An Empirical Evaluation of the Individual Elements in the Nuclear Diamagnetic Shielding Tensor by the Atom Dipole Method

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Abstract: Following earlier work on evaluating the average diamagnetic susceptibility and electric multipole moments by the atom dipole method we now extend the atom dipole model to evaluate the individual elements in the nuclear diamagnetic shielding tensor. The successful evaluation of the diamagnetic shielding tensor elements provides the link between the experimental determination of the spin-rotation constants and the total magnetic shielding tensor elements (or the shielding anisotropy).

It is now well known that the elements in the nuclear magnetic shielding tensor, σ_{xx}, can be separated into two dominant terms which are the diamagnetic ($\sigma_{xx}{}^{\mathrm{d}}$) and the paramagnetic ($\sigma_{xx}{}^{\mathrm{p}}$) terms.[1]

$$\sigma_{xx} = \sigma_{xx}{}^{\mathrm{d}} + \sigma_{xx}{}^{\mathrm{p}}$$

$$\sigma_{xx}{}^{\mathrm{d}} = \frac{e^2}{2mc^2}\left\langle 0\left|\sum_i \frac{(y_i{}^2 + z_i{}^2)}{r_i{}^3}\right|0\right\rangle$$

$$\sigma_{xx}{}^{\mathrm{p}} = \frac{e^2}{2mc^2}\sum_{k>0}\left[\frac{\left\langle 0\left|\sum_i L_{xi}/r_i{}^3\right|k\right\rangle\left\langle k\left|\sum_i L_{xi}\right|0\right\rangle + \mathrm{cc}}{\epsilon_0 - \epsilon_k}\right] \tag{1}$$

e and m are the electron charge and mass, c is the speed of light, $\langle 0|$ indicates the ground-state wave function, the sum over i is over all electrons (the nuclear origin is appropriate for all properties), the sum over k is over all excited electronic states, cc indicates complex conjugate, and ϵ_0 indicates the energy of the 0th or ground state of the system.

$\sigma_{xx}{}^{\mathrm{p}}$ is intimately related to the spin-rotation interaction constant, M_{xx}, which is defined through a $\mathcal{H} = -(1/\hbar^2)\mathbf{I}\cdot\mathbf{M}\cdot\mathbf{J}$ interaction in a rotating molecule ($\mathbf{I}$ and $\mathbf{J}$ are the nuclear and rotational angular momenta, respectively); M_{xx} also contains a sum over excited electronic states. M_{xx} and $\sigma_{xx}{}^{\mathrm{p}}$ are directly related by[1,2]

$$\sigma_{xx}{}^{\mathrm{p}} = \frac{e^2}{2mc^2}\left[(M_{xx}I_{xx}c/e\hbar\mu_0 g_{\mathrm{I}}) - \sum_n{}' \frac{Z_n}{r_n{}^3}(y_n{}^2 + z_n{}^2)\right] \tag{2}$$

μ_0 is the nuclear magneton, g_{I} is the nuclear g value, I_{xx} is the moment of inertia, Z_n is the atomic number of the nth nucleus, r_n and y_n are the coordinates from the nucleus in question to the nth nucleus, and the prime on the summation over n indicates that the shielded nucleus is omitted. Thus if the molecular structure is known, $\sigma_{xx}{}^{\mathrm{p}}$ can be obtained from M_{xx} or *vice versa*.

The major share of experimental data involving the parameters in eq 1 and 2 is through the average shielding obtained primarily from chemical shifts in liquids.

$$\sigma_{\mathrm{av}} = \sigma_{\mathrm{av}}{}^{\mathrm{d}} + \sigma_{\mathrm{av}}{}^{\mathrm{p}} = \frac{1}{3}(\sigma_{xx}{}^{\mathrm{d}} + \sigma_{xx}{}^{\mathrm{d}} + \sigma_{zz}{}^{\mathrm{d}}) + \frac{1}{3}(\sigma_{xx}{}^{\mathrm{p}} + \sigma_{yy}{}^{\mathrm{p}} + \sigma_{zz}{}^{\mathrm{p}}) = \frac{e^2}{3mc^2}\left\langle 0\left|\sum_i \frac{1}{r_i}\right|0\right\rangle + \frac{e}{2\hbar mc\mu_0 g_{\mathrm{I}}}(M_{xx}I_{xx} + M_{yy}I_{yy} + M_{zz}I_{zz}) - \frac{e^2}{3mc^2}\sum_n{}' \frac{Z_n}{r_n} \tag{3}$$

Flygare and Goodisman[3] have proposed a reliable method of evaluating $\sigma_{\mathrm{av}}{}^{\mathrm{d}}$ which has been helpful in evaluating σ_{av} from the spin-rotation constants, the molecular structure, and eq 3. This equation is[3,4]

$$\sigma_{\mathrm{av}}{}^{\mathrm{d}} \cong \sigma_{\mathrm{av}}{}^{\mathrm{d}}(\text{free atom}) + \frac{e^2}{3mc^2}\sum_n{}' \frac{Z_n}{r_n} \tag{4}$$

Values of $\sigma_{\mathrm{av}}{}^{\mathrm{d}}$(free atom) are well known. The error involved in using eq 4 for the diamagnetic shielding was shown, by using the Hellman–Feynman theorem, to be equal to the ratio of the bonding energy of an atom to the total electronic energy of the atom.[3] Equation 4 has also been used along with eq 3 to evaluate the previously unknown signs of the spin-rotation constants in a number of linear and spherical top molecules.[3,5] In spite of the success of using eq 4 to evaluate $\sigma_{\mathrm{av}}{}^{\mathrm{d}}$ for a nucleus in a molecule, attempts by Flygare and Goodisman[3] to extend the method to evaluate the individual elements in the diamagnetic shielding tensor, $\sigma_{xx}{}^{\mathrm{d}}$, were not as successful. The equation analogous to eq 4 to evaluate the individual elements in the diamagnetic shielding tensor is

$$\sigma_{xx}{}^{\mathrm{d}} \cong \sigma^{\mathrm{d}}(\text{free atom}) + \frac{e^2}{2mc^2}\sum_n{}' \frac{Z_n}{r_n{}^3}(y_n{}^2 + z_n{}^2) \tag{5}$$

Because of the many methods now available[6,7] to measure the individual elements (or anisotropies) in the

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[1] N. F. Ramsey, *Phys. Rev.*, 78, 699 (1950).

[2] W. H. Flygare, *J. Chem. Phys.*, 41, 793 (1964).

[3] W. H. Flygare and J. Goodisman, *ibid.*, 49, 3122 (1968).

[4] See also Figure 1 in N. F. Ramsey, *Amer. Sci.*, 49, 509 (1961).

[5] H. L. Tigelaar and W. H. Flygare, *Chem. Phys. Lett.*, 7, 254 (1970); see also a discussion of other attempts at estimating $\sigma_{\mathrm{av}}{}^{\mathrm{d}}$ in this reference.

[6] For example, see a new pulsed nmr method in M. Mehring, R. G. Griffin, and J. S. Waugh, *J. Chem. Phys.*, 55, 746 (1971), and references cited therein which also describe the orientated molecule methods.

[7] The molecular Zeeman effect can also be used to directly measure the magnetic shielding anistropy; see ref 4; W. Hüttner and W. H. Flygare, *ibid.*, 47, 4137 (1967); and F. H. DeLeeuw and A. Dynamus, *Chem. Phys. Lett.*, 15, 288 (1970).

total shielding, it is desirable to develop an easy method to evaluate $\sigma_{xx}{}^{\mathrm{d}}$.

In this paper we propose an evaluation of $\sigma_{xx}{}^{\mathrm{d}}$ by using an atom dipole model.[8] This atom dipole model has been used quite successfully to evaluate molecular electric dipole and quadrupole moments and the molecular diamagnetic susceptibilities. This model assumes that bonded atoms retain a major share of their free atom electron densities and that the change in density associated with bonding can be represented by localized empirical atom dipoles. Comparison of our calculated values of $\sigma_{zz}{}^{\mathrm{d}}$ (with this model) with the known values is quite good. We will also show from this viewpoint why Flygare and Goodisman were successful in the use of eq 4 and not as successful in the use of eq 5 for the calculation of diamagnetic shielding.

Theory

Equation 3 for the average diamagnetic shielding may be rewritten in the following way

$$\sigma_{\mathrm{av}}{}^{\mathrm{d}}(A) = \frac{e^2}{3mc^2}\left\langle 0\left|\sum_j \frac{1}{r_j}\right|0\right\rangle = \frac{e^2}{3mc^2}\left[\left\langle 0\left|\sum_k^{Z_A} r_k{}^{-1}\right|0\right\rangle + \sum_n{}'\left\langle 0\left|\sum_{i_n}^{Z_n} r_{i_n}{}^{-1}\right|0\right\rangle\right] \qquad (6)$$

where we have merely partitioned the sum of all j electrons into the k electrons "on" nucleus A and the i_n electrons "on" the other n nuclei. If the bonded atom retains a major share of the free atom electron distribution we have

$$\frac{e^2}{3mc^2}\left\langle 0\left|\sum_k^{Z_A} r_k{}^{-1}\right|0\right\rangle = \sigma_{\mathrm{atom}}{}^{\mathrm{d}}(A) \qquad (7)$$

Accurate values for the diamagnetic shielding of many free atoms have been calculated by Malli and Froese.[9]

To evaluate the second term in eq 6, we use the coordinate transformation discussed in detail by Gierke, Tigelaar, and Flygare (GTF).[8]

$$\mathbf{r}_{i_n} = \mathbf{r}_n + \boldsymbol{\varrho}_{i_n} \qquad (8)$$

The second term in eq 6 now becomes

$$\sum_n{}'\left\langle 0\left|\sum_{i_n}^{Z_n}(r_{i_n})^{-1}\right|0\right\rangle = \sum_n{}'\left\langle 0\left|\sum_{i_n}^{Z_n}{}'(|\mathbf{r}_n + \boldsymbol{\varrho}_{i_n}|)^{-1}\right|0\right\rangle$$

This equation can be expanded in a Taylor series about the nth nucleus. Retaining the first three terms of the expansion gives

$$\sum_n{}'\langle 0|(r_{i_n})^{-1}|0\rangle = \sum_n{}'\frac{Z_n}{r_n} - \sum_n{}'(r_n)^{-3}(\mathbf{r}_n\cdot\langle\boldsymbol{\varrho}\rangle_n) + \sum_n{}'\left[-\frac{\langle\rho^2\rangle_n}{2r_n{}^3} + \left(\frac{3}{2r_n{}^5}\right)(x_n{}^3\langle x^2\rangle_n + y_n{}^2\langle y^2\rangle_n + z_n{}^2\langle z^2\rangle_n) + (3/r_n{}^5)(x_ny_n\langle xy\rangle_n + x_nz_n\langle xz\rangle_n + y_nz_n\langle yz\rangle_n)\right] \qquad (9)$$

where we have used the Born–Oppenheimer approximation, we have assumed the molecule is a rigid rotor, and we have defined

$$\langle\boldsymbol{\varrho}\rangle_n \equiv \left\langle 0\left|\sum_{i_n}^{Z_n}\boldsymbol{\varrho}_{i_n}\right|0\right\rangle$$
$$\langle\rho^2\rangle_n \equiv \left\langle 0\left|\sum_{i_n}^{Z_n}\rho_{i_n}{}^2\right|0\right\rangle \qquad (10)$$

with similar definitions for $\langle x\rangle_n$ and $\langle x^2\rangle_n$. Values for the quantities defined in eq 10 (*i.e.*, the atom dipoles and atom electronic second moments) for several atoms in different bonding situations are given in GTF.[8] To a good approximation[8] the charge distribution on the nth atom will be nearly spherical so that

$$\langle x^2\rangle_n \cong \langle y^2\rangle_n \cong \langle z^2\rangle_n \cong \langle\rho^2/3\rangle_n \qquad (11)$$

and

$$\langle xy\rangle_n \cong \langle xz\rangle_n \cong \langle yz\rangle_n \cong 0 \qquad (12)$$

Substituting the results of eq 7, 9, 11, and 12 into eq 6, we obtain the average diamagnetic shielding in terms of the atom dipoles.

$$\sigma_{\mathrm{av}}{}^{\mathrm{d}}(A) = \underbrace{\sigma_{\mathrm{atom}}{}^{\mathrm{d}}(A)}_{\mathrm{I}} + \underbrace{\frac{e^2}{3mc^2}\sum_n{}'\frac{Z_n}{r_n}}_{\mathrm{II}} - \underbrace{\frac{e^2}{3mc^2}\sum_n{}'\frac{\mathbf{r}_n\cdot\langle\boldsymbol{\varrho}\rangle_n}{r_n{}^3}}_{\mathrm{III}} \qquad (13)$$

The result for the individual diagonal tensor elements is

$$\sigma_{xx}{}^{\mathrm{d}}(A) = \underbrace{\sigma_{\mathrm{atom}}{}^{\mathrm{d}}(A)}_{\mathrm{I}} + \underbrace{\frac{e^2}{2mc^2}\sum_n{}'\frac{Z_n}{r_n{}^3}(y_n{}^2 + z_n{}^2)}_{\mathrm{II}} + \underbrace{\frac{e^2}{2mc^2}\sum_n{}'[(2r_n{}^{-3})(y_n\langle y\rangle_n + z_n\langle z\rangle_n) - (3r_n{}^{-5})(y_n{}^2 + z_n{}^2)(\mathbf{r}_n\cdot\langle\boldsymbol{\varrho}\rangle_n)]}_{\mathrm{III}} + \underbrace{e^2/2mc^2\sum_n{}'[2(r_n{}^{-3})\langle\rho^2/3\rangle_n - 3(r_n{}^{-5})(y_n{}^2 + z_n{}^2)\langle\rho^2/3\rangle_n]}_{\mathrm{IV}} \qquad (14)$$

The diamagnetic shielding tensors for a large number of molecules have been calculated with eq 13 and 14, and some representative results are listed in the first column of Table I. The necessary $\langle\rho\rangle_n$ and $\langle\rho^2\rangle$ parameters are from ref 8. The known calculated (*ab initio*) results are listed in the second column of Table I.

Discussion

In eq 13 and 14 there are four types of contributions to the diamagnetic shielding tensor. The first two terms are identical with those used by Flygare and Goodisman,[3] the free atom contribution (I) and the contribution of the electronic point charges centered at the other n nuclei II. The third term, III, arises if the point charges are not centered on the nth nucleus but are displaced by a distance $\langle\rho\rangle_n$. This term (the dipole term) is in general quite small (on the order of a few

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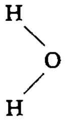
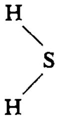
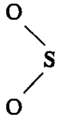
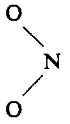
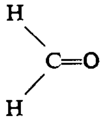
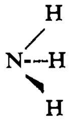
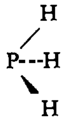
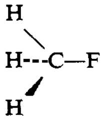
(8) T. D. Gierke, H. L. Tigelaar, and W. H. Flygare, *J. Amer. Chem. Soc.*, 94, 330 (1972); from this point to be referred to as GTF.

(9) G. Malli and C. Froese, *Int. J. Quantum Chem., Suppl.*, 1, 95 (1967).

Table I. Magnetic Shielding in Several Molecules[a]

Molecule y ↑ └→ x	Atom	$\left.\begin{matrix}\sigma_{av}^d\\ \sigma_{xx}^d\\ \sigma_{yy}^d\\ \sigma_{zz}^d\end{matrix}\right\}^b$	$\left.\begin{matrix}\sigma_{av}^d\\ \sigma_{xx}^d\\ \sigma_{yy}^d\\ \sigma_{zz}^d\end{matrix}\right\}^c$
H—H	H	31.9	32.0[n]
		34.7	
		30.4	
		30.4	
F—F	F	530.5	529.5[d]
		480.5	
		555.4	
		555.4	
H—F	H	109.2	108.9[d]
		54.3	
		136.6	
		136.6	
	F	484.4	481.6[d]
		479.8	
		486.7	
		486.7	
H—Cl	H	142.6	142.3[e]
		54.4	45.3
		186.7	190.1
		186.7	190.1
	Cl	1151.7	1150.3[e]
		1146.0	1148.6
		1154.6	1152.2
		1154.6	1152.2
N≡N	N	384.0	380.9,[f] 384.5[d]
		348.9	338.4
		401.6	407.1
		401.6	407.1
C≡O	C	326.1	326.4[g]
		280.4	271.2
		349.0	354.1
		349.0	354.1
	O	443.7	444.5[g]
		418.7	410.5
		456.2	461.5
		456.2	461.5
	H	103.4	102.8[h]
		102.7	102.8
		78.4	75.3
		129.1	130.2
	O	420.9	415.6[i]
		420.3	415.5
		416.7	415.0
		425.7	416.3
	H	136.1	136.1[e]
		120.5	124.0
		109.3	109.0
		178.6	187.0
	S	1066.7	1065.0[e]
		1064.5	1063.4
		1063.9	1064.7
		1071.9	1066.7
	O	530.0	531.2[j]
		553.9	553.0
		452.4	451.3
		583.6	588.6
	S	1152.8	1151.8[j]
		1163.0	1160.5
		1100.9	1095.7
		1194.4	1199.4
	O	482.7	483.8[k]
		505.8	508.5
		423.1	423.8
		513.0	519.2
	N	448.5	446.3[k]
		472.9	471.2
		379.3	369.8
		493.5	497.8
	H	106.4	111.5[g]
		87.3	92.6
		94.0	94.7
		137.8	147.1
	C	338.0	338.5[g]
		294.2	288.5
		355.7	355.3
		364.2	370.6
	O	452.0	452.0[g]
		418.3	415.8
		467.6	465.2
		470.0	475.1
	H	95.4	95.0,[l] 96.0[h]
		110.6	110.7, 112.1[h]
		60.4	87.7 56.8
		115.1	119.1
	N	360.1	355.0[l]
		364.5	354.5
		358.0	355.2
		358.0	355.2
	H	127.2	127.8[e]
		136.6	135.7
		80.4	79.2
		164.8	168.0
	P	983.8	981.0[e]
		984.7	979.8
		983.3	981.4
		983.3	981.4
	H	121.5	121.9[h]
		112.3	114.1
		96.8	93.7
		155.3	158.0
	F	526.4	527.0[m]
		489.9	494.0
		544.6	543.0
		544.6	543.0

[a] Units are ppm. The first column gives the results of this paper compared with known results in the second column. [b] Calculated with eq 13 and 14; the known structures and the parameters are in ref 8. [c] Theoretical *ab initio* calculations. [d] C. W. Kern and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 260 (1962). [e] S. Rothenberg, R. H. Young, and H. F. Schaefer, *J. Amer. Chem. Soc.*, **92**, 3243 (1970). [f] E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Chem. Phys.*, **54**, 4269 (1971). [g] D. B. Neumann and J. W. Moscowitz, *ibid.*, **50**, 2216 (1969). [h] G. P. Arrighini, M. Maestro, and R. Moccia, *ibid.*, **52**, 6111 (1970). [i] G. P. Arrighini and C. Guidotti, *Chem. Phys. Lett.*, **6**, 436 (1970). [j] S. Rothenberg and H. F. Schaefer, *J. Chem. Phys.*, **53**, 3015 (1970). [k] S. Rothenberg and H. F. Schaefer, *Mol. Phys.*, **21**, 317 (1971). [l] J. F. Harrison, *J. Chem. Phys.*, **47**, 2990 (1967). [m] C. W. Kern and M. Karplus, unpublished, 1964; see S. C. Wofsey, J. S. Muenter, and W. Klemperer, *ibid.*, **55**, 2014 (1971). [n] W. Kolos and L. Wolniewicz, *ibid.*, **41**, 3674 (1964).

Table II. Magnetic Shielding Anisotropies (ppm) in Several Molecules

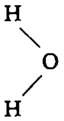
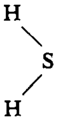
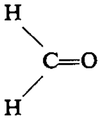
Molecule	Atom	Shielding anisotropy, calcd	I[a]	II[b]	III[c]
CH_3F	F	$2\sigma_{xx}^d - \sigma_{yy}^d - \sigma_{zz}^d$	−109.0	−147.0	−98.0
	H	$2\sigma_{xx}^d - \sigma_{yy}^d - \sigma_{zz}^d$	−27.5	−4.0	−23.5
H_2O	H	$\sigma_{zz}^d - \sigma_{xx}^d - \sigma_{yy}^d$	−52.0	−17.7	−47.9
H_2CO	H	$\sigma_{zz}^d - \sigma_{xx}^d - \sigma_{yy}^d$	−43.5	−17.7	−40.2
H_2S	H	$\sigma_{zz}^d - \sigma_{xx}^d - \sigma_{yy}^d$	−51.2	−17.7	−46.1

[a] Calcd with eq 13 and 14. [b] Calcd from ref 3 or eq 14 with term IV omitted. [c] Theoretical *ab initio* calculations. References and axes are in Table I.

parts per million) relative to the preceding terms. The quadrupole term (IV) which appears only in σ_{xx}^d in eq 14 arises because the electronic charge distribution on the nth nucleus is not a point charge but is spatially extended. Ignoring this term may result in significant errors in σ_{xx}^d. This explains why eq 4 gives accurate estimates for the average diamagnetic shielding (no quadrupole term), but eq 5 gives only fair estimates for the individual tensor elements (quadrupole term is nonzero). This is particularly evident if we consider

Table III. Magnetic Shielding Computed with Eq 13 and 14 and the Spin-Rotation Constants[a]

Molecule y ↑ └→ x	Atom	σ_{xx}^{d} σ_{yy}^{d} σ_{zz}^{d} σ_{av}^{d}	σ_{xx}^{p} σ_{yy}^{p} σ_{zz}^{p} σ_{av}^{p}	σ_{xx} σ_{yy} σ_{zz} σ_{av} [b]	σ_{xx}(exptl) σ_{yy} σ_{zz} σ_{av}
H—H	^{1}H	35.7	0.0[y]	34.7	
		30.4	−8.4	22.0	
		30.4	−8.4	22.0	
		32.9	−5.6	26.3	26.6[c]
H—F	^{1}H	54	0[d]	54	
		137	−119	18	
		137	−119	18	
		109	−80	29	29.2[c]
	^{19}F	480	0[d]	480	
		487	−94	393	
		487	−94	393	
		484	−63	421	415[c]
H—Cl	^{1}H	54	0[e]	54	
		187	−166	21	
		187	−166	21	
		143	−111	32	31.5[c]
	^{35}Cl	1146	0[e]	1146	
		1155	−300	854	
		1155	−300	854	
		1152	−200	952	
H—Br	^{1}H	54	0[f]	54	
		350	−321	29	
		350	−321	29	
		251	−214	37	35[h]
	^{79}Br	3124	0[g]	3124	
		3132	−768	2364	
		3132	−768	2364	
		3129	−512	2617	
H—I	^{1}H	56	0[f]	56	
		465	−424	41	
		465	−424	41	
		329	−283	46	44[h]
	^{127}I	5503	0[g]	5503	
		5511	−1496	4015	
		5511	−1496	4015	
		5508	−998	4510	
F—F	^{19}F	480	0[i]	480	
		555	−1124	−569	
		555	−1124	−569	
		530	−750	−219	−210[h]
H—C≡N	^{14}N	348	0[j]	348	
		398	−627	−229	
		398	−627	−229	
		381	−418	−37	
	^{1}H	48	0[f]	49	
		121	−109	12	
		121	−109	12	
		97	−71	26	28[k]
Cl—C≡N	^{35}Cl	1152	0[j]	1152	
		1223	−930	293	
		1223	−930	293	
		1199	−620	579	
	^{14}N	350	0[j]	350	
		475	−1110	−635	
		475	−1110	−635	
		434	−740	−306	
Cl—F	^{19}F	488	0[l]	488	
		609	197	806	
		609	197	806	
		569	132	700	667[l]
	^{35}Cl	1149	0	1149	
		1218	−2458[j]	−1240	
		1218	−2458	−1240	
		1195	−1639	−444	−408[l]
N≡N	^{15}N	349	0[m]	349	
		402	−729	−327	
		402	−729	−327	
		384	−486	−102	−101[h]

Molecule y ↑ └→ x	Atom	σ_{xx}^{d} σ_{yy}^{d} σ_{zz}^{d} σ_{av}^{d}	σ_{xx}^{p} σ_{yy}^{p} σ_{zz}^{p} σ_{av}^{p}	σ_{xx} σ_{yy} σ_{zz} σ_{av} [b]	σ_{xx}(exptl) σ_{yy} σ_{zz} σ_{av}
C≡O	^{13}C	280	0[n]	280	
		349	−484	−135	
		349	−484	−135	
		326	−323	+3	
	^{17}O	419	0[o]	419	
		456	−690	−234	
		456	−690	−234	
		444	−460	−16	
O=C=S	^{13}C	299	0[p]	299	
		483	−579	−96	
		483	−579	−96	
		421	−386	35	
	^{17}O	421	0[j]	421	
		538	−978	−440	
		538	−978	−440	
		499	−652	−153	
	^{33}S	1060	0[j]	1060	
		1141	−810	331	
		1141	−810	331	
		1114	−540	574	
H—C≡C—H	^{1}H	50	0[f]	50	
		120	−99	21	
		120	−99	21	
		97	−66	31	29.4[h]
	^{1}H	103	−71[q]	31	
		78	−37	41	
		129	−108	21	
		103	−72	31	30.2[h]
	^{1}H	120	−88[r]	32	
		109	−71	39	
		179	−154	24	
		136	−104	32	30.8[h]
	^{1}H	87	−69[s]	18	
		94	−70	24	
		137	−120	17	
		106	−86	20	21.3[u]
	^{17}O	418	−1600[t]	−1182	
		468	−870	−402	
		470	−10	460	
		452	−827	−375	
Ph—F	^{19}F	519	−64[v]	455	
		649	−373	276	
		679	−415	264	
		616	−284	332	333[h]
CH$_3$F	^{1}H	112	−85[c]	27	
		97	−98	29	
		155			
		121	−91	30	26.9[c]
	^{19}F	490	−63[c]	426	423.5[c]
		545	−52	493	489.5
		544	−52	493	489.5
		526	−56	471	467.5
NH$_3$	^{1}H	111	−88[w]	23	
		60	−16	44	
		115	−104	11	
		95	−67	28	30.8[c]
	^{14}N	364	−117[w]	247	
		358	−78	280	
		358	−78	280	
		360	−91	269	266[h]
PH$_3$ ↑ y └→ z	^{1}H	80	−88[x]	35	
		165			
		136	−108	28	
		127	−98	29	28.3[c]
	^{31}P	983	−370[x]	612	
		983	−370	612	
		985	−421	564	
		984	−387	597	

Footnotes to Table III:

[a] Units are ppm. The last column gives the experimental results. The references in the second column under σ^p are for the spin rotation constants. [b] Not vibrationally corrected. [c] See footnote *m* of Table I and references cited therein. [d] R. Weiss, *Phys. Rev.*, **131**, 659 (1963). [e] E. W. Kaiser, *J. Chem. Phys.*, **53**, 1686 (1970). [f] N. F. Ramsey, ref 4. [g] F. C. DeLucia, P. Helminger, and W. Gordy, *Phys. Rev.*, *A*, **3**, 1849 (1971). [h] A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967. [i] M. R. Baker, C. H. Anderson, and N. F. Ramsey, *Phys. Rev.*, *A*, **133**, 1533 (1964). [j] C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1955. [k] W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.*, **28**, 601 (1958). [l] W. N. Lipsccmb, *Advan. Magn. Resonance*, **2**, 137 (1966). [m] W. H. Flygare, ref 3. [n] I. Ozier, L. M. Crapo, and N. F. Ramsey, *J. Chem. Phys.*, **49**, 2315 (1968). [o] W. H. Flygare and V. W. Weiss, *ibid.*, **45**, 2785 (1966). [p] F. H. DeLeeuw and A. Dymanus, *Chem. Phys. Lett.*, **7**, 288 (1970). [q] J. Verhoeven and A. Dymanus, *J. Chem. Phys.*, **52**, 3222 (1970). [r] F. C. DeLucia and J. W. Cederberg, *J. Mol. Spectrosc.*, **40**, 52 (1971). [s] T. Shigenari, *J. Phys. Soc. Jap.*, **23**, 404 (1967); S. G. Kukolich and D. J. Ruben, *J. Mol. Spectrosc.*, **38**, 130 (1971); K. D. Tucker, G. R. Tomasevich, and P. Thaddeus, *Astrophys. J.*, 169, 429 (1971). [t] W. H. Flygare and J. T. Lowe, *J. Chem. Phys.*, **43**, 3654 (1965). [u] B. L. Shapiro, R. M. Kopchik, and S. J. Ebersole, *ibid.*, 39, 3154 (1963). [v] A. S. Dubin and S. I. Chan, *ibid.*, **46**, 1749 (1967). [w] S. G. Kukolich and S. C. Wofsy, *ibid.*, **52**, 5477 (1970). [x] P. O. Davies, R. M. Neuman, S. C. Wofsy, and W. Klemperer, *ibid.*, **55**, 3564 (1971). [y] N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

some diamagnetic shielding anisotropies in Table II, which were chosen so that the point charge and dipole contributions would be small. It is evident that the results in Tables I and II obtained by the method of atom dipoles are in good agreement with those obtained by the *ab initio* calculations.

Assuming that reliable estimates for the diamagnetic shielding tensor can be obtained by using eq 13 and 14, we will now evaluate the total shielding tensor in several molecules in which the spin-rotation constants are known. Using experimental spin-rotation constants, the paramagnetic shieldings of several molecules were calculated (eq 2) and combined with the diamagnetic shielding calculated using eq 13 and 14 to give the total shielding tensor (the atom dipoles used are from ref 8). The results are given in Table III along with a comparison with the experimental values when available. The agreement is generally quite good. In most examples of Table III, errors in the experimental spin-rotation constants are the limiting factors in the calculation of the total shielding tensor. Of course, since the individual elements of the total shielding tensor are obtained, we can also evaluate the nuclear magnetic shielding anisotropy, $\Delta\sigma$. A few results obtained in this manner are compared with experiment in Table IV. The axis systems of the experimental shielding anisotropies generally coincide with the symmetry axes of the molecules. The shielding anisotropy observed is the difference between the average of the two tensor elements perpendicular to axis of highest symmetry and the tensor element parallel to this symmetry axis.

Of course, the above methods may be reversed. If the elements of the shielding tensor are known, eq 13 and 14 may be used to evaluate the spin-rotation interaction tensor. Kukolich and Nelson[10] have recently obtained the shielding anisotropy of fluorine in CH_2F_2 by high resolution molecular Zeeman measurement.[11] Their results were $2\sigma_{cc} - \sigma_{aa} - \sigma_{bb} = -335 \pm 15$ and $\sigma_{aa} - \sigma_{bb} = 9 \pm 13$, where *a*, *b*, and *c* are the principle inertial axes. These may be combined with the average shielding of $\sigma_{av} = 361$[12] and the diamagnetic shielding tensor calculated with eq 14 ($\sigma_{aa}{}^d = 511$, $\sigma_{bb}{}^d = 576$, $\sigma_{cc}{}^d = 595$) to yield the spin-rotation constants of $M_{aa} = -30.2 \pm 3$, $M_{bb} = -6.5 \pm 1$, and $M_{cc} = -11.2 \pm 1$ kHz. Errors are due chiefly to errors in the measured shielding anisotropies. We can also evaluate the spin-rotation interaction of a given rotational level.[1,2]

Table IV. Calculated and Experimental Shielding Anisotropies, $\Delta\sigma = (\sigma_\perp)_{av} - \sigma_\parallel$

Molecule	Atom	Calcd	Exptl	Method
CH_3F	^{19}F	+66	$+61 \pm 15^a$	sr[b]
			$+66 \pm 8^c$	cl[d]
			$+159.2 \pm 0.6^e$	lc[f]
	$^1H^g$	+0.4	$+0.6 \pm 0.5^e$	lc
			-1.9 ± 10^a	sr
OCS	^{13}C	−395	-372 ± 42^h	Other
PH_3	^{31}P	−49	$\lvert 41\rvert^i$	Other
Ph—F	^{19}F	−185	-115^j	lc
			-40^k	lc
HCN	^{13}C	$-326^{l,n}$	-285 ± 20^m	lc
	^1H	−37	$+4 \pm 1^m$	lc
H—C≡C—H	^1H	−29	-8.1 ± 2.2^o	lc
S═C═S	^{13}C	−458	-425 ± 16^p	Other
			-438 ± 44^q	Other

[a] See footnote *m* of Table I. [b] Indicates value is derived from experimental spin-rotation interaction and *ab initio* calculation of diamagnetic shielding. [c] E. Hunt and H. Meyer, *J. Chem. Phys.*, **41**, 353 (1964). [d] Indicates clathrate experiment. [e] R. Bernheim and T. R. Krugh, *J. Amer. Chem. Soc.*, **89**, 6784 (1967). [f] Indicates liquid crystal experiment. [g] The anisotropy measured here is actually $^1/_2(\sigma_{xx} + \sigma_{yy}) - \sigma_{zz}$ where *z* is the C_{3v} axis. [h] F. H. DeLeeuw and A. Dynamus, *Chem. Phys. Lett.*, **7**, 288 (1970). [i] C. Deverall, *Mol. Phys.*, **18**, 319 (1970), gives a positive sign for $\Delta\sigma$, but K. T. Gillen, *J. Chem. Phys.*, **56**, 1573 (1972), indicates a negative sign is appropriate. [j] C. S. Yannoni, B. P. Dailey, and G. P. Ceasar, *J. Chem. Phys.*, **54**, 4023 (1971). [k] J. Nehring and A. Saupe, *ibid.*, **52**, 1307 (1970). [l] Calculated from measured chemical shifts: $\sigma_{HCN} = 75.4 + \sigma_{CS_2}{}^m$, $\sigma_{CO} = 11.5 + \sigma_{CS_2}{}^n$, and $\sigma_{CO} = +5$; see discussion (footnote *n*, Table III). [m] F. Millet and B. P. Dailey, *J. Chem. Phys.*, **54**, 5343 (1971). [n] R. Ettinger, P. Blume, A. Patterson, Jr., and P. C. Lauterbur, *ibid.*, **33**, 1597 (1960). [o] G. Englert, A. Saupe, and J. P. Weber, *Z. Naturforsch. A*, **23**, 152 (1968). [p] A. Pines, W.-K. Rhim, and J. S. Waugh, *J. Chem. Phys.*, **54**, 5438 (1971). [q] H. W. Spiess, D. Schweitzer, U. Häeberlen and K. H. Hauser, unpublished results.

$$C(J_{K_-K_+}) = -\sum_g M_{gg}\langle J_g{}^2\rangle/J(J+1) \tag{15}$$

We obtain $C(3_{01}) - C(2_{12}) = -4.8 \pm 1.5$ kHz. The experimental result is -3.2 ± 0.5.[10b] Moreover, in the case of spherical tops and linear molecules the spin-rotation tensor reduces to a scalar. Therefore if the average shielding and rotational constant are known, the spin-rotation constant and the elements of the paramagnetic shielding tensor may be predicted. This process was used for the calculated value of $\Delta\sigma_{^{13}C}$ of HCN and CS_2 in Table IV, where the diamagnetic shielding tensor elements of ^{13}C calculated with eq 14 are for HCN and CS_2 respectively $\sigma_\perp{}^d = 345$, $\sigma_\parallel{}^d = 287$, and $\sigma_\perp{}^d = 531$, $\sigma_\parallel{}^d = 301$.

One final point should be mentioned with respect to the diamagnetic shielding tensor. The expansion de-

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(10) (a) S. G. Kukolich and A. C. Nelson, *J. Chem., Phys.*, **56**, 4446 (1972); (b) private communication from same authors.

(11) For a discussion of the Hamiltonian and energy levels, see W. Hüttner and W. H. Flygare, *J. Chem. Phys.*, **47**, 4137 (1967).

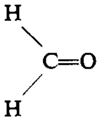
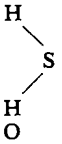
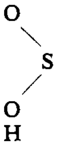
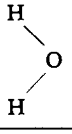
(12) J. W. Emsley and L. Phillips, *Progr. Nucl. Magn. Resonance Spectrosc.*, 7, 1 (1971).

veloped in this paper may also be applied to the off-diagonal elements which are defined in eq 16. Expanding eq 16 as before with the assumptions in eq 11 and 12 gives eq 17, where the shielded nucleus is assumed to be nearly spherical and does not contribute to the shielding. A few results are given in Table V.

$$\sigma_{xy}{}^{\mathrm{d}} = -\frac{e^2}{2mc^2}\left\langle 0\left|\sum_i \frac{x_i y_i}{r_i{}^3}\right|0\right\rangle \tag{16}$$

$$\sigma_{xy}{}^{\mathrm{d}} = \underbrace{-\frac{e^2}{2mc^2}\sum_n{}' \frac{Z_n x_n y_n}{r_n{}^3}}_{\mathrm{II}} - \underbrace{\frac{e^2}{2mc^2}\left[\sum_n{}' \frac{x_n\langle y\rangle_n + y_n\langle x\rangle_n}{r_n{}^3} - 3\sum_n \frac{x_n y_n[r_n\cdot\langle \varrho\rangle_n]}{r_n{}^5}\right]}_{\mathrm{III}} + \underbrace{\frac{e^2}{2mc^2}\sum_n \frac{3x_n y_n\langle x^2\rangle_n}{r_n{}^5}}_{\mathrm{IV}} \tag{17}$$

Table V. Off-Diagonal Elements of the Diamagnetic Shielding Tensor

Molecule $\overset{y}{\uparrow}\!\rightarrow x$		Calcd, eq 17	*Ab initio*	Ref
	$\sigma_{yz}{}^{\mathrm{d}}$(H)	+48	+43	*a*
	$\sigma_{xy}{}^{\mathrm{d}}$(H)	+61	+65	*b*
	$\sigma_{xy}{}^{\mathrm{d}}$(O)	+52	+51	*c*
	$\sigma_{xy}{}^{\mathrm{d}}$(H)	+33	+38	*d*

[a] Footnote *g*, Table I. [b] Footnote *e*, Table I. [c] Footnote *j*, Table I. [d] Footnote *h*, Table I.

The significance of these results is that by using eq 14 and 17 all of the tensor elements of the diamagnetic shielding tensor may be evaluated in any convenient axis system. The principle axis system (the set of axes which diagonalize the diamagnetic shielding tensor) can then be easily found, and knowing the diamagnetic shielding tensor in the principle axis system makes it easier to visualize the molecular charge distribution of a molecule as measured by the diamagnetic shielding.

Conclusion

We have extended the atom dipole model proposed in GTF[8] to the evaluation of the diamagnetic shielding tensor, and the method was used to correlate the experimental results of the spin-rotation interaction, the average shieldings, and the shielding anisotropy of nuclei in molecules. In this respect it was shown that there may be significant diamagnetic contributions to the shielding tensor which previously have been ignored, specifically terms III and IV of eq 14.

The methods developed here may, in theory, be used to evaluate other properties with r^{-n} radial dependence. In particular, we have examined the electric field, electric field gradient, and electrostatic potential energy defined in eq 18, 19, and 20, respectively,[13]

$$E_x(A) = |e|\left[\sum_n{}' \frac{X_n}{r_n{}^3} - \left\langle 0\left|\sum_i (X_i/r_i{}^3)\right|0\right\rangle\right] \tag{18}$$

$$q_{xx}(A) = |e|\left[\sum_n{}' \frac{Z_n(2X_n{}^2 - Y_n{}^2 - Z_n{}^2)}{r_n{}^5} - \left\langle 0\left|\sum_i \frac{2X_i{}^2 - Y_i{}^2 - Z_i{}^2}{r_i{}^5}\right|0\right\rangle\right] \tag{19}$$

$$V = \frac{e^2}{2}\sum_A\sum_n{}'\left\{\frac{Z_A Z_n}{r_{An}} - Z_A\left\langle 0\left|\sum_j r_{Aj}{}^{-1}\right|0\right\rangle - Z_n\left\langle 0\left|\sum_i r_{ni}{}^{-1}\right|0\right\rangle + \left\langle 0\left|\sum_i\sum_j r_{ij}{}^{-1}\right|0\right\rangle\right\} + \frac{e^2}{2}\sum_A\left\{\left\langle 0\left|\sum_i\sum_{i\neq i} r_{ii}{}^{-1}\right|0\right\rangle - 2\left\langle 0\left|\sum_i r_{Ai}{}^{-1}\right|0\right\rangle\right\} \tag{20}$$

where the sums are over all *A* nuclei in the molecules, all *n* nuclei excluding *A*, all *j* electrons "on" the *n*th nucleus, and all *i* electrons "on" the *A*th nucleus. The factors of $^1/_2$, where they appear, are to compensate for counting a pair twice.

When the electronic terms of these equations are expanded as in eq 6–14, four basic terms will appear which we have previously called the free atom term, nuclear point charge term, dipole term, and quadrupole term. In the expressions for the electric field and field gradient note that the nuclear terms will be of opposite sign and cancel. Furthermore the free atom term will be more sensitive to the bonding environment relative to the free atom term in the diamagnetic shielding. This problem arises because the electric field and field gradient are a measure of the *distortion* of the electronic charge whereas the diamagnetic shielding measures the *spatial extent* of electronic charge. The relative size of these effects has been discussed in GTF. The spatial extent of a bonded atom's electron distribution has been shown to be quite insensitive to the bonding environment.[8] This is only approximately true of the *distortion* in charge. Therefore we expect the electric field and field gradient to be extremely sensitive to the value assigned to the free atom term, which suggests that the atom dipole method will not be as effective in these cases.

The expansion of the electrostatic potential energy in terms of atom dipoles is more complex. The final result is given by

$$V = \frac{e^2}{2}\sum_A\sum_n{}'\left[\frac{\langle \varrho\rangle_A\cdot\langle \varrho\rangle_n}{r_{An}} - \frac{3(\mathbf{r}_{An}\cdot\langle \varrho\rangle_A)(\mathbf{r}_{An}\cdot\langle \rho\rangle_n)}{r_{An}{}^5}\right] + \frac{e^2}{2}\sum_A V_{\mathrm{atom}}(A) \tag{21}$$

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(13) For definitions, see W. H. Flygare, *Rec. Chem. Progr.*, 28, 63 (1967).

where

$$V_{\text{atom}}(A) \equiv \left\langle 0 \left| \sum_{i}\sum_{i' \neq i} r_{ii'}{}^{-1} \right| 0 \right\rangle - 2\langle 0|r_{Ai}{}^{1}-|0\rangle \tag{22}$$

The first term in eq 2 is just the potential energy arising from the dipole–dipole interaction of the atom dipoles. If the free atom terms do not change with respect to internal rotation and kinetic energy effects are neglected, we should be able to evaluate the barrier to internal rotation by calculating the change in the dipole–dipole interaction using the parameters in GTF for the atom dipoles. For ethane we found the dipole–dipole contribution to be $\Delta V_{\text{dip}} = 392$ cal/mol compared to the experimental barrier of 2928 ± 25 cal/mol.[14] This result indicates that barriers to internal rotation may arise from subtle changes in V_{atom}.[15] The magnitude of these changes can be estimated in ethane where $e^2 \cdot V_{\text{atom}}(\text{H}) = (4mc^2/e^2N)\sigma_{\text{av}}{}^{\text{d}}(\text{H})$. We found that a 0.07% change in $V_{\text{atom}}(\text{H})$ would account for the observed barrier. Subtle changes in the calculated electron distribution of ethane have been noted by Jorgensen and Allen.[16]

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

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(14) J. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 962 (1968).

(15) The origin of the barrier may, however, be due to kinetic energy effects or structural changes, both of which were ignored.

(16) W. L. Jorgensen and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 567 (1971).

Physical Evidence for Complex Formation between Olefins and *trans*-Glyoxal ^3A_u

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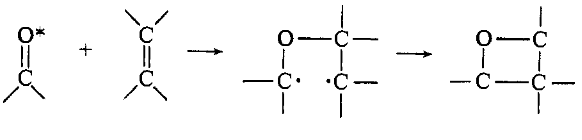
Abstract: The gas-phase quenching of *trans*-glyoxal ^3A_u (lowest energy n,π* triplet state) by the olefins ethylene, butene-1, and isobutylene at 300°K has been examined by a time-resolved phosphorescence technique using tunable dye laser excitation. Significant deviations from Stern–Volmer quenching behavior are observed. The results may be explained by assuming that a collision complex is reversibly formed during olefin–glyoxal ^3A_u collisions. A number of rate constants concerning the formation and subsequent reactions of the complex may be derived. The nature of the collision complex is discussed in terms of current observations on the photochemistry of n,π* triplet states.

The triplet n,π* excited electronic states of carbonyl-containing compounds undergo a large number of important photochemical and photophysical processes.[2a] The rich photochemistry of these molecules is presumably a reflection of (1) the relatively long (~milliseconds) lifetimes of n,π* triplets and (2) the nucleophilic and electrophilic behavior of the C atom and O atom, respectively, or the radical-like behavior of n,π* electronic configurations. Of particular interest has been the photochemical reaction of n,π* triplets with olefins to produce oxetanes when electronic energy transfer to the olefin is energetically unfavorable.[2b] Stereochemical studies have suggested that oxetane formation is preceded by biradical formation.[3]



Recently Kochevar and Wagner[4] have presented chemical evidence that the biradical formation itself may be preceded by the rate-limiting formation of a charge-transfer complex. In this paper we report physical evidence for the formation of a relatively stable collision complex between *trans*-glyoxal ^3A_u (n,π* triplet) and several olefins. It is possible that this collision complex is either the charge-transfer complex or the biradical.

There is a considerable amount of photophysical and photochemical information available concerning glyoxal (HCOCOH). Spectroscopic studies have shown the presence of two low-lying electronic states of *trans*-glyoxal: a ^1A_u (n,π*) state lying 21,978 cm^{-1} above the ^1A_g ground state and a ^3A_u(n,π*) state 19,198 cm^{-1} above the ground state.[5] Although theory predicts additional singlet and triplet B_g states in the same energy region,[6] recent calculations[7] supported by photoelectron spectroscopy[8] indicate that these states may be much higher in energy than the A_u states. Glyoxal may also exist in the cis form. The $^1B_1$ excited state of the cis form lies 350 cm^{-1} *below* the ^1A_u state of the trans form.[9] However, this state does not correlate with the ^1A_u and may thus be thought of as a separate molecular species. Also, the $^3B_1$ state of *cis*-glyoxal is

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(1) Alfred P. Sloan Foundation Fellow.

(2) (a) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); (b) D. R. Arnold, R. L. Hinman, and A. H. Blick, *Tetrahedron Lett.*, 1425 (1964).

(3) See, for instance, J. Saltiel, K. R. Neubergen, and M. Wrighton, *J. Amer. Chem. Soc.*, 91, 3658 (1969), or N. J. Turro and P. A. Wriede, *ibid.*, **92**, 320 (1970).

(4) I. H. Kochevar and P. J. Wagner, *ibid.*, **92**, 5742 (1970).

(5) (a) W. Goetz, A. J. McHugh, and D. A. Ramsay, *Can. J. Phys.*, **48**, 1 (1970); (b) J. Paldus and D. A. Ramsay, *ibid.*, **45**, 1389 (1967).

(6) (a) H. L. McMurry, *J. Chem. Phys.*, **9**, 231 (1941); (b) *ibid.*, **9**, 241 (1941).

(7) J. R. Swenson and R. Hoffman, *Helv. Chim. Acta*, **53**, 2331 (1970).

(8) D. W. Turner, A. D. Baker, C. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley, New York, N. Y., 1970.

(9) G. N. Currie and D. A. Ramsay, *Can. J. Phys.*, **49**, 317 (1971).