where basis function p is taken to be centered on atom A and U_{pp} and γ_{AB} are the diagonal atomic "core" matrix element and the two-center Coulomb integral defined in ref 34. The other elements are given as

$$H_{\mathrm{pq}}{}^{\mathrm{r}} = 0$$

$$H_{\mathrm{pq}}{}^{\mathrm{i}} = -\frac{eh}{2mc}\boldsymbol{\beta}\cdot\int \chi_{\mathrm{p}}{}^{0}(\mathbf{r}_{\mathrm{q}} \times \boldsymbol{\nabla})\chi_{\mathrm{q}}{}^{0}\,\mathrm{d}\tau \tag{A.3}$$

where p ≠ q, but both are centered on the same atom, and

$$\begin{aligned} H_{\mathrm{pq}}{}^{\mathrm{r}} &= \cos\left(\frac{e}{2\hbar c}\mathbf{B}\cdot\mathbf{R}_{\mathrm{q}} \times \mathbf{R}_{\mathrm{p}}\right)\frac{1}{2}(\beta_{\mathrm{p}}{}^{0} + \beta_{\mathrm{q}}{}^{0})S_{\mathrm{pq}}{}^{0} \\ H_{\mathrm{pq}}{}^{\mathrm{i}} &= \sin\left(\frac{e}{2\hbar c}\mathbf{B}\cdot\mathbf{R}_{\mathrm{q}} \times \mathbf{R}_{\mathrm{p}}\right)\frac{1}{2}(\beta_{\mathrm{p}}{}^{0} + \beta_{\mathrm{q}}{}^{0})S_{\mathrm{pq}}{}^{0} \end{aligned} \tag{A.4}$$

in the London approximation for the case where p and q refer to different atoms. In eq A.2–A.4 it has been assumed that a valence basis set of s and p Slater-type atomic orbitals is used. The elements of **G** become

$$\begin{aligned} G_{\mathrm{pp}}{}^{\mathrm{r}} &= \sum_{\mathrm{B}}^{\mathrm{atoms}} \sum_{\mathrm{q}}^{\mathrm{B}} 2R_{\mathrm{qq}}{}^{\mathrm{r}}\gamma_{\mathrm{AB}} - R_{\mathrm{pp}}{}^{\mathrm{r}}F^{0} \\ G_{\mathrm{pp}}{}^{\mathrm{i}} &= 0 \end{aligned} \tag{A.5}$$

where p is taken to be on atom A and $F^{0} = \gamma_{\mathrm{AA}}$. Also

$$\begin{aligned} G_{\mathrm{sp}_\alpha}{}^{\mathrm{r}} &= R_{\mathrm{sp}_\alpha}{}^{\mathrm{r}}(G^{1} - F^{0}) \\ G_{\mathrm{sp}_\alpha}{}^{\mathrm{i}} &= R_{\mathrm{sp}_\alpha}{}^{\mathrm{i}}\left(F^{0} - \frac{1}{3}G^{1}\right) \\ G_{\mathrm{p}_\alpha\mathrm{p}_\beta}{}^{\mathrm{r}} &= R_{\mathrm{p}_\alpha\mathrm{p}_\beta}{}^{\mathrm{r}}\left(\frac{11}{25}F^{2} - F^{0}\right) \\ G_{\mathrm{p}_\alpha\mathrm{p}_\beta}{}^{\mathrm{i}} &= \frac{1}{2}R_{\mathrm{p}_\alpha\mathrm{p}_\beta}{}^{\mathrm{i}}\left(F^{0} - \frac{1}{5}F^{2}\right) \end{aligned} \tag{A.6}$$

where s and p refer to s and p type atomic orbitals centered on the same atom and G^{1} and F^{2} are the Slater–Condon parameters given in ref 34. If p and q are centered on different atoms A and B, then

$$\begin{aligned} G_{\mathrm{pq}}{}^{\mathrm{r}} &= -R_{\mathrm{pq}}{}^{\mathrm{r}}\gamma_{\mathrm{AB}} \\ G_{\mathrm{pq}}{}^{\mathrm{i}} &= R_{\mathrm{pq}}{}^{\mathrm{i}}\gamma_{\mathrm{AB}} \end{aligned} \tag{A.7}$$

Semiempirical Magnetic Susceptibilities of Benzene Derivatives[1]

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Abstract: We applied a previously derived semiempirical theory of diamagnetic susceptibilities to a series of conjugated hydrocarbons that are composed of phenyl groups and saturated or unsaturated hydrocarbon chains. With the exception of diphenylethylene and mesitylene the agreement between theoretical and experimental values is better than 0.5%.

In a previous series of papers we developed a semiempirical theory of the diamagnetic susceptibilities of organic molecules. In the first paper[2a] we applied the theory to saturated hydrocarbons, in the second paper[2b] to oxygen containing molecules, and in the third paper[3] to polyacenes. In each of these calculations we applied the theory to all molecules of a given type for which the experimental susceptibility values are known and we expressed the susceptibilities in terms of a small number of adjustable parameters. In the present paper we extend the theory to conjugated hydrocarbon molecules which are not polyacenes; these are molecules such as toluene, styrene, biphenyl, etc. Again, we consider all molecules of this type for which the experimental diamagnetic susceptibilities are known.

We follow the same procedure as in the treatment of the polyacenes.[3] We represent the diamagnetic susceptibility of a molecule as a sum of bond contributions and of bond–bond interactions; in addition, we must also consider the π-electron susceptibility. For example, the susceptibilities χ_{benzene} and χ_{toluene} of benzene and toluene are written as

$$\begin{aligned} \chi_{\mathrm{benzene}} &= 6\chi_{\mathrm{C}} + 6\chi_{\sigma} + 6\chi_{\mathrm{CH}} - 6\chi_{\sigma,\sigma} - \\ &\qquad 12\chi_{\sigma,\mathrm{CH}} - 6\chi_{\pi,\mathrm{CH}} - 12\chi_{\sigma,\pi} + D \\ \chi_{\mathrm{toluene}} &= 7\chi_{\mathrm{C}} + 7\chi_{\sigma} + 8\chi_{\mathrm{CH}} - 8\chi_{\sigma,\sigma} - 13\chi_{\sigma,\mathrm{CH}} - \\ &\qquad 5\chi_{\pi,\mathrm{CH}} - 13\chi_{\sigma,\pi} - 3\chi_{\mathrm{CH,CH}} + K_{\mathrm{toluene}}D \end{aligned} \tag{1}$$

Here, the π-electron susceptibility is calculated by means of a method that was proposed by London[4] and it is expressed in terms of the π-electron susceptibility D of the benzene molecule. In this way we use the ratios of the London-type π-electron results between different molecules; we feel that these ratios are much more reliable than the absolute values.

We have found that the many parameters in these expressions occur in certain fixed combinations so that the molecular susceptibilities can usually be expressed in terms of a relatively small numbers of parameters. In the present case, where we consider the molecules that are listed in Table I, we can express the susceptibilities in terms of some parameters that we have introduced previously and in terms of some additional,

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[1] Work supported by the Advanced Research Projects Agency.

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Table I. Theoretical and Experimental Diamagnetic Susceptibilities of Conjugated Hydrocarbons (in Terms of -10^{-6} cgs Units)

Molecule	χ_{theor}	χ_{exptl}	χ_{theor}
Toluene	$A + Q + 1.0028D^*$	66.11^a	66.285
Ethylbenzene	$A + B + Q + 1.0028D^*$	77.2^a	77.545
Styrene	$A + B + Q + R + 0.919D$	68.2^b	68.212
Biphenyl	$2A + T + 1.868D$	103.25^c	103.371
Bibenzyl	$2A + 2B + T + 2.0056D^*$	126.8^c	127.445
Phenylbutadiene	$A + 3B + Q + 2R + S + 0 + 0.903D$	85.7^b	85.673
Stilbene	$2A + 2B + R + S + T + 1.794D$	120^b	120.176
p-Diphenylbenzene	$3A + 2T + 2.729D$	152^d	151.533
p-Xylene	$A + 2Q + 1.0114D^*$	76.78^a	77.507
Mesitylene	$A + 3Q + 0.9956D^*$	$92.32^{a,f}$	88.453
Hexamethylbenzene	$A + 6Q + 1.026D^*$	122.5^d	122.171
Tetraphenylethylene	$4A + 2B + R + S' + 3T + 3.581D$	217.4^e	217.236
1,1-Diphenylethylene	$2A + 2B + C + R + S + T + 1.856D$	$118^{b,f}$	121.447
Diphenylmethane	$2A + B + T + 2.0056D^*$	115.7^c	116.185

* These values were calculated by us, assuming the Coulomb integral in toluene to be $\alpha + 0.1\beta$ for the carbon attached to the methyl group. The other values were taken from ref 5. [a] S. Broersma, *J. Chem. Phys.*, **17**, 873 (1949). [b] "International Critical Tables," Vol. VI, McGraw-Hill, New York, N. Y., 1929. [c] A. Bose, *Phil. Mag.*, **21**, 1119 (1936). [d] A. Pacault, *Bull. Soc. Chim. Fr.*, **16**, 371 (1970). [e] E. Muller, *Z. Elektrochem.*, **45**, 593 (1939). [f] These values were excluded in fitting the parameters.

new parameters. The previously introduced parameters are

$$\begin{aligned} A &= 6\chi_{\text{C}} + 6\chi_\sigma + 6\chi_{\text{CH}} - 6\chi_{\sigma,\sigma} - 12\chi_{\sigma,\text{CH}} - \\ &\qquad 6\chi_{\pi,\text{CH}} - 12\chi_{\sigma,\pi} \\ B &= \chi_{\text{C}} + 2\chi_{\text{CH}} + \chi_\sigma - \chi_{\sigma,\sigma} - 4\chi_{\sigma,\text{CH}} - \chi_{\text{CH,CH}} \qquad (2) \\ C &= -\chi_{\sigma,\sigma} + 2\chi_{\sigma,\text{CH}} - \chi_{\text{CH,CH}} \end{aligned}$$

The first of these parameters is the susceptibility of the benzene σ electrons. It may be seen from eq 1 that the benzene susceptibility is given by

$$\chi_{\text{benzene}} = A + D \qquad (3)$$

where the first term represents the σ-electron susceptibility (together with the interaction term between the σ and the π electrons) and the second term the π-electron susceptibility. The parameter B represents the addition of a CH_2 group to an alkane chain[2] and the parameter C accounts for branching in a hydrocarbon chain.[2]

In order to express the susceptibilities of the molecules of Table I we must also introduce the new parameters

$$\begin{aligned} Q &= \chi_{\text{C}} + \chi_\sigma + 2\chi_{\text{CH}} - 2\chi_{\sigma,\sigma} - \chi_{\sigma,\text{CH}} + \\ &\qquad \chi_{\pi,\text{CH}} - \chi_{\pi,\sigma} - 3\chi_{\text{CH,CH}} \\ R &= -2\chi_{\text{CH}} + 3\chi_{\sigma,\text{CH}} - 3\chi_{\pi,\text{CH}} - 3\chi_{\pi,\sigma} - 3\chi_{\text{CH,CH}} \\ S &= \chi_{\sigma,\text{CH}} + \chi_{\pi,\text{CH}} - \chi_{\pi,\sigma} - \chi_{\text{CH,CH}} \qquad (4) \\ T &= -2\chi_{\text{CH}} + \chi_\sigma - 4\chi_{\sigma,\sigma} + 4\chi_{\sigma,\text{CH}} + 2\chi_{\pi,\text{CH}} - \\ &\qquad 2\chi_{\pi,\sigma} \end{aligned}$$

It is easily verified that the parameter Q represents the difference between the σ-electron susceptibilities of toluene and benzene. The parameter R represents a double C–C bond in a hydrocarbon chain. The parameter S contains only bond–bond interactions and it should be expected that its value is much smaller than the values of the other parameters. Finally, the parameter T is associated with a σ bond between phenyl groups (such as in biphenyl). In Table I we have listed the expressions of the molecular susceptibilities in terms of the above parameters.

Calculations

Before we can determine the values of the various susceptibility parameters we must calculate the various London π-electron susceptibilities. Some of the values that we need have been calculated already by Pullman and Pullman[5] but the others had to be evaluated by us. In Table I we have used an asterisk to denote the values that we calculated; the other numbers were taken from the work by Pullman. In our calculations we have to assume a value for the Coulomb integral for those carbon atoms in the benzene ring that are attached to a methyl or an alkyl group; we took this value as $\alpha + 0.1\beta$.

Some of the parameters in Table I were introduced in previous work and we decided to make use of the values that we derived previously. In our work on the alkane molecules[2a] we found that

$$B = 11.260 \qquad C = 0.570 \qquad (5)$$

and in our work on the polyacenes[3] we found that

$$A = 43.8286 \qquad D = 11.3003 \qquad (6)$$

If we substitute the above values into the expressions of Table I we find that we have four adjustable parameters Q, R, S, and T for describing the susceptibilities of the 14 molecules. We determined the best values of the parameters by means of the least-squares method. It turned out that the susceptibility values of the molecules mesitylene and 1,1-diphenylethylene could not be accurately represented so we excluded these values in determining the parameter values. By using the least-squares method for the remaining 12 molecules we found that

$$\begin{aligned} Q &= 11.12469 \\ R &= -7.79428 \\ S &= 1.73365 \\ T &= -5.26061 \end{aligned}$$

By substituting these values, together with the values of

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(5) B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie, Paris, 1952, p 545.

eq 5 and 6, we obtain the numbers in the last column of Table I.

It may be seen that the agreement between the experimental and the theoretical susceptibilities is quite satisfactory except for the molecules mesitylene and 1,1-diphenylethylene which we excluded from the parameter fitting. Still, for these two molecules the difference between the experimental and theoretical susceptibilities is less than 5%, which is within the possible experimental error.

Theoretical Study of the Fluorine–Fluorine Nuclear Spin Coupling Constants. I. The Importance of Orbital and Spin Dipolar Terms

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Abstract: The indirect F–F coupling constants of various fluorine-containing compounds are studied theoretically. All the contributions to the F–F couplings are examined by using INDO-MO's and the sum-over-states perturbation method. For F–F couplings, the orbital (OB) and spin dipolar (SD) terms are very important and sometimes make decisive contributions over the Fermi contact (FC) term. By the inclusion of the OB and SD terms, the experimental signs of geminal F–F couplings and trans F–F couplings for fluoro olefins are reproduced. Both the OB and SD terms become small in magnitude for F–F couplings separated by more than four bonds and the FC term becomes significant. Surprisingly large long-range couplings originate from the FC term through the transitions of the F–F antibonding σ orbitals to the corresponding bonding orbitals, for the s-cis conformations of FC=CC=CF (a) and FCCCF (b). These large long-range couplings are named as "fragment couplings" through the quantum chemical considerations.

The theory of the indirect nuclear spin–spin coupling constant is based on the original work of Ramsey.[1] For light nuclei, the indirect nuclear spin–spin coupling constant originates from three electron-nucleus interaction hamiltonians; they are the orbital (OB), spin dipolar (SD), and Fermi contact (FC) terms. The OB term represents the interaction between the nuclear spin and the induced dipole moment due to the orbital motion of electrons, and the SD and FC terms represent respectively the dipole–dipole and Fermi contact interactions between nuclear spin and electron spin.

Among these mechanisms, the FC term was found to be predominant for the proton couplings originally by Ramsey and Purcell,[1] and most of the latter theoretical studies[2–4] based only on this term have been successful in the explanation of proton couplings. However, uncritical extension of this treatment to the couplings between other nuclear pairs is very dangerous.[2,3a,5,6] Indeed, in a previous study,[7] we found extraordinarily large contributions of the OB and SD terms to the F–F coupling constants of some fluorine-containing compounds.

Many experimental values of F–F coupling constants have now accumulated, and interestingly the observed trends of the F–F coupling constants are far different from those seen in the H–H coupling constants. In order to explain these tendencies, Sederholm[8] advanced the concept of the "through space" couplings, although many criticisms[9] have thrown on this concept. Our view is that part of the experimental complexity of the F–F coupling constants may be due to the importance of the OB and SD term in addition to the FC term.

At present, extensive theoretical studies of the F–F coupling constants seem to be very limited, compared with those of the proton couplings, and moreover it seems that no satisfactory rule has yet been developed to provide a unified explanation of the experimental trends of the F–F couplings. Thus, in this series of papers, we will present a systematic theoretical study of the F–F coupling constants. All the mechanisms are considered by using the INDO-MO's[10] and the sum-over-states perturbation theory.

In the first paper, we examine the relative importance of the FC, SD, and OB mechanisms for the F–F couplings in various chemical situations. They are the geminal, vicinal, and long-range couplings in various fluoroalkanes, -alkenes, and -cycloalkanes. Then, we advance to explain the observed trends of the F–F couplings from the above point of view. They are the signs of the coupling constants, the substituent effects, through space couplings, near-zero couplings, etc.

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