organic substrate can change that situation. For example, in the case of the original BZ reaction (substrate: malonic acid) it was demonstrated spectrophotometrically by Franck and Geiseler[18] that the concentration of Br_2 fluctuates in synchronization with the concentration of Ce^{4+}

The malonic acid and other substrates of the homogeneous BZ reaction can remove the produced Br_2 chemically. In the case of the oxalic acid reaction discussed here the bromine is swept out by a gas stream. As one of our referees pointed out to us all effects are similar. Even the mathematical description of the Br_2 removal is identical: in both cases it has the form of a pseudo-first-order chemical reaction. In this respect it is important to mention the oscillations discovered by Körös and Orbán[19,20] with phenolic and anilinic substrates in the absence of metal ion catalyst.

Finally we want to emphasize that the mechanism proposed here is by no means the only one which may account for the effects of elemental bromine in the BZ reaction. Experimental work is in progress in our laboratory to examine the role of Br^- and of Br_2 in the original BZ reaction.

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Orbital Contributions to the Nuclear Spin–Spin Coupling Constants of Molecules

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Abstract: This paper presents ab initio values for the "paramagnetic" orbital contributions J^{1b} to the spin–spin coupling constants of the molecules methane, water, hydrogen fluoride, hydrogen cyanide, hydrogen isocyanide, acetylene, ethylene, ethane, acetonitrile, and methyl isocyanide. These values are compared with those obtained from previous semiempirical studies.

I. Introduction

The isotropic nuclear spin–spin coupling constant is the sum of four experimentally indistinguishable terms: the Fermi contact term J^3, the "diamagnetic" and "paramagnetic" orbital terms (J^{1a} and J^{1b}), and the spin-dipolar term (J^2).[1] Following the pioneering treatment of J_{HD} by Ramsey,[1] most theoretical studies have concentrated on the Fermi contact term. However, recently there has been renewed interest in the orbital and dipolar terms.[2,3]

The principal theoretical method which has been used to calculate the orbital contribution is the coupled Hartree–Fock (CHF) perturbation theory.[5] It has been implemented semiempirically in the INDO approximation by Blizzard and Santry[6] and in the MINDO/3 approximation by Dewar et al.[7a] and Schulman.[7b] Another form of semiempirical theory which has been used for the orbital term is the sum-over-states perturbation theory.[8]

From a theoretical point of view ab initio values of J^{1b} in CHF perturbation theory should be more accurate than their semiempirical counterparts. We report here our results for all coupling constants in the molecules methane, water, hydrogen fluoride, hydrogen cyanide, acetylene, ethylene, ethane, acetonitrile, and methyl cyanide. A contracted Gaussian 6-31G basis set[9] was employed, the 4-31G basis giving similar results. For HCN and C_2H_2 we also used the larger contracted basis of Dunning $(10s^56p^3/5s^3)$[10] which gave results differing from those of the 6-31G set by about 15%. The orbital term therefore appears to be much less sensitive to the basis set than the Fermi contact term.

II. Theory

Only a brief recounting of the theory for the orbital term is necessary since the CHF method for second-order properties has been adequately discussed by Thomsen et al.[5] The contribution $J_{AB}{}^{1b}$ for the coupled nuclei A and B is obtained from the energy bilinear in the perturbations H_A and H_B, and is given in the Ramsey treatment by

$$J_{AB}{}^{1b} = (-8\beta^2\hbar^2\gamma_A\gamma_B/3h) \times \sum_m \frac{\left\langle 0 \left| \sum_k^{2n} \mathbf{h}_A(k) \right| m \right\rangle \cdot \left\langle m \left| \sum_{k'}^{2n} \mathbf{h}_B(k') \right| 0 \right\rangle}{E_m - E_0} \quad (1)$$

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where $|0\rangle$ and $|m\rangle$ are the ground- and excited-state singlet wave functions, respectively, for the $2n$-electron system. The perturbations are

$$\mathbf{H}_A = 2\beta h\gamma_A \sum_k [-ir_{kA}^{-3}(\mathrm{r}_{kA} \times \nabla_k)] \equiv 2\beta\hbar\gamma_A \sum_k \mathbf{h}_A(k) \tag{2}$$

In the coupled Hartree–Fock approximation partial account is taken of the correlation contribution to $J_{AB}{}^{1b}$ by employing as an *ansatz* the lowest energy $2n$-electron Slater determinant of orbitals self-consistent in the external perturbation $\mathbf{h}_A$. In this approximation $J_{AB}{}^{1b}$ is given by

$$(J_{AB}{}^{1b})_{CHF} = (-16\beta^2\hbar^2\gamma_A\gamma_B/3h)\sum_{k=1}^{n}{}' \langle\phi_k{}^{(0)}|\mathbf{h}_B|\cdot i\boldsymbol{\phi}_k{}^{(1)}\rangle \tag{3}$$

where the $\phi_k{}^{(0)}$ are the ordinary zeroth-order molecular orbitals of Hartree–Fock theory in the absence of perturbations and the $i\boldsymbol{\phi}_k{}^{(1)}$ are the corresponding first-order (vector) corrections.

The molecular orbitals $\phi_k{}^{(0)}$ were obtained using the GAUSSIAN 70 program.[12] We required the matrix representation of the perturbing operator $\mathbf{h}_A$ in the basis of contracted Gaussian-type functions θ on two molecular centers, say P and Q, where θ on center P, for example, is a linear combination of primitive Gaussians of the form

$$\theta(P, \alpha_p, l_p, m_p, n_p) = (x - x_p)^{l_p}(y - y_p)^{m_p}(z - z_p)^{n_p}e^{-\alpha_p r_A{}^2} \tag{4}$$

Integrals required for the evaluation of matrix elements of h_A in a Gaussian basis are known as field integrals and formulas for them are given by Matsuoka.[13] Their evaluation, in turn, involves quantities called G_i by Taketa, Huzinaga, and O-ohata.[14] A convenient test on the integration formulas is to check the matrix elements for hermitivity:

$$\langle\theta(P, \ldots)|\mathbf{h}_A|\theta(Q, \ldots)\rangle = \langle\theta(Q, \ldots)|\mathbf{h}_A|\theta(P, \ldots)\rangle^*$$

In doing so we found two errors in eq 3.2 of ref 14. For the case $l_p + l_q = 2$, G_0 should be amended to $f_0 + f_2/2\nu$ and G_1 to $-f_1p - f_2/2\nu$. We also required two-electron integrals over molecular orbitals; an efficient transformation program was written to obtain them.

III. Results

Table I contains the coupled Hartree–Fock values of ${}^nJ_{AB}$ for the 41 coupling constants in the ten molecules considered.[15] While the coupled J^{1b}'s are not the major contributor to the experimental ${}^nJ_{AB}$, they are often a significant percentage of it. Among the one-bond coupling constants important contributions of $({}^1J_{AB}{}^{1b})_{CHF}$ occur (with their percentages of the experimental value in parentheses) for ${}^1J_{HF}{}^{1b}$ (36%), ${}^1J_{HO}{}^{1b}$ (13%), ${}^1J_{CC}{}^{1b}$ of acetylene (9%), ${}^1J_{CC}{}^{1b}$ of ethylene (14%), and ${}^1J_{CN}{}^{1b}$ of acetonitrile (25%). Among the two-bond coupling constants significant orbital contributions occur for ${}^2J_{HH}{}^{1b}$ of water (47%), ${}^2J_{CH}{}^{1b}$ of acetylene (14%), ${}^2J_{CH}{}^{1b}$ of ethylene (67%), and ${}^2J_{NH}{}^{1b}$ of HCN (55%). Finally, among the three-bond values ${}^3J_{HH}{}^{1b}$ of acetylene is 30% of the experimental value.

The present results confirm our earlier suggestion[2] that ${}^1J_{CN}{}^{1b}$ is an important contributor to ${}^1J_{CN}$ of acetonitrile. However, our ab initio value for methyl isocyanide, −1.2 Hz, is much smaller than the previous semiempirical value, −8.2 Hz.

Some statement should be made about the adequacy of the basis sets used here. The calculations for HCN and C_2H_2 were made in both the 6-31G and $(10s^56p^3/5s^3)$ bases, the latter containing considerably more contracted Gaussian basis functions. Since the results differed by only 15% the orbital

Table I. Coupled Hartree–Fock Values of ${}^nJ_{AB}{}^{1b}$ (Hz)[a,b]

${}^nJ_{AB}$	molecule	$({}^nJ_{AB}{}^{1b})_{CHF}$	exptl ${}^nJ_{AB}$
${}^1J_{HF}$	HF	191.5	+530[c]
${}^1J_{HO}$	H_2O	−11.0	±79[d]
${}^1J_{HN}$	HNC	0.7	
${}^1J_{HC}$	CH_4	1.4	+125.0[e]
	HCN	−3.7 (−3.8)	+275,[f] 269[g]
	C_2H_2	−3.7 (−3.8)	+248.7[h]
	C_2H_4	0.1	+156.2[h]
	C_2H_6	1.2	+125.0[h]
	CH_3CN	1.1	+136.1[i,j]
	CH_3NC	0.8	+145.2[k]
${}^1J_{CC}$	C_2H_2	13.7 (15.3)	+170.6[h]
	C_2H_4	−9.7	67.2[h]
	C_2H_6	0.2	−4.8[h]
	CH_3CN	−1.7	+56.5[i]
${}^1J_{CN}$	HCN	−5.2 (−6.0)	
	CH_3CN	−4.4	−17.5[j]
	HNC	−0.5	
	CH_3NC (double bond)	−1.2	−8.9,[l] −9.1[m]
	CH_3NC (single bond)	0.4	−10.7[k]
${}^2J_{HH}$	H_2O	3.4	+7.2[n]
	CH_4	1.1	−12.4[o]
	C_2H_4	1.4	2.3[h]
	C_2H_6	1.0	
	CH_3CN	1.0	
	CH_3NC	1.0	
${}^2J_{CH}$	C_2H_2	6.6 (6.8)	49.7[h]
	C_2H_4	−1.6	−2.4[h]
	C_2H_6	0.2	−4.8[h]
	CH_3CN	−0.2	−9.8,[g] −10.0[j]
	HNC	4.8	
${}^2J_{NH}$	HCN	−4.6 (−4.8)	8.7[f]
	CH_3NC	−0.0	3.3[k,l]
${}^2J_{CC}$	CH_3NC	−0.9	
${}^2J_{CN}$	CH_3CN	0.4	3.0[j]
${}^3J_{HH}$	C_2H_2	2.6 (2.9)	9.8[h]
	C_2H_4 (trans)	0.5	19.1[h]
	C_2H_4 (cis)	−0.2	11.5[h]
	C_2H_6 (gauche)	0.2	8.0[p]
	C_2H_6 (trans)	1.0	
${}^3J_{NH}$	CH_3CN	−0.2	
${}^3J_{CH}$	CH_3NC	0.2	

[a] Values of the orbital term obtained by the coupled Hartree–Fock method using eq 3 in the 6-31G basis set. Values for HCN and C_2H_2 in parentheses were obtained with the $(10s^56p^3/5s^3)$ basis set. [b] The nuclei involved are ${}^1H$, ${}^{13}C$, ${}^{15}N$, ${}^{17}O$, and ${}^{19}F$. [c] J. S. Muenter and W. Lemperer, *J. Chem. Phys.*, **52**, 6033 (1970). [d] A. E. Florin and M. Alei, *ibid.*, **47**, 4268 (1967). [e] N. Muller and D. E. Pritchard, *ibid.*, **31**, 768 (1959). [f] G. Binsch and J. D. Roberts, *J. Phys. Chem.*, **72**, 4310 (1968). [g] G. Olah and T. E. Kiovsky, *J. Am. Chem. Soc.*, **90**, 4666 (1968). [h] R. M. Lynden-Bell and N. Sheppard, *Proc. R. Soc. London, Ser. A*, **269**, 385 (1962); D. M. Graham and C. E. Holloway, *Can J. Chem.*, **41**, 2114 (1963). [i] G. A. Gray, Ph.D. Dissertation, University of California, Davis, Sept 1967. [j] W. McFarlane, *Mol. Phys.*, **10**, 603 (1966). [k] W. McFarlane, *J. Chem. Soc. A*, 1660 (1967). [l] N. J. Koole, D. Knol, and M. J. A. DeBie, *J. Magn. Reson.* **21**, 499 (1976). [m] I. Morishima, A. Mizuno, and T. Yonezawa, *Chem. Commun.*, 1321 (1970). [n] J. R. Holmes, D. Kivelson, and W. C. Drinkard, *J. Chem. Phys.*, **37**, 150 (1962). [o] R. A. Bernheim and J. Lavery, *ibid.*, **42**, 1464 (1965). [p] The measured value is an average over the rotamers.

Table II. Comparison of the Present Results for $(J_{AB}{}^{1b})_{CHF}$ with Previous Semiempirical Values (Hz)

molecule	atom pair	present results	semiempirical results (A-E)				
			A[a]	B[b]	C[c]	D[d]	E[e]
ethane	CC	0.2	−1.87	−2.9	0.3	−1.1	−2.3[e]
ethylene	CC	−9.7	−11.34	−18.6	−3.76	−6.4	
acetylene	CC	13.7 (15.3)	12.5	23.6	4.13	0.0	
acetonitrile	CN	−4.4	−1.02				−7.9[f]

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term appears to be well described in the 6-31G basis. On the other hand, use of the minimal STO-3G basis gave very different results. Another test of the bases used here is to compare the present results with those of ref 11 for CH_4, HF, and H_2O, where very large basis sets were used. For ${}^1J_{HF}{}^{1b}$ the present value, 191.5 Hz, agrees well with the value of 182.8 Hz in a (11s7p/6s) uncontracted set. For water, our values of ${}^1J_{OH}{}^{1b} = -11.0$ and ${}^2J_{HH} = 3.4$ Hz are close to the −10.7 and 4.5 Hz of ref 11. Finally, for methane the present ${}^1J_{CH}{}^{1b} = 1.4$ and ${}^2J_{HH}{}^{1b} = 1.1$ Hz compare well with their 1.7 and 1.4 Hz for a $(1s^56p^3/5s^3)$ contracted basis.

Table II contains the present ab initio coupled Hartree-Fock results ${}^1J_{CC}{}^{1b}$ and ${}^1J_{CN}{}^{1b}$ along with several semiempirical values. All of the latter have the correct signs for ethylene, acetylene, and acetonitrile, although there are some cases of large errors in magnitude. Only method C yields the correct sign for ${}^1J_{CC}$ of ethane; however, the ab initio value, 0.2 Hz, is so small that a negative value might be obtained using a much larger basis set.

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Triplet [2 + 2] Cycloadditions. Spin-Inversion Control of Stereoselectivity

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Abstract: Spin-inversion mechanisms in triplet $[_\pi2_s + {}_\pi2_s]$ complexes fall into three classes. These differ in their stereochemical results: (a) bis pyramidalization (BP) which leads to 2s + 2s product; (b) intramolecular disrotation (ID) which leads to 2s + 2a product; (c) bis intramolecular disrotation (BID) which leads to 2a + 2a product. The polarity (i.e., the donor-acceptor relationship) and the triplet excitation energies of the olefins will determine the relative efficiency of these mechanisms; when the olefin pair is nonpolar (i.e., both olefins are electron donors or electron acceptors) 2s + 2s is the main product. As polarity increases, 2s + 2a becomes the major product. Further increase of polarity results again in 2s + 2s cycloaddition. On the other hand, decreasing the triplet excitation energies of the olefins at constant polarity will increase 2s + 2s production. The efficiency of ID and BP is larger in short intermolecular distances and hence anti regiochemistry is expected. Photochemical data (e.g., cycloaddition of olefins to cyclohexenones, type A rearrangement, and the di-π-methane rearrangement) are discussed in the light of these predictions.

I. Introduction

The organic chemistry of molecules in their triplet state is considered to be exclusively a chemistry of diradicals.[1] It was argued that, since product formation is prohibited by the spin conservation principle, the reaction must involve an intermediate diradical which inverts a spin in a subsequent slow step yielding singlet product.[1a]

Though useful for understanding the loss of stereochemical information often encountered in triplet reactions, several other features, such as formation of highly strained trans-fused four-membered rings and head-to-tail regiochemistry,[2] re-

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