction of a moderate amount of configuration interaction (*i.e.*, employment of a multideterminantal wave function) often times can remedy this situation. The rotational barrier of ethylene provides an excellent example of this phenomenon. The SCF method is inadequate for calculating the barrier height in this case because antiplanar ethylene, in marked contrast to the planar equilibrium form of the molecule, is not a closed-shell system; as a result the barrier height is greatly overestimated by the SCF method. A simple CI calculation allowing the lowest (SCF) configurations in both geometries to mix with their respective lowest excited species, however, obtains a much more satisfactory balance of treatment.[9] In addition, a more sophisticated form of CI has been used by Das and Wahl[10] to give accurate predictions of the heats of atomization of H_2, Li_2, and F_2, where the Hartree–Fock method has failed to do so by a great margin.

In view of this discussion and the fact that cyclobutadiene, unlike tetrahedrane, is not a closed-shell system (at least in its square geometry), it seems apparent that the SCF method by itself is not reliable for calculating the difference in stability between these two systems. Another observation supporting this same general conclusion can be made by examining (Table III) the electronic configurations of both molecules relative to the C_{2v} subgroup commonly shared by them (square

Table III. Correlation of the Molecular Orbitals of Square Cyclobutadiene and Tetrahedrane with Respect to a Common C_{2v} Subgroup[a]

	Square Cyclobutadiene D_{4h}	C_{2v}
4 × 1s AO's	a_{1g}, b_{2g}, e_u	2 × a_1, b_1, b_2
4 × CH bonds	a_{1g}, b_{2g}, e_u	2 × a_1, b_1, b_2
4 × CC bonds	a_{1g}, b_{1g}, e_u	a_1, a_2, b_1, b_2
π_1	a_{2u}	a_1
π_2	$^1/_2$ × e_g	$b_1(b_2)$
Total occupied	3 × a_{1g}, 1 × b_{1g}, 2 × b_{2g}, $^1/_2$ × e_g, 1 × a_{2u}, 3 × e_u	6 × a_1, 1 × a_2, 4(3) × b_1, 3(4) × b_2
Unoccupied		
π_3	$^1/_2$ × e_g	b_2 (b_1)
π_4	b_{1u}	a_1
	Tetrahedrane T_d	C_{2v}
4 × 1s AO's	a_1, t_2	2 × a_1, b_1, b_2
4 × CH bonds	a_1, t_2	2 × a_1, b_1, b_2
6 × CC bonds	a_1, t_2, e	3 × a_1, a_2, b_1, b_2
Total occupied	3 × a_1, 3 × t_2, 1 × e	7 × a_1, 1 × a_2, 3 × b_1, 3 × b_2
Unoccupied		
π^*	t_1	a_2, b_1, b_2

[a] The first column categorizes the MO's according to their VB description.

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(7) S. Peyerimhoff, *J. Chem. Phys.*, **43**, 998 (1965).

(8) "Selected Values of Properties of Hydrocarbons," Circular C461, National Bureau of Standards, Washington, D. C., 1947.

(9) R. J. Buenker, *J. Chem. Phys.*, **48**, 1368 (1968).

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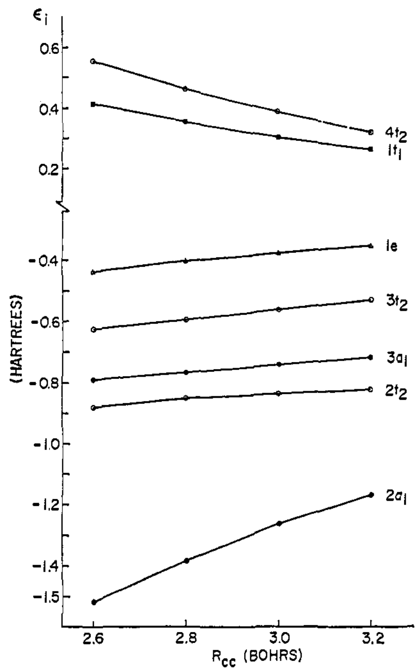

Figure 1. Total energy E_T (hartrees) as a function of the CC distance (bohrs) for several states of tetrahedrane as obtained from the SCF and the CI treatment.

cyclobutadiene but not the rectangular form has such a subgroup). Evidently tetrahedrane occupies one more a_1 MO in place of either the b_1 or b_2 orbitals which are degenerate in square cyclobutadiene. The ground state of tetrahedrane thus correlates with a doubly excited state of cyclobutadiene in which both the lowest and highest π orbitals are doubly occupied; in this electronic configuration the two alternating π bonds of cyclobutadiene are replaced by diagonal ones (since the b_{1u} is bonding along each diagonal but antibonding along each bond of the perimeter, thereby nullifying the bonding everywhere except along the diagonals), leading to the following structure.

IV

This system is clearly what one would expect from compressing all six tetrahedrane CC bonds into one plane; it is also closely related to the bicyclobutadiene biradical species (III) mentioned by Baird and Dewar, obtained by allowing one of the b_{1u} electrons of IV to revert back to the more stable e_u level.

The fact that tetrahedrane and cyclobutadiene possess different electronic configurations implies that single determinantal wave functions representing the ground states of these systems are not related by a continuous transformation throughout the geometry change connecting their nuclear arrangements; fortunately, this discontinuity can be removed rather easily by carrying out a CI calculation, the details of which can be deduced from Table III. What apparently is necessary is that cyclobutadiene be allowed *via* CI to use its highest two π MO's in the treatment so that it can compensate for its open-shell nature and also choose additional a_1 character, obviously preferred by tetrahedrane. In like manner, the CI for tetrahedrane should allow interaction with the t_1 MO in order that the necessary b_1 and b_2 character preferred in cyclobutadiene make its contribution. The CI calculation for cyclobutadiene (in which excitations among all four π MO's are considered) has already been reported,[5] while that suggested for tetrahedrane (in which all excitations between the e and t_1 orbitals are taken into account) is considered in the next section.

Configuration Interaction

There are 100 determinants with $M_s = 0$ for each tetrahedrane geometry calculated which can be formed by choosing the last four occupied spin orbitals from among the ten formed from the e and t_1 spatial MO's; the multiplets resulting from each set of these determinants are listed in Table IV. The CI calculation mixes configurations of the same symmetry with one another, thereby producing the potential curves shown in Figure 1. More complete details concerning the CI technique employed are given elsewhere.[11]

Table IV. Multiplets Deriving from 1e → $1t_1$ Excitations in Tetrahedrane

Spatial irreducible representation	Singlet	Triplet	Quintuplet
A_1	5	1	
A_2	2	2	
E	5	3	1
T_1	4	7	
T_2	7	5	1

The lowering in total energy for the ground state $^1A_1$ relative to its SCF value is rather small (about 0.03 hartree) when compared with the analogous change found for cyclobutadiene;[5] this result is, of course, a quantitative realization of the previous observation to the effect that cyclobutadiene is not a closed-shell system in contrast to tetrahedrane. The equilibrium CC distance is increased slightly by the CI to 1.566 Å and the force constant is lowered to 4.4 mdyn/Å per CC bond; both of these results are easily related to the fact that the CI exchanges antibonding t_1 character for that of the bonding e MO (see Figure 2 for the variation of SCF orbital energies with CC stretch).[12]

The most significant result of the CI calculations, however, is the finding that cyclobutadiene (in its rectangular ground state) is more stable than tetrahedrane by 70.3 kcal, a much larger difference than obtained strictly by the SCF method. Clearly, the larger number is a much more reliable estimate of the energy difference since it results from the more balanced treatment offered by the CI calculations. Dewar and coworkers[4,13] have calculated the heats of atomization of tetrahedrane and cyclobutadiene to be 745.9 and 830.1 kcal/mole, respectively, thus finding the planar isomer to be more stable by a margin of 84.2 kcal, in good agreement with the present *ab initio* CI result. Surprisingly enough, however, the *ab initio* calculations obtain the large energy difference only after CI and geometry

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(11) R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta*, 12, 183 (1968).

(12) It is certainly not surprising that the highest occupied levels of tetrahedrane are bonding in light of the fact that these MO's represent the CC single bonds (Table III).

(13) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, 87, 3255 (1965).

variations are taken into account; the *SCF energy* of tetrahedrane for its equilibrium CC bond distance is actually 10 kcal/mole lower than the SCF energy obtained for *square* cyclobutadiene using the analogous basis set.

Excited Configurations

The CI calculations for these two systems also yield some interesting information regarding their excited states. For the tetrahedral geometry the most significant point is that none of the low-lying excited states is bound with respect to CC stretch, in contrast to the behavior of the ground state; apparently promotion of a single electron from the bonding e to the antibonding t_1 MO is sufficient to destroy the stability of the tetrahedral nuclear arrangement.

Of the doubly excited states of cyclobutadiene, that which most closely corresponds to structure IV is calculated to lie over 300 kcal above the ground state, thereby giving a quantitative indication of the strain energy created by crowding six CC single bonds into one C_4 plane. The triplet associated with the corresponding single excitation (^3E_u), which can be identified with the bicyclobutadiene biradical (III), is found to prefer a square geometry with an excitation energy relative to the cyclobutadiene ground state of 120 kcal/mole. The CI treatment undoubtedly overestimates this quantity, however, since the MO's employed are those of the SCF ground state; previous experience indicates that the resulting discrepancy should be approximately 1.0 eV, thus making the best estimate of the ^3E_u transition energy to be 100 kcal. This estimate places the biradical energy some 30 kcal/mole above that of tetrahedrane, a finding which disagrees somewhat with the qualitative conclusion based on the aforementioned semiempirical calculations[4] to the effect that the two species are thermoneutral.

C_4H_4 and Two Acetylenes

Also of interest in the study of C_4H_4 isomers is the question of their stability relative to two acetylene molecules. In the previous study of cyclobutadiene,[5] it was pointed out that the SCF method by itself again cannot give a reliable estimate of this separation energy; in addition, the CI calculation necessary to balance the treatment in this case appears to be of rather impractical size. As a result only upper and lower limits of this energy difference could be determined, placing its value somewhere between 0 and 30 kcal/mole in favor of two acetylenes.

Because of the fact that tetrahedrane possesses a closed-shell electronic configuration, it might be expected that SCF calculations could succeed in this comparison with two C_2H_2 molecules where it had failed with cyclobutadiene. Closer analysis in terms of correlation of electronic configurations (Table V), however, renders such a conclusion somewhat uncertain. Consideration of two acetylenes separated at infinity with their CC axes perpendicular to one another (C_{2v} point group) leads to a ground-state configuration for this system which again differs from that of tetrahedrane. Also, a preliminary investigation of the effect of CI on both systems indicates that the acetylenes are much more responsive to this improvement in the treatment than is tetrahedrane, suggesting as before in the case of cyclobutadiene, that the SCF method is likely to yield poor results in such an energy comparison. Furthermore, as with cyclobutadiene, it is difficult to judge at which level a CI calculation (at least one of practical size) could be said to offer a balanced treatment for the combined molecule and separated products. Thus the aforementioned estimate that cyclobutadiene is from 0 to 30 kcal/mole less stable than two acetylenes remains the best inference one can draw in this connection from the *ab initio* calculations.

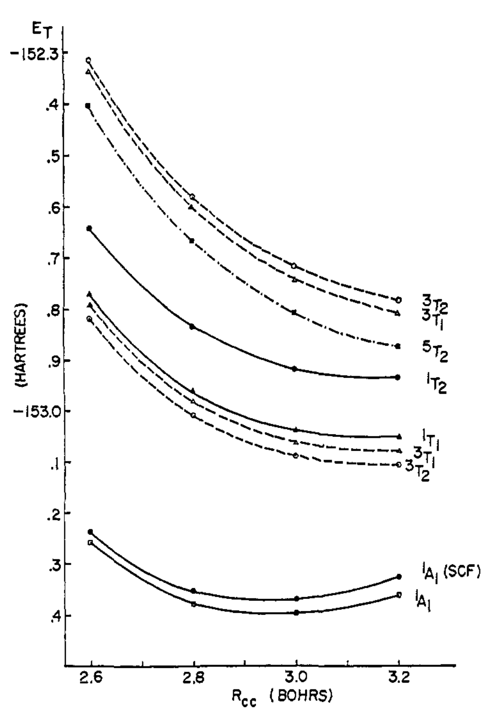

Figure 2. Orbital energies ϵ_i (hartrees) as a function of the CC distance in tetrahedrane.

Table V. Correlation of Molecular Orbitals of Two Acetylenes Separated at Infinity with Their Major Axes Perpendicular to One Another[a]

	Two C_2H_2 molecules $D_{\infty h}$	C_{2v}
4 × 1s AO's	$2 \times \sigma_g$, $2 \times \sigma_u$	$2 \times a_1, b_1, b_2$
4 × CH bonds	$2 \times \sigma_g$, $2 \times \sigma_u$	$2 \times a_1, b_1, b_2$
2 × CC bonds	$2 \times \sigma_g$	$2 \times a_1$
$2 \times \pi$ (∥ and ⊥)	$2 \times \pi_u$	$2 \times a_1, b_1, b_2$
Total occupied	$6 \times \sigma_g$, $4 \times \sigma_u$, $2 \times \pi_u$	$8 \times a_1$, $3 \times b_1$, $3 \times b_2$
Unoccupied		
$2 \times \pi^*$ (∥ and ⊥)	$2 \times \pi_g$	$2 \times a_2, b_1, b_2$

[a] The first column categorizes the MO's according to their VB description.

Nevertheless, this finding appears to be considerably at odds with that of Gleicher and Dewar,[13] which predicts cyclobutadiene to be *more* stable than two acetylenes by some 50 kcal/mole. It should be pointed out, however, that their value is obtained by comparing with the experimental C_2H_2 heat of atomization rather than with the corresponding semiempirically calculated value;[14] if the semiempirical number is chosen instead, the energy difference is considerably smaller (2.1 kcal/

mole, with the acetylenes still less stable), in much better agreement with the *ab initio* results. By the same token the analogous benzene–acetylene comparison,[14] which differs from experiment by only 4 kcal/mole if the acetylene experimental heat of atomization is employed, shows a discrepancy of 70 kcal/mole if the semiempirical value is taken. While it certainly can be argued that the benzene result supports the practice of assuming the experimental acetylene energy for purposes of comparison, it also seems fair to suggest that failure to obtain good agreement between experiment and semiempirical calculation for the heat of atomization of acetylene, a relatively small molecule, might be symptomatic of an occasional spurious result for larger systems. In any event, it seems clear that both *ab initio* and semiempirical methods are on safest grounds when used to compare the stability of molecules of roughly the same size; thus it seems quite certain that cyclobutadiene is substantially more stable than its tetrahedral isomer.

Acknowledgments. The authors wish to thank Dr. J. Harper for suggesting the investigation of tetrahedrane and for several illuminating discussions during the course of this work. The services and computer time made available by the University of Nebraska Computer Center have been essential to this study and are hereby gratefully acknowledged.

[14] M. J. S. Dewar and G. Klopman, *J. Am. Chem. Soc.*, **89**, 3089 (1967).

Valence-Bond Studies of Contact Nuclear Spin–Spin Coupling. III. π-Electron Coupling in Aromatic and Cyclic Unsaturated Hydrocarbons

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Abstract: Theoretical calculations of π-electron contributions to contact proton spin–spin coupling constants in aromatic and cyclic unsaturated systems are performed by means of a previously developed formalism which uses the generalized product approximation with intergroup configuration interaction and valence-bond wave functions. Theoretical results for a number of aromatic and unsaturated cyclic fragments are compared with the experimental data, and their significance for coupling mechanisms are discussed. Agreement of theoretical results with experiment is best for small, long-range coupling constants. Theoretical values for all of the indene long-range coupling constants should be useful for the detailed spectral analysis. Comparisons of the calculated and experimental results for cycloheptatriene suggest that the unsaturated portion of the molecule is very nearly planar in the liquid phase.

The first paper[1] in this series introduced a theoretical valence-bond (VB) description of contact nuclear spin–spin coupling which avoids the empirical choice of an "average excitation energy." [2] The method, which includes an explicit sum over a finite set of triplet-state VB wave functions in the second-order perturbation expression,[3] was used[4] to calculate H–H coupling constants in a large number of unsaturated molecular fragments. The agreement of the semiempirical results with pertinent experimental data was quite satisfactory, but the rapid increase in the number of triplet states with an increasing number of electrons limited the calculations to systems which could be described in terms of eight electron fragments. A subsequent theoretical formulation[5] by means of density matrix theory and the generalized product approximation with intergroup configuration interaction[6–8] provided a generalization of many existing theories of nuclear spin coupling. One advantage of this formulation is that it permits extension to many electron systems in which separate groups can be recognized. For example, it is often convenient to recognize the σ- and π-electron systems as separate groups. Furthermore, within the simple VB schemes[9,10] in which atomic orbital overlap is ignored, any separation of the molecule into groups is permissable.

It is the purpose of this investigation to make use of the generalized product approximation formalism[5] to extend the VB calculations[1,4] of contact nuclear spin–spin coupling constants to molecular fragments with as many as 16 electrons. This permits coupling constant calculations to be performed in the important examples of aromatic and cyclic unsaturated hydrocarbons. Since there have been no previous calculations for most of these systems in which a number of coupling paths are of importance, the results are of significance in discussing mechanisms of contact coupling and should be of use in making detailed analyses of the complex nuclear magnetic resonance (nmr) spectra.

Theoretical Formulation. Integral Parameters

Contact nuclear spin–spin coupling constants were calculated from the second-order perturbation ex-

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