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.

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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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[6] R. McWeeny, *Rev. Mod. Phys.*, **32**, 335 (1960).
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pression of Ramsey[3] which has been cast into the density matrix notation by McWeeny and Mizuno.[8] Since methods for calculating VB transition spin densities and triplet-state energies were discussed in previous papers in this series,[1,4] the formalism which uses the generalized product approximation with intergroup configuration interaction[5] will be reviewed briefly to aid in the discussion.

For the case of two groups, R and S, the generalized single configuration wave function, $^1\Phi_0$, is given by

$$^1\Phi_0 = \mathcal{A}[^1\phi_{\mathrm{R}0}(1, 2, \ldots, N_{\mathrm{R}}) \times {}^1\phi_{\mathrm{S}0}(N_{\mathrm{R}} + 1, \ldots, N_{\mathrm{R}} + N_{\mathrm{S}})] \qquad (1)$$

where $\mathcal{A}$ is an operator which produces a normalized antisymmetric wave function and $^1\phi_{\mathrm{R}0}$ denotes the lowest singlet-state wave function of group R with N_{R} electrons. Similarly, generalized single configuration triplet-state wave functions, $^3\Phi_{\mathrm{R}r_m}$ $(m = +1, 0, -1)$ are obtained by excitation to the r_mth triplet of group R.

$$^3\Phi_{\mathrm{R}r_m} = \mathcal{A}[^3\phi_{\mathrm{R}r_m}{}^1\phi_{\mathrm{S}0}] \qquad (2)$$

Now consider configurational mixing between the ground state, $^1\Phi_0$, and those configurations, $^1\Phi_{\mathrm{RS}}$, which arise by exciting both groups to triplets and spin coupling to a singlet function

$$^1\Phi_{\mathrm{RS}} = 3^{-1/2}(\Phi_{\mathrm{R}r_{+1}\mathrm{S}s_{-1}} - \Phi_{\mathrm{R}r_0\mathrm{S}s_0} + \Phi_{\mathrm{R}r_{-1}\mathrm{S}s_{+1}}) \qquad (3)$$

where, for example

$$\Phi_{\mathrm{R}r_{+1}\mathrm{S}s_{-1}} = \mathcal{A}[^3\phi_{\mathrm{R}r_{+1}}{}^3\phi_{\mathrm{S}s_{-1}}] \qquad (4)$$

Configurational mixing between $^1\Phi_0$ and $^1\Phi_{\mathrm{RS}}$ gives

$$^1\Psi_0 = c_0{}^1\Phi_0 + \sum_{r,s} c_{rs}{}^1\Phi_{\mathrm{RS}} \qquad (5)$$

with energy $^1E_0$ and the summation is over all of the triplets of groups R and S. The coefficients are obtained by solving the appropriate secular determinant. Matrix element expressions have been reported previously.[5]

In the triplet manifold configurational mixing occurs between a given triplet, $^3\Phi_{\mathrm{R}r_m}$, and those which are obtained by exciting to the triplets of group S. For the $m = 0$ component of the R group triplets, the most general expression is

$$^3\Psi_{\rho 0} = \sum_{r_0} c_{\rho 0, r_0}{}^3\Phi_{\mathrm{R}r_0} + \sum_{s_0} c_{\rho 0, s_0}{}^3\Phi_{\mathrm{S}s_0} \qquad (6)$$

with energy $^3E_\rho$ and coefficients obtained from diagonalizing the secular determinant.[5] An expression analogous to eq 6 is obtained for the S group triplets.

With the foregoing expressions for the wave functions and energies and the assumption that the electron densities of the coupled nuclei, N and N′, are only nonnegligible for group R, the expression for the contact nuclear spin–spin coupling constant is

$$J_{\mathrm{NN}'} = (2h)^{-1}(16\pi\beta\hbar/3)^2\gamma_{\mathrm{N}}\gamma_{\mathrm{N}'} \times \left[\sum_{\rho 0}\left\{\frac{\sum_{r_0}\{c_0 c_{\rho 0, r_0} - (1/\sqrt{3})\sum_{s_0} c_{rs} c_{\rho 0, s_0}\}^2 \times Q_1(0r_0|1_{\mathrm{N}};1_{\mathrm{N}})Q_1(0r_0|1_{\mathrm{N}'};1_{\mathrm{N}'})}{^3E_\rho - {}^1E_0}\right\} + \sum_{\sigma 0}\left\{\frac{\sum_{r_0}\{c_0 c_{\sigma 0, r_0} - (1/\sqrt{3})\sum_{s_0} c_{\sigma 0, s_0} c_{rs}\}^2 \times Q_1(0r_0|1_{\mathrm{N}};1_{\mathrm{N}})Q_1(0r_0|1_{\mathrm{N}'};1_{\mathrm{N}'})}{^3E_\sigma - {}^1E_0}\right\}\right] \qquad (7)$$

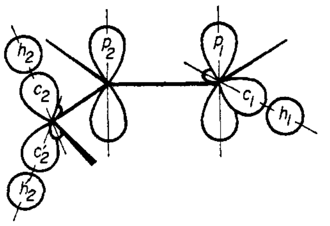

Figure 1. Labeling of atomic and hybrid orbitals in an unsaturated three-carbon fragment.

Ground-state wave functions in the VB method are of the form

$$^1\phi_{\mathrm{R}0} = \sum_j c_{rj}{}^1\psi_j \qquad (8)$$

where the c_{rj}'s are the coefficients corresponding to the lowest eigenvalue of the secular determinant and the $^1\psi_j$'s are the nonionic singlet canonical structures in the Rumer–Pauling bond diagram method.[9,10] Valence-bond triplet-state wave functions $(m = 0)$ are of the form

$$^3\phi_{\mathrm{R}r_0} = \sum_l c_{r_0,l}{}^3\psi_l \qquad (9)$$

where the $^3\psi_l$'s are the nonionic triplet-canonical structures.[11,12] Valence-bond transition spin densities between $^1\phi_{\mathrm{R}0}$ and $^3\phi_{\mathrm{R}r_0}$ for use in eq 7 and in calculating the matrix elements of the secular determinants for eq 5 and 6 are given by [5,12]

$$Q_1(0r_0|1;1') = \sum_{jl} c_{rj} c_{r_0,l}(1/2)^{n-i_{jl}} \sum_a a(1)a^*(1')f^a{}_{jl} \qquad (10)$$

where a denotes an atomic orbital in R, and in the superposition diagrams of the singlet and triplet canonical structures, i_{jl} is the number of islands, and $f^a{}_{jl}$ is $+1$ if atomic orbital a is part of an island which contains a broken bond and is in the even subset of an alternant system. However, $f^a{}_{jl}$ equals -1 if a is part of an island which contains a broken bond and is in the odd subset. In all other cases this factor is zero.

Because of the very large number of terms (784 for the 16 electron case) which arise for the summation in eq 5, corresponding to configuration interaction (CI) in the singlet manifold, perturbation theory was used to calculate the ground-state wave functions and energies. However, CI in the triplet manifold was performed by diagonalizing a secular determinant over all of the R and S group triplet states.[13]

A FORTRAN computer program was written to calculate coupling constants from eq 7. Representative computation time for a 16-electron fragment is approximately 2 min on a CDC 6400 digital computer.

Entered in Table I are the semiempirical molecular and atomic exchange integral parameters, $K(a,b)$, for orbitals a and b in the unsaturated hydrocarbon fragment depicted in Figure 1. These integrals were used in previous calculations of spin–spin coupling constants,[4] triplet-state energies,[12] and esr hyperfine cou-

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(13) This procedure should be more accurate than that used in ref 5 in which CI in the triplet manifold was performed by successive diagonalization of secular determinants for each of the R-group triplets. However, results for the nonaromatic systems discussed in ref 5 are only slightly affected by this modification.

pling constants.[14] An exception is the one-center exchange integral, $K(p_1,c_1)$, where p_1 and c_1 denote atomic orbitals centered on an *aromatic* carbon. An empirical value of 1.06 eV for this integral was obtained by fitting the experimental value of −0.62 Hz between the α-methyl and *para* hydrogens in toluene,[15] since this six-bond coupling is expected to be dominated by a σ–π configuration interaction mechanism. The lower value of this integral for aromatic systems suggests a significant reduction in the extent of σ–π configuration interaction, but this cannot be justified on the basis of theoretical considerations[14] of esr hyperfine coupling constants. Perhaps inadequacies in the VB description of aromatic systems and changes in the other parameters have been compensated by this change.

Table I. Molecular and Atomic Exchange Integrals, $K(a,b)$, for Orbitals *a* and *b* in Unsaturated and Aromatic Systems[a]

$K(p_1,p_2) = -2.256$ eV (1.337 Å)[b]
-1.892 (1.40 Å)[b]
-1.583 (1.46 Å)[b]
-1.483 (1.474 Å)[b]
$K(p_1,c_1) =$ 1.26 (ethylenic)[c]
1.06 (aromatic)[d]
$K(p_1,h_1) = 0.792$[c]
$K(c_1,h_1) = -3.916$[c]
$K(p_2,c_2) = -0.52 \cos^2 \phi$[e]
$K(c_2,h_2) = -3.80$[f]

[a] Orbitals are labeled as in Figure 1. [b] C. A. Coulson and W. T. Dixon, *Tetrahedron*, **17**, 215 (1962); D. Clarkson, C. A. Coulson, and T. H. Goodwin, *ibid.*, **19**, 2153 (1963). [c] Reference 14. [d] Empirical value from this work. [e] Reference 4. [f] Reference 2.

σ-Electron contributions to spin–spin coupling constants have not been included in these calculations because they would require the introduction of many more orbitals and exchange integral parameters.

Results and Discussion

A. Benzene. Existing theoretical calculations[16–18] of π-electron contributions to spin–spin coupling in aromatic molecules made use of empirical hyperfine coupling constant data from the electron spin resonance spectra of aromatic free radicals. Although the assumption of single determinant molecular orbital (MO) wave functions in conjunction with the "average energy approximation" led to necessarily positive or zero H–H coupling constants,[16] the use of VB wave functions with the "average energy approximation" led[17] to negative π-electron contributions to the coupling between *meta* protons in benzene.

Calculated results for benzene are based on ten-electron fragments consisting of a six-electron group for the π system of benzene and a four-electron group consisting of two C–H bonds in the appropriate positions. The calculated VB ground to triplet-state energies, ${}^3E_\kappa - {}^1E_0$, and the contribution of each triplet to the *ortho*, *meta*, and *para* coupling constants are entered in Table II. Triplet states, which correspond to those for the π-electron system of benzene, have been labeled by the symmetry species appropriate to the D_{6h} point group. Total calculated π-electron contributions to the three types of coupling are given at the bottom of Table II. As noted previously,[4] total values depend critically on the cancellation between two large contributions with opposite signs. The results appear to converge since contributions from the higher triplets are negligible. The triplet-state assignments for benzene are consistent with those based on the *ab initio* calculations of Buenker, Whitten, and Petke;[19] however, the lowest triplet state is about 1 eV smaller than the experimental value (3.65 eV).[20] Several interesting discussions have been given of the symmetry properties[21–23] of the triplet contributions to the nuclear spin–spin coupling constants in the Ramsey perturbation formulation.[3] These symmetry properties are apparent in the contributions of each of the triplets in Table II to the *ortho*, *meta*, and *para* π-electron coupling constants in benzene. Magnitudes of contributions from species which are degenerate in D_{6h} symmetry are not necessarily the same because E_{1u}, for example, correlates with $A_1 + B_1$ in C_{2v} symmetry but correlates with $B_{2u} + B_{3u}$ in D_{2h} symmetry.[24]

Table II. Calculated VB Ground to Triplet-State Energies, ${}^3E_\kappa - {}^1E_0$, and the π-Electron Contributions, ${}^3J^\pi{}_{HH'}(\kappa)$, ${}^4J^\pi{}_{HH'}(\kappa)$, ${}^5J^\pi{}_{HH'}(\kappa)$, of Each Triplet, κ, to the *ortho*, *meta*, and *para* Coupling Constants in Ten-Electron Fragments for the Benzene Molecule[a]

κ	${}^3E_\kappa - {}^1E_0$, eV	${}^3J^\pi{}_{HH'}(\kappa)$, Hz	${}^4J^\pi{}_{HH'}(\kappa)$, Hz	${}^5J^\pi{}_{HH'}(\kappa)$, Hz
1	2.59($^3B_{1u}$)[b]	1.17	−1.17	1.17
2	5.76($^3E_{1u}$)[b]	−0.41	0.41	0.54
3	5.76($^3E_{1u}$)[b]	0.14	−0.14	0.00
4	6.82($^3E_{2g}$)[b]	3.08	3.09	−4.11
5	6.82($^3E_{2g}$)[b]	−1.05	−1.04	0.00
6	7.84	263.11	263.32	−262.69
7	7.85	−265.29	−265.07	265.73
8	11.05($^3B_{1u}$)[b]	0.01	−0.01	0.01
9	12.50($^3A_{2g}$)[b]	0.00	0.00	0.00
10	13.56($^3E_{1u}$)[b]	0.00	0.00	0.00
11	13.56($^3E_{1u}$)[b]	0.00	0.00	0.00
12	15.66	0.00	0.00	0.00
	$\sum_\kappa J^\pi{}_{HH'}(\kappa) =$	0.76	−0.61	0.65

[a] It was assumed that r(C–C) = 1.40 Å. [b] Triplet states which correlate with those for the π-electron system of benzene.

Entered in Table III are the calculated π-electron contributions to the *ortho*, *meta*, and *para* coupling

Table III. Comparison of a Number of *ortho*, *meta*, and *para* Coupling Constants in Benzene with the Experimental Values

	$J^\pi{}_{HH'}$ (VB),[a] Hz	$J^\pi{}_{HH'}$ (VB),[b] Hz	$J_{HH'}$ (CNDO),[c] Hz	$J_{HH'}$ (INDO),[c] Hz	$J_{HH'}$ (exptl),[d] Hz
ortho	0.76	0.47	7.55	8.15	7.54
meta	−0.61	−0.21	1.90	2.13	1.37
para	0.65	0.23	0.44	1.15	0.69

[a] This work. [b] Reference 17. [c] Reference 31. [d] J. M. Read, R. E. Mayo, and J. H. Goldstein, *J. Mol. Spectrosc.*, **22**, 419 (1967).

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(17) H. M. McConnell, *J. Chem. Phys.*, 30, 126 (1959).

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constants in benzene, theoretical coupling constants obtained by other investigators, and the experimental results. The π-electron results obtained here are two to three times larger than the values obtained by McConnell[17] by means of VB wave functions and the "average energy approximation." An increase by this amount seems to be typical of the use of VB finite sum methods[1] instead of the "average energy approximation" but with the same exchange integral parameters.

The large discrepancies between the calculated *ortho* and *meta* coupling constants in the first column of Table III and the corresponding experimental values in the last column can be attributed to the neglect of significant *positive* contributions which arise within the σ-electron framework.[25-27] The *para* H–H coupling constant appears to be dominated by a π-electron mechanism, *i.e.*, a σ–π configuration interaction mechanism,[17] but there have been some theoretical discussions[28-30] which suggest small, positive σ-electron contributions for coupling over five bonds.

Recent theoretical results for aromatic coupling constants have been based on self-consistent perturbation theory[31] with CNDO[32] (complete neglect of differential overlap) and INDO[33] (intermediate neglect of differential overlap) wave functions. Calculated aromatic coupling constants based on these types of wave functions are entered in the third and fourth columns of Table III. The INDO method differs from the CNDO method in the inclusion of one-center exchange integrals. As a consequence, the difference between the results of the two methods is indicative of the importance of σ–π configuration interaction to the spin–spin coupling. The differences between the CNDO and INDO results for *ortho* and *para* coupling are close to those obtained by the VB method, but this difference for *meta* coupling is somewhat smaller in magnitude and of a different sign.

B. Toluene and the Xylenes. Recent accurate experimental coupling constant data for toluene[15,34] provide good experimental criteria for the theoretical calculations. Acrivos[18] reported results for the related system, *sym*-trimethylbenzene, and obtained theoretical results based on a method which is similar to that introduced by Karplus,[35] but which includes a sum over occupied and unoccupied Hückel molecular orbitals for the π system of benzene.

In Table IV are entered the calculated π-electron contributions to the long-range H–H coupling constants for toluene (items 1–3) and *o*-, *m*-, and *p*-xylenes (items 4–6). The calculations were based on ten-electron fragments similar to those for benzene. Also included in Table IV are the theoretical results of Acrivos[18] and pertinent experimental data.[15,18] As noted previously, the one-center exchange integral, $K(c_1,p_1)$, for an aromatic carbon was fitted to the experimental value for the α-Me to *p*-H coupling in toluene (item 3). This experimental value was chosen because any contributions to this coupling over six bonds by direct or indirect σ-electron mechanisms[30] are expected to be minimal. For a freely rotating or hindered methyl group, the average value $K(c_2,p_2)_{av} = -0.26$ eV was chosen.[4]

Table IV. Calculated π-Electron Contributions to the Long-Range H–H Coupling Constants in Ten-Electron Fragments for the Toluene and Xylene Molecules and Available Experimental Data

Molecule	$J^{\pi}_{HH'}$ (calcd),[a] Hz	$J^{\pi}_{HH'}$ (calcd),[b] Hz	$J_{HH'}$ (exptl), Hz
Toluene			
1. CH_3 to *o*-H	−0.73	−0.87	−0.75[c]
2. CH_3 to *m*-H	0.59	...	0.36[c]
3. CH_3 to *p*-H	(−0.62)[d]	−0.37	−0.62[c,d]
Xylenes			
4. CH_3 to *o*-CH_3	0.74	...	...
5. CH_3 to *m*-CH_3	−0.60	−0.32	$<\lvert 0.35\rvert$[b]
6. CH_3 to *p*-CH_3	0.63	...	...

[a] This work. [b] Reference 18. [c] Reference 15. [d] Exchange integral, $K(c_1,p_1)$, fitted to this value.

With the parameterization discussed above, the calculated toluene α-methyl to *o*-H coupling constant (item 1) is in good agreement with the experimental value. Crude, semiempirical VB calculations[27] for the similar case of *allylic* coupling indicated a small *positive* contribution to $^4J_{HH'}$ from indirect, σ-electron mechanisms, but empirical observations[36] suggest that σ-electron contributions should vanish for the *cis* relationship of the protons. The calculated five-bond coupling between the α-methyl and *meta* proton (item 2) in toluene is almost twice the experimental value. This is probably due to inclusion in the VB formalism of too much correlation between electrons in the same subset of an alternant system.

It is interesting that the calculated *o*-, *m*-, and *p*-xylene coupling constants (items 4–6) have almost identical magnitudes to the analogous values in toluene even though different exchange integrals are used. The calculated methyl to *m*-methyl coupling (item 5) is too large, presumably for the reason cited above. On this basis the calculated *o*-xylene and *p*-xylene couplings should be in better agreement with experimental values but these are not yet available.

C. Cyclopentadiene and Indene. Since experimental results for cyclopentadiene[37] and indene[38,39] are based on partial analyses of the complex nmr spectra, many of the smaller coupling constants were not determined. However, the calculated results are consistent with many aspects of the spectra and in the case of indene many prove of value in performing a detailed analysis.

Calculated π-electron contributions to the H–H coupling constants for fragments of the cyclopentadiene (I) and indene (II) molecules and the experimentally determined values are entered in Table V. In both

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(25) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(26) M. Barfield, *ibid.*, **46**, 811 (1967).

(27) M. Barfield, *ibid.*, **41**, 3825 (1964).

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(35) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

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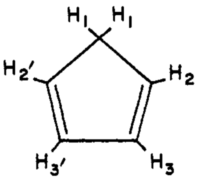

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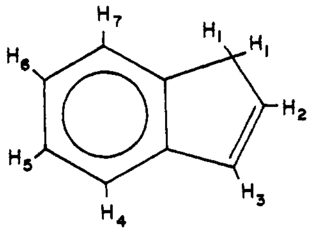

II

cases the ring systems were assumed to be planar with tetrahedral HCH angles bisected by the planes of the rings. Results reported here are based on fragments with a single C–H bond for the methylene group since satisfactory exchange integral parameters for a tetrahedral CH_2 group have not been established unambiguously.[2,40] As additional justification for this procedure, it should be noted that calculations with empirically determined parameters for the CH_2 groups gave essentially the same results as those in which a single C–H bond was considered.

Table V. Calculated π-Electron Contributions to Spin Coupling in Fragments of the Cyclopentadiene and Indene Molecules Compared with Available Experimental Data

Cyclopentadiene^{a}			Indene^{b}		
HH′	$J^{\pi}_{HH'}$ (calcd), Hz	$J_{HH'}$ (exptl), Hz	HH′	$J^{\pi}_{HH'}$ (calcd), Hz	$J_{HH'}$ (exptl), Hz
12	1.76	1.20^{d}	12	2.22	2.02^{c}
13	−1.58	−1.31^{d}	13	−2.09	−1.98^{c}
22′	1.10	1.94^{d}	14	0.56	. . .
33′	0.86	1.94^{d}	15	−0.67	. . .
23′	−0.95	1.09^{d}	16	0.60	. . .
			17	−0.83	. . .
23	2.29	5.06^{d}	23	2.39	5.58^{c}
			24	0.32	. . .
			25	−0.25	. . .
			26	0.27	. . .
			27	−0.26	. . .
			34	−0.34	. . .
			35	0.27	. . .
			36	−0.29	. . .
			37	0.27	~|0.7|^{e}

^{a} Calculations were based on eight-electron fragments if the coupling constant included the 1 protons, and ten-electron fragments in all other cases. The ring system was assumed to be planar with $r(C{=}C) = 1.337$ Å, $r(C{-}C) = 1.483$ Å, and the HCH angle was assumed to be tetrahedral. ^{b} Calculations were based on 12-electron fragments if the calculated coupling constant included the 1 proton; 14-electron fragments were used in all other cases. In the aromatic ring it was assumed that $r(C{-}C) = 1.40$ Å, and in the five-membered ring $r(C{=}C) = 1.337$ Å, $r(C{-}C) = 1.483$ Å, and the HCH angle was assumed to be tetrahedral. ^{c} Reference 38. ^{d} Reference 37. ^{e} Reference 39.

The nmr spectrum of cyclopentadiene was partially analyzed[37,38] by double-resonance techniques with irradiation of the methylene protons. Results for J_{12} and J_{13} in Table V are of particular interest because both the experimental and theoretical values are significantly less than the corresponding values in indene. These two coupling constants each include contributions of different magnitude and sign for the two possible coupling paths around the five-membered rings. For example, the calculated J^{π}_{12} in cyclopentadiene reflects contributions of about 2.8 Hz along the three-bond path and ~−1.1 Hz along the six-bond path. The J^{π}_{13} coupling in I is attributable to contributions of about −2.5 Hz along the four-bond path and ~1.0 Hz along the five-bond path. The other calculated π-electron coupling constants for cyclopentadiene in Table V are consistent with nonnegligible contributions from the σ-electron framework. If a nominal value of 1.2 Hz[27] is ascribed to σ-electron contributions for the all *trans* arrangement of the four-bond H–H coupling constant, the total estimated value for $J_{22'}$ (2.3 Hz) is reasonable but we have underestimated $J_{23'}$ (0.25 Hz) if a positive sign for the experimental value is assumed.

The calculated indene coupling constants, J^{π}_{12} and J^{π}_{13} in Table V, have larger magnitudes than the corresponding values for cyclopentadiene because contributions for the six- and five-bond paths which include the aromatic ring protons are ~−0.5 and ~+0.5 Hz, respectively. These values are about one-half of those for coupling through a nonaromatic π-electron system. Smaller magnitudes for transmission of spin "information" through an aromatic ring seem to be general and a consequence of the partial bond orders in such systems.[35] The methylene protons also are coupled to some or all of the aromatic ring protons.[38] Since these protons are the X_2 part of an $ABCDKLX_2$-type spectrum,[38,41] first-order analysis is not sufficient to determine the sign and magnitude of the long-range coupling constants. However, the long-range coupling constant with the largest calculated magnitude ($J^{\pi}_{17} = -0.83$ Hz) is consistent with the observation[39] that methyl substitution in the 7 position of indene removes the largest splitting in the spectrum of the methylene group protons. By analogy with the results for the α-methyl to *m*-H long-range coupling in toluene (Table IV), it seems likely that J^{π}_{16} and J^{π}_{14} in Table V may be too large by a factor of about 2.

The 3 proton of indene is also split by several aromatic protons and the largest splitting appears to be ±0.7 Hz. This is consistent with long-range coupling to the 7 proton if in addition to the calculated value of 0.27 Hz a contribution of about 0.4 Hz arises from the σ-electron framework in the all *trans* arrangement of the bonds linking the 3 and 7 protons.[30] The width of the observed spectral lines[38] for the 2 proton in indene is consistent with the calculated long-range coupling constants in Table V, but a detailed analysis is clearly necessary.

D. Cycloheptatriene and Cyclooctatetraene. In contrast to the fragments considered above, the π-electron systems of cycloheptatriene and cyclooctatetraene exhibit substantial deviations from planarity.[42,43] It may be anticipated that the decreased delocalization will have a marked effect on the values of the spin–spin coupling constants. Complicating features in the nmr spectra at room temperature are equilibration of nonplanar cycloheptatriene conformers[44–46] and valence

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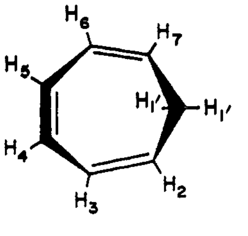
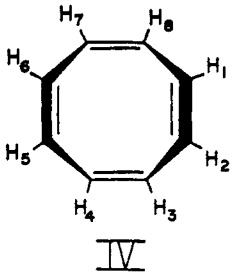
tautomerism in cyclooctatetraene.[47,48]

The calculated π-electron contributions for fragments of the cycloheptatriene (III) and cyclooctatetraene (IV) molecules are entered in Table VI along with the available experimental data.[48,49] Two different conformations were assumed for the cycloheptatriene fragments corresponding to different values for the angle β between the planes formed by C_3–C_4–C_5–C_6 and C_2–$C_3\cdots C_6$–C_7. In one set of calculations on the cyclooctatetraene fragments, β was taken to be 40°, which is close to the microwave result of 40.5 ± 2°,[42] and in the other calculations this angle was taken to be 0° in accordance with the X-ray diffraction results[50] for the $Mo(CO)_3$ complex of III. In both sets of calculations the dihedral angles for the methylene protons were assumed to be 90 and 330°. The absence[49] of any π-electron enhancement[51] of the geminal coupling constant, $J_{11'}$, provides further evidence for a conformation in which one of the methylene protons is in the nodal plane of the adjacent π electrons. In the room-temperature nmr spectrum[44,46] of III the methylene protons are equivalent, corresponding to equilibrium between two equivalent conformers. Thus, coupling constants involving the methylene protons were taken as the average of the two values (J^{π}_{12}, J^{π}_{13}, and J^{π}_{14} in Table VI).



III



IV

Table VI. Calculated π-Electron Contributions to the Spin–Spin Coupling Constants in Fragments of the Cycloheptatriene and Cyclooctatetraene Molecules Compared with Available Experimental Data

Cycloheptatriene[a]				Cyclooctatetraene[b]		
	$J^{\pi}_{HH'}$ (calcd), Hz		$J_{HH'}$ (exptl),[c]		$J^{\pi}_{HH'}$ (calcd),	$J_{HH'}$ (exptl),[d]
HH'	β = 40°	β = 0°	Hz	HH'	Hz	Hz
12	0.93[e]	0.86[e]	6.7	12	2.42	11.0
13	−0.91[e]	−0.82[e]	<0.4	13	−2.58	...
14	0.50[e]	0.04[e]	<0.1	14	0.22	...
23	2.48	2.33	8.9	15	−0.22	...
24	−1.64	−1.04	1.48[f]	16	2.34	...
25	0.55	1.14		23	4.53	2.0
26	−0.34	−0.42	...			
27	0.09	0.51	...			
34	3.06	0.95	5.51			
35	−1.99	−0.47	0.72			
36	1.26	0.36	0.69			

[a] Calculations were based on 10-electron fragments if the coupling included the 1 protons, and 12-electron fragments otherwise. The ring system was assumed to be nonplanar with r(C=C) = 1.337 Å, r(C—C) = 1.483 Å, and the HCH angle was assumed to be tetrahedral. [b] Calculations were based on 12-electron fragments with the "tub" conformation and r(C=C) = 1.337 Å, r(C—C) = 1.46 Å. [c] Reference 49. [d] Reference 48. [e] Values taken as the average for the 1' and 1 protons. [f] $J_{24} + J_{25}$ = 1.48 Hz.

Since the 2 to 7 protons in cycloheptatriene are separated from the methylene (1 and 1') protons by an odd/even number of bonds along one path of the ring and an even/odd number of bonds along the other path, the first three calculated values of $J_{HH'}$ in Table VI arise as sums of contributions with opposite signs. The magnitudes of the calculated VB π-electron contributions decrease steadily with the number of intervening bonds in a linear polyene system; thus, the signs of the couplings to the 1 protons are determined by the sign of the coupling along the shorter path. The calculated values for J^{π}_{12} and J^{π}_{13} are consistent with significant σ-electron contributions.

Of the two sets of calculated coupling constants for cycloheptatriene, only that for β = 0° in Table VI appears to be completely consistent with the experimental results. For example, the observed value for $J_{24} + J_{25}$ is +1.48 Hz, but for β = 40° the sign of the calculated sum is *negative*. However, for the β = 0° conformation, addition of +1.2 Hz due to σ-electron coupling in the all-*trans* arrangement of the bonds linking the 2 and 4 protons gives a total estimated value of +1.30 Hz, which is in good agreement with the experimental results. Similarly, an addition of +1.2 Hz to the calculated value of −0.47 Hz for J_{35} in the β = 0° conformation leads to an estimated value of +0.73 Hz, which is in very good agreement with the experimental value of +0.72 Hz. For the β = 40° conformation the calculated value for J_{35} is of the wrong sign. Also, with the expectation of positive contributions from the σ-electron framework to the five-bond coupling constant[29], J_{36}, the value obtained for this coupling in the β = 0° conformation is the only one which is consistent with the experimental results. Thus, it appears that the 0° value[50] for β is the correct one for cycloheptatriene in solution.

Cyclooctatetraene was assumed to be in the "tub" conformation. The dihedral angles between adjacent double bonds were assumed to be 70°. Calculated results in Table VI are based on 12-electron fragments consisting of one group with eight $2p_{\pi}$ electrons and another with two C–H bonds. The large values calculated for J^{π}_{13}, J^{π}_{16}, and J^{π}_{23} in Table VI can be attributed to the very favorable relationship between the C–H bonds containing the coupled protons and the π-electron system. Very small calculated values for J^{π}_{14} and J^{π}_{15} arise because of the near orthogonality of the individual double bonds which comprise the extended π-electron system. The geometry of cyclooctatetraene is such that the coupling constants should have minimal contributions from the σ-electron framework. Exceptions, of course, are coupling constants of the J_{12} type.

Conclusions

On the basis of the comparison of a large number of calculated coupling constants in aromatic and cyclic unsaturated hydrocarbons with the experimental data,

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the following general observations can be made in regard to the mechanisms.

(a) A π-electron (σ–π configuration interaction) mechanism is dominant for *para* H–H coupling in benzene, α-methyl to H coupling in toluene, and methyl to methyl coupling in the xylenes. σ contributions to *ortho* and *meta* coupling in benzene are considerably larger than the π contributions.

(b) An aromatic π-electron system is less effective in transmitting spin information than a linear polyene system; *i.e.*, the magnitudes are smaller.

(c) Contributions to π-electron coupling from different paths are approximately additive.

(d) The VB calculations appear to overestimate the π-electron coupling constants between nuclei which are associated with $2p_\pi$ electrons in the same subset of an alternate system.

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Spectroscopic Studies of Alkali Metal Ions and Ammonium Ions in 2-Pyrrolidones[1]

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Abstract: The far-infrared spectra of alkali metal salts in 2-pyrrolidones exhibit bands which are not present in either the pure solvent or the pure salt. The band frequencies are dependent on the nature of the cation and solvent but not on the anion. The experimental evidence indicates that the observed bands are due to vibrations of the cations in a solvent cage. Nuclear magnetic resonance and far-infrared mole-ratio studies were used to determine the coordination number of lithium ion in a mixed solvent system, 1-methyl-2-pyrrolidone (1M2PY) and dioxane. Both techniques indicate that the lithium ion is solvated by four molecules of the pyrrolidone. Examination of the carbonyl band frequency in 1M2PY indicates that the cation interacts strongly with the oxygen of the carbonyl group. The absence of Raman lines in 1M2PY solutions of lithium salts suggest that the bond with solvent is essentially ionic.

It was pointed out in our previous publications,[2] as well as those of Edgell and coworkers, that the combination of nmr and far-infrared spectroscopic techniques offers a new approach to the study of ionic solvation. These publications reported spectroscopic studies on solvation of alkali metal salts in dialkyl sulfoxides[2a–c] and other solvents.[2d–f] A model for the alkali metal vibration in solvent cage was proposed.[2d–f] It was of interest to us to extend these studies to other solvents, both polar and nonpolar, so as to determine the influence of solvent properties on the formation, the stoichiometry, and the structure of the solvation cage around metal ions. In this paper, we report the study of the alkali metal ion solvation in 2-pyrrolidone and its derivatives.

In general, 2-pyrrolidones are polar compounds with a dielectric constant of 27[3] for the 2-pyrrolidone and 32[4] for the 1-methyl-2-pyrrolidone (hereafter abbreviated 2PY and 1M2PY, respectively). The pyrrolidones also act as nucleophilic reagents and form complexes with both transition[5] and nontransition metal ions.[6,7] Studies on the solvent properties of 1M2PY indicate that it is an excellent dissociating solvent.[8,9] Preliminary investigation indicated that at least 2PY and 1M2PY have reasonable transparencies in the far-infrared spectral region.

Experimental Section

Apparatus. All far-infrared spectra were obtained with a Perkin-Elmer 301 far-infrared spectrophotometer. Demountable liquid cells with Teflon spacers and polyethylene windows (Barnes Engineering Co.) were used. Cell thicknesses were usually kept at 0.05 or 0.1 mm. Between runs, the cells were flushed with acetone and then with pentane and dried in a current of dry air. The spectrophotometer was used in the double-beam mode. A dry nitrogen purge was always maintained when running below 320 cm^{-1} but the purge was not necessary above this frequency. Concentrations of salt solutions were varied between 0.1 and 2.0 *M*. Most measurements, however, were carried out with 0.5 *M* solutions.

Ultraviolet spectra were obtained on a Cary 14 spectrophotometer. Infrared spectra from 4000 to 600 cm^{-1} were obtained on either a Perkin-Elmer 237B or a Unicam SP 200 spectrophotometer.

The nmr measurements were made on a 60-Mc Varian A-60 spectrometer. All sample tubes were equilibrated at 35° before they were placed in the probe. This practice ensured reaching thermal

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