

Theory of Magnetic Susceptibilities and NMR Chemical Shifts in Terms of Localized Quantities. 3. Application to Hydrocarbons and Other Organic Molecules

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Abstract: A method for the ab initio calculation of magnetic susceptibilities (χ) and chemical shifts (σ) based on individual gauge for localized orbitals (IGLO) is applied to a wealth of organic molecules. Calculations with a double- ζ basis (DZ) are possible for molecules as large as Me_4Si or benzene and lead to acceptable results. For somewhat larger basis sets with polarization functions, good agreement with experiment is found. The anisotropies of χ and σ are also obtained satisfactorily. Both χ and σ are directly obtained as sums of contributions of the various localized orbitals that have a direct physical meaning. These contributions are to some extent transferable, which allows the construction of an ab initio increment system.

1. Introduction

In paper 1 of this series¹ a coupled Hartree-Fock theory for diamagnetic susceptibilities (χ) and chemical shifts (σ) in terms of localized MO's and individual gauge origins for different MO's has been derived. The theory has been recapitulated in a more compact form and been applied to the molecules H_2 , $(\text{H}_2)_2$, LiH, BH, BH_3 , B_2H_6 , HF, F_2 , H_2O , NH_3 , CH_4 , CH_3^+ , and H_2CO in paper 2 of this series.² We now want to report our calculations on organic molecules, mainly hydrocarbons, which are too large for calculations of magnetic properties by traditional methods but where our method yields rather reliable results.

In addition to the straightforward calculation of chemical shifts, we have also studied the theoretical basis for the various increment systems proposed in the literature, and we present a purely ab initio increment system for hydrocarbons.

2. Theory

Since the theory has been outlined previously,^{1,2} we need only summarize it very briefly. The basic idea is to solve the coupled Hartree-Fock equations (written here in a form that is valid in a localized representation as well as in terms of canonical Hartree-Fock orbitals) with a different gauge origin for the different orbital labels k . In (2.1) and (2.2) the φ_{k0} are the (localized)

$$(1 - P_0)F_0\varphi_{k0} = 0 \quad (2.1)$$

$$[(1 - P_0)F_1 - P_1F_0]\varphi_{k0} + (1 - P_0)F_0\varphi_{k1} = 0 \quad (2.2)$$

"unperturbed" Hartree-Fock orbitals, F_0 is the Fock operator, and P_0 the projection operator onto the space spanned by the (doubly) occupied φ_{k0} . The φ_{k1} is the first-order perturbation correction to the orbitals, P_1 is defined as

$$P_1 = \sum_{k=1}^n [|\varphi_{k1}\rangle\langle\varphi_{k0}| - |\varphi_{k0}\rangle\langle\varphi_{k1}|] \quad (2.3)$$

(where n is the number of doubly occupied orbitals), and F_1 is given as

$$F_1 = h_1 - \sum_{k=1}^n K_1^k \quad (2.4)$$

$$h_1 = \frac{e}{2mci}(\vec{B} \times \vec{r}) \cdot \vec{p} \quad (2.5)$$

where h_1 is the first-order perturbation operator corresponding to the external magnetic field (with \vec{B} the magnetic field strength,

\vec{r} , and \vec{p} position and momentum vectors of the electron, respectively) and where K_1^k is an exchange operator. If we further introduce the perturbation h_1' due to the magnetic moment $\vec{\mu}$ of the nucleus at position \vec{p} , and the second-order perturbation operators h_2 and h_2'

$$h_1' = \frac{e}{2mci} \frac{\vec{\mu} \times (\vec{r} - \vec{p}) \cdot \vec{p}}{|\vec{r} - \vec{p}|^3} \quad (2.6)$$

$$h_2 = \frac{e^2}{8mc^2}(\vec{B} \times \vec{r})^2 \quad (2.7)$$

$$h_2' = \frac{e^2}{2mc^2} \frac{(\vec{B} \times \vec{r})(\vec{\mu} \times [\vec{r} - \vec{p}])}{|\vec{r} - \vec{p}|^3} \quad (2.8)$$

the magnetic susceptibilities and chemical shifts are given as

$$\chi = \sum_{k=1}^n \langle \varphi_{k0} | h_2 | \varphi_{k0} \rangle - \sum_{k=1}^n \langle \varphi_{k0} | h_1' | \varphi_{k1} \rangle \quad (2.9)$$

$$\sigma = 2 \left(\sum_{k=0}^n \langle \varphi_{k0} | h_2' | \varphi_{k0} \rangle - \langle \varphi_{k0} | h_1' | \varphi_{k1} \rangle \right) \quad (2.10)$$

The direct solution of (2.1, 2.2) is rather hopeless except for very small molecules. The reason is that one has to choose a "gauge origin" within the molecule, from which all position vectors are measured. The exact results for χ and σ are independent of this gauge origin; however, approximate solutions of (2.1, 2.2) lead to results that are very sensitive to the choice of the gauge origin and also to the size of the basis. Both χ and σ are, as seen from (2.9, 2.10), small differences of two large quantities, the first of which (containing the φ_{k0} only but not the φ_{k1}), called the "diamagnetic term", is easily calculated rather accurately, while the second, called the "paramagnetic term", is usually much in error except for nearly spherically symmetrical systems, where the paramagnetic term is rather small and the diamagnetic one dominates.

Our approach consists in introducing new orbitals ψ_k related to the $\varphi_k = \varphi_{k0} + \varphi_{k1} + \dots$ via

$$\varphi_k = e^{i\Lambda_k} \psi_k \quad (2.11)$$

$$\Lambda_k = \frac{e}{2c\hbar}(\vec{R}_k \times \vec{B}) \cdot \vec{r} \quad (2.12)$$

and to choose the point \vec{R}_k as the center of gravity of the localized orbital φ_{k0} . (Other choices \vec{R}_k and even of the functional form of Λ_k are possible). We find that

$$\psi_{k0} = \varphi_{k0} \quad (2.13)$$

(1) W. Kutzelnigg, *Isr. J. Chem.*, **19**, 193 (1980).

(2) M. Schindler, and W. Kutzelnigg, *J. Chem. Phys.*, **76**, 1919 (1982).

Table 1. Susceptibilities (Absolute Values in ppm-cgs, i.e., in Units of $4\pi \times 10^{-12} \text{ J T}^{-2} \text{ mol}^{-1}$)

molecule	IGLO			CHF DZ	IGLO INC.	experimental	
	DZ	I	II			gas	liquid
CH ₄	20.8	19.5	19.4	24.8	17.0	18.7 ^a	17.4 ^b
C ₂ H ₆	35.7	31.1	30.9	62.0	30.3	27.4 ^c	26.8 ^b
C ₃ H ₈	50.4			128.3	43.5	40.5 ^c	38.6 ^b
n-C ₄ H ₁₀					56.6		
iso-C ₄ H ₁₀					56.9		51.7 ^e
n-C ₅ H ₁₂					69.7		63.1 ^e
iso-C ₅ H ₁₂					70.3		
neo-C ₅ H ₁₂	79.6				70.4	63.1 ^c	63.0 ^b
adamantane					119.5		94.3 ^e
c-C ₃ H ₆	48.5					39.9 ^c	39.2 ^b
bicyclo[1.1.0]butane	60.6						
bicyclo[1.1.1]pentane	64.5						
tetrahydrene	60.0						
Si(CH ₃) ₄	95.2						74.9 ^d
C ₂ H ₄	24.1	22.7	22.6	41.8	23.2	19.7 ^a	18.8 ^b
propene	39.1	35.7			36.3	31.5 ^c	30.7 ^b
cis-2-butene	54.3				49.4		42.6 ^e
trans-2-butene	53.9				49.4		42.6 ^e
trans-1,3-butadiene	44.1	40.6			42.2		32.1 ^b
1,3,5-hexatriene	65.7						35.6 ^e
2-methyl-2-butene					62.5		53.2 ^e
2,3-dimethyl-2-butene					75.6		
2,3-dimethyl-1,3-butadiene					68.4		57.2 ^e
2,5-dimethyl-2,4-hexadiene					94.6		78.7 ^e
H ₂ CO	10.49	9.73	9.63	34.77		6.85 ^f	
CH ₃ CHO	26.85	24.56					22.70 ^e
CH ₃ OH	26.91	23.72					21.40 ^e
CH ₃ CH ₂ OH	42.15						33.72 ^e
HCOOH	25.40						19.90 ^e
cyclopropenone	31.56						30.7 ^h
oxirane	39.47						43.1 ^c
furane	53.9						44.8 ⁱ
CH ₃ F	23.40	20.30				17.8 ^b	
CH ₃ CH ₂ F	38.91	33.56					33 ± 4 ¹
CH ₂ F ₂	27.52	24.29					24.0 ^g
CHF ₃	33.33	30.32					30 ^g
CF ₄	39.95	36.52					36 ^g
OCF ₂	30.83	28.58					26.4 ^g
1,1-difluoroethene	37.83	34.34					28.6 ^g
trans-1,2-difluoroethene	35.42	31.31					
cis-1,2-difluoroethene	35.94	31.92					27.2 ^g
allene	35.52		31.89			25.3 ± 0.8 ^b	
ketene	31.14		28.99				
diazomethane		25.66	25.40				

^a J. G. Oldenzel, N. J. Trappeniers, *Physica A (Amsterdam)*, 82A, 565, 581 (1976). ^b C. Barter, R. G. Meisenheimer, and D. P. Stevenson, *J. Chem. Phys.*, 64, 1312 (1960). ^c J. W. Emsley, J. Feeney, L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 1, Pergamon Press, New York, 1967. ^d F. H. A. Rummens and F. M. Mourits, *Can. J. Chem.*, 55, 3021 (1977). ^e W. Haberditzl in "Theory and Applications of Molecular Diamagnetism", L. N. Mulay, E. A. Bourdaux, Ed., Wiley, New York, 1976. ^f S. G. Kukolich, *J. Chem. Phys.*, 54, 8 (1971). ^g B. R. Appleman, B. P. Dailey, *Adv. Magn. Reson.*, 7, 231 (1974). ^h E. Hamer, D. H. Sutter, *Z. Naturforsch. A*, 31a, 265 (1976). ⁱ Landolt-Börnstein, "Zahlenwerte und Funktionen", K. H. Hellwege, Ed., New Series 11/6, Springer, Berlin, 1974.

and get for ψ_{k1} the system of equations

$$[(1 - P_0)\bar{F}_{k1} - \bar{P}_{k1}F_0]\psi_{k0} + (1 - P_0)F_0\psi_{k1} = 0 \quad (2.14)$$

which replaces (2.2). For the definition of \bar{F}_{k1} and \bar{P}_{k1} as well as for the final expressions for σ and χ , we must refer to previous publications.^{1,2} The essential difference of (2.14) as compared to (2.2) is that in (2.14) the position vector \bar{r} of an electron in the orbital ψ_k is measured with respect to the center of gravity of φ_{k0} . Since the localized orbitals are not too different from spherical shape, the local paramagnetic contributions are rather small, and errors in them affect the final results only slightly.

One no longer obtains χ and σ as small difference of two large numbers, and one no longer needs very large basis sets in order to get an acceptable accuracy.

There is, of course, a price to pay since new contributions arise that were not present in the theory with a common gauge origin.

These new terms have been called^{1,2} "resonance" and "exchange" corrections. The former cause no problem at all, while the latter—which are usually very small—are calculated in an approximate way (eq 50 in paper 1 of this series) that is based on

the replacement of an operator product by a matrix product. These corrections show up explicitly only in the final expressions (eq 32 and 33 in paper 2) for the susceptibilities χ , not in those (eq 37 in paper 2) for the chemical shifts σ . These are only affected indirectly by the above-mentioned corrections, since the equations (eq 29 in paper 2) from which the perturbing orbitals ψ_{k1} are determined contain exchange and resonance terms. So formally σ is obtained as a sum of a (local) diamagnetic term σ_d and a local paramagnetic term σ_p , while χ contains also contributions χ_r and χ_x , which are usually quite small.

Both χ and σ are, of course, tensor quantities, and we are interested in the isotropic part as well as in the anisotropy $\Delta\chi$ or $\Delta\sigma$.

In order to avoid confusion, we should point out that our method has nothing to do with GIAO's (gauge invariant atomic orbitals)³

(3) This term has been coined by Hameka;⁴ other authors have criticized it; Pople⁵ has for example suggested to call them rather "gauge dependent atomic orbitals".

(4) H. F. Hameka, *Mol. Phys.*, 1, 203 (1958).

(5) J. A. Pople, *Discuss. Faraday Soc.*, 34, 7 (1962).

Table II. ¹H NMR Shifts Relative to CH₄ (in ppm)

molecule		IGLO			CHF DZ	IGLO INC	experimental		
		DZ	I	II			gas	liquid	
CH ₄		0	0	0	0	0	0		
C ₂ H ₆		0.08	0.59	0.58	2.18	0.45	0.75 ^a		
C ₃ H ₈	CH ₃	-0.18			10.3	0.62	0.68 ^b		
	CH ₂	0.03			-23.3	0.90	1.16 ^{b,c}		
<i>n</i> -C ₄ H ₁₀	CH ₃					0.78			
	CH ₂					1.07			
<i>iso</i> -C ₄ H ₁₀	CH ₃					0.79		0.66 ^h	
	CH					1.35		1.33	
<i>n</i> -C ₅ H ₁₂	CH ₃	0.53				0.78		0.76 ⁱ	
	CH ₂	0.63				1.23		1.12	
	CH ₂	0.85				1.24		1.12	
<i>iso</i> -C ₅ H ₁₂	CH ₃					0.94			
	CH ₂					1.24			
	CH					1.52			
	2CH ₃					0.95			
C(CH ₃) ₄	0.86						0.84 ^d	0.82 ^a	
<i>c</i> -C ₃ H ₆	-0.21							0.07 ^a	
bicyclobutane	CH	2.44							1.26 ^h
	CH _{2ax}	0.08							0.32
	CH _{2eq}	1.19							1.26
bicyclo[1.1.1]pentane	CH	2.82							
	CH ₂	1.62							
tetrahydrane	4.99								
Si(CH ₃) ₄	-0.25						-0.13 ^e	-0.14 ^a	-0.23 ^h
adamantane	CH ₂					2.22			1.6 ^k
	CH					2.82			1.7
C ₂ H ₄ propene		6.12	5.26	5.23	12.58	5.33		5.18 ^a	
	CH ₃	0.83	1.13			0.79			1.59 ^e
	CH	6.75	5.64			5.97			5.60
	CH ₂ trans	6.14	4.53			4.87			4.75
	CH ₂ cis	6.17	4.90			4.85			4.83
<i>cis</i> -2-butene	CH ₃	0.76				0.90			1.47 ^k
	CH	6.53				5.28			5.32
	CH ₂	0.90				0.90			1.50 ^k
<i>trans</i> -2-butene	CH ₃	0.90				5.26			5.30
	CH	6.08				6.17			4.47 ^l
2-methylpropene	CH ₃					1.24			1.47 ⁱ
	CH					6.17			4.47 ^l
2-methyl-2-butene	CH ₃					1.11			1.40 ⁱ
	CH ₃ <i>cis</i>					1.35			1.40
	CH ₃ <i>trans</i>					1.45			1.40
	CH					5.57			5.08 ^l
2,3-dimethyl-2-butene	CH ₃					1.56			
2,3-dimethyl-1,3-butadiene	CH ₃					1.37			1.64 ^k
	CH ₂ <i>cis</i>					5.23			4.67
	CH ₂ <i>trans</i>					5.38			4.75
2,5-dimethyl-2,4-hexadiene	CH ₃ <i>cis</i>					1.35			
	CH ₃ <i>trans</i>					1.45			
	CH					5.99			
<i>trans</i> -butadiene	CH	6.11	5.91			6.07			6.14 ^e
	CH ₂ <i>trans</i>	6.18	5.14			4.75			4.93
	CH ₂ <i>cis</i>	5.96	4.93			4.88			5.03
hexatriene	CH ₂ <i>trans</i>	6.11							
	CH ₂ <i>cis</i>	6.33							
	CH <i>trans</i>	6.38							
	CH <i>cis</i>	6.59							
	CH ₂	-0.02	0.27						0.79 ^e
<i>c</i> -C ₃ H ₄	CH	9.10	7.79						6.88
<i>c</i> -C ₄ H ₆	CH ₂	1.28							2.41 ^e
	CH	7.64							5.84
benzene		8.69							7.24 ^e
<i>c</i> -C ₇ H ₈	CH _{2ax}	1.33							1.31 ^f
	CH _{2eq}	2.02							2.69 ^f
	CH _{op}	8.04							6.37
	CH _{ip}	6.23							5.96
	CH ₂ CH	7.87							5.14
<i>c</i> -C ₄ H ₄	A ^m	7.25							5.12 ^g
	B ^m	3.63							
C ₂ H ₂	3.99	2.10	2.04	21.08			1.34 ^a		1.67 ^e
allene	5.29		4.55	23.26					4.54 ^h
ketene	2.95		2.41						
CH ₂ NN			3.49						2.85 ^e
H ₂ CO	10.66	9.37	9.29				12.3 ± 2 ^j		9.3 ⁱ
CH ₃ CHO	CH ₃	1.52	1.42				1.79 ^e		2.05 ^h
	CH	10.88	8.82						9.59
CH ₃ OH	CH ₃	2.11	2.55						3.26 ^h
	OH	-4.05	-0.50						

Table II (Continued)

molecule		IGLO			CHF DZ	IGLO INC	experimental	
		DZ	I	II			gas	liquid
CH ₃ CH ₂ OH	CH ₃	0.60					1.05 ^h	
	CH ₂	2.01					3.46	
	OH	-2.47						
HCOOH	HC	9.72						
	OH	5.41						
cyclopropenone		11.45						
oxirane		1.61						2.41 ^h
furan	OCH	9.71						7.27 ^h
	CH	8.13						6.17
CH ₃ F		3.03	3.64				4.00 ^e	4.12 ^h
CH ₃ CH ₂ F	CH ₃	0.25	0.35				1.14 ^e	1.11 ^h
	CH ₂	0.99	3.75				4.23	4.23
		4.31	4.60					5.32 ^h
CH ₂ F ₂		5.51	5.45					6.12 ^h
CHF ₃		4.95	6.19					
1,1-difluoroethene		7.97						
<i>trans</i> -1,2-difluoroethene		7.19						
<i>cis</i> -1,2-difluoroethene								

^a L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1174 (1961). ^b J. B. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961). ^c R. E. Wasylshen and T. Schaefer, *Can. J. Chem.*, **52**, 3247 (1974); $\sigma(\text{CH}_3) - \sigma(\text{CH}_2) = -0.435$. ^d W. T. Raynes and M. A. Raza, *Mol. Phys.*, **17**, 157 (1969). ^e J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 2, Pergamon Press, New York, 1968. ^f H. Guenther, "NMR Spectroscopy", Wiley, New York, 1980. ^g G. Meier and A. Alzerra, *Angew. Chem.*, **85**, 1056 (1973); value for tri-*tert*-butyl-*c*-butadiene. ^h L. M. Jackmann and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, New York, 1969. ⁱ F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, 1969. ^j S. G. Kukolich, *J. Am. Chem. Soc.*, **97**, 5704 (1975); assuming $\sigma(\text{CH}_4) = 30.611$ ppm as the best experimental value, given by Raynes (W. T. Raynes, in "Nuclear Magnetic Resonance", R. K. Harris, Ed., The Chemical Society, London, 1978, Vol. 7). ^k M. Hesse, H. Meier, and B. Zeeh, "Spektroskopische Methoden in der organischen Chemie", Thieme, 1979. ^l A. Zschunke, "Kernmagnetische Resonanzspektroskopie in der organischen Chemie", Akademie Verlag, Berlin, 1971. ^m Bond Lengths for cyclobutadiene A 1.57 and 1.34 Å and B 1.46 and 1.42 Å.

that have been introduced by F. London⁶ and have since been used or analyzed by various authors;^{7-12,31-42} an efficient ab initio approach based on the use of GIAO has been formulated by Dichtfield.^{31,32} In GIAO methods the basis AO's are multiplied by individual gauge factors like in (2.11) while in the IGLO method each localized *molecular* orbital is multiplied by a gauge factor. This latter choice has the advantage that one only needs the two-electron integrals over the original MO's while in GIAO methods the integrals over the GIAO's are needed, which is much more time consuming and probably the decisive step in Dichtfield's program. Dichtfield uses the finite perturbation method; i.e., he performs one SCF calculation of the molecule with and one without the magnetic field. This is formally equivalent to the coupled Hartree-Fock method. Of the existing programs the one by Dichtfield is probably the one which is the most competitive with ours. If our program is significantly faster (we have only made some very preliminary comparisons), this is probably so because the GIAO integrals are not needed.

While there is (as just mentioned) a vast literature on GIAO's, IGLO's have, to the author's knowledge, not been used before, although a method proposed by Okninski and Sadlej⁴³ is somewhat related to ours.

3. Basis Sets, Localization, and Sign Convention

For the calculations in this paper mainly three types of basis sets have been used. DZ is a double- ζ basis set, namely a (7,3/3) Huzinaga¹³ set in the contraction (4,1,1,1;2,1/2,1). Basis I is a (95;5) Huzinaga set, contracted to triple- ζ (51111; 311/311), plus one set of polarization functions, i.e., *d* on carbon and *p* on hy-

drogen with exponents of 1.0 and 0.7, respectively. Basis II differs only in the contraction of the *p* groups (51111;2111).

We choose this notation for the basis sets in order to be consistent with paper 2,² where basis I and II were the smallest and where the largest basis was V. For the much larger molecules studied now, we had to be more modest in the choice of the basis.

The localized MO's are constructed according to the criterion of Boys,¹⁴ which was applied separately to the set of core MO's (K for first-row and K, and L for second-row atoms) and valence MO's. For multiple bonds the localization leads to banana bonds.

The sign convention for the absolute shifts $\sigma(\text{C})$ and $\sigma(\text{H})$ is such that diamagnetic (shielding) terms are positive and paramagnetic (antishielding) terms negative. The relative shifts are defined as

$$\delta(\text{X}) = \sigma(\text{CH}_4) - \sigma(\text{X})$$

i.e., $\delta(\text{X}) < 0$ means that the nucleus is more shielded than in CH₄. This is the usual sign convention for relative shifts.

Since all molecules of this study are diamagnetic, we always give the absolute value $|\chi|$, since χ should be negative.

The geometries used are, unless stated otherwise, experimental gas-phase r_0 geometries as compiled in ref 15 and 16.

4. Susceptibilities of Hydrocarbons and Other Organic Molecules

The list of molecules that we have studied (see Tables I-III) includes aliphatic hydrocarbons up to C₃H₁₂, olefins and dienes, cyclic and polycyclic hydrocarbons up to benzene, cycloheptatriene, bicyclo[1.1.1]pentane, and tetrahedrane, oxygen-containing hydrocarbons up to furan, various fluorine-substituted hydrocarbons, and the common standard Me₄Si.

We have performed IGLO calculations with a DZ basis for most molecules in the list, for some selected molecules the larger

(6) F. London, *J. Phys. Radium*, **8**, (1937).
 (7) J. A. Pople, *J. Chem. Phys.*, **37**, 53 (1962); **37**, 60 (1962).
 (8) R. McWeeny, *Mol. Phys.*, **1**, 311 (1958).
 (9) R. McWeeny, *Chem. Phys. Lett.*, **9**, 341 (1971).
 (10) H. F. Hameka, *Rev. Mod. Phys.*, **34**, 87 (1962), and references quoted therein.
 (11) P. A. Dobosh, P. D. Ellis, and Yu-Chung Chou, *J. Magn. Reson.*, **36**, 439 (1979).
 (12) A. R. Barber, P. D. Ellis, K. Seidman, and K. Schade, *J. Magn. Reson.*, **34**, 1 (1979).
 (13) S. Huzinaga, Approximate Atomic Functions. 1., University of Alberta, 1971.

(14) S. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 296, 303, 305 (1960).
 (15) M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendeman, D. A. Ramsey, F. J. Lovas, W. J. Lafferty, and A. G. Maki, *J. Phys. Chem. Ref. Data*, **8**, 619 (1979).
 (16) Landolt-Börnstein, "Zahlenwerte und Funktionen", K. H. Hellwege, Ed., New Series, II/7, Springer, Berlin, 1976.

Table III (Continued)

molecule		IGLO			CHF DZ	IGLO INC	experimental	
		DZ	I	II			gas	liquid
ketene	CH ₂	21.9		6.8				4.8 ^c
	C	209.1		203.5				196.3
diazomethane	CH ₂			34.3				25.4 ^c
	H ₂ CO	199.6	201.8	202.2			196 ^g	
CH ₃ CHO	CH ₃	25.1	32.7				33.5 ^c	
	CH	203.7	203.8				203.8	
CH ₃ OH	CH ₃	42.8	52.0				51.3 ^c	
	CH ₂	14.6					19.9 ^c	
CH ₃ CH ₂ OH	CH ₃	63.6					59.3	
	CH ₂	175.5					168.3 ^c	
HCOOH	OC	159.1					155.1 ^d	
	C=C	166.4						
oxirane		29.8					43.1 ^c	
furan	OC	151.8					145.9 ^d	
	CC	121.0					112.7	
CH ₃ F		55.6	69.4				78.9 ^h	77.5 ^m
	CH ₃ CH ₂ F	8.8	16.5					15.6 ^c
CH ₂ F ₂	CH ₂	55.6	71.0					80.3
		89.3	100.2				117.6 ^h	113.3 ⁿ
CHF ₃		103.5	105.6				126.7 ^h	120.9 ⁿ
		112.6	108.2				130.7 ^h	122.0 ^o
CF ₄		148.2	137.9					
		158.9	162.4					164 ⁱ
1,1-difluoroethene	F ₂ C	76.0	67.9					66
	H ₂ C	143.6	149.7					147 ⁱ
<i>trans</i> -1,2-difluoroethene		137.0	140.2					139 ⁱ
<i>cis</i> -1,2-difluoroethene								

^a K. Jackowski, W. T. Raynes, *Mol. Phys.*, **34**, 465 (1977). ^b L. J. M. van DeVen, J. W. de Haan, *J. Chem. Soc., Chem. Commun.*, 94 (1978). ^c E. Breitmaier and W. Voelter, "13C Spectroscopy", 2nd ed., Verlag Chemie, Weinheim/Bergstr., Germany, 1978. ^d G. C. Levy, R. L. Lichter, and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed., Wiley, New York, 1980. ^e G. Maier, S. Pfriem, K.-D. Malsch, H.-O. Kalinowski, and K. Dehnicke, *Chem. Ber.*, **114**, 3988 (1981), estimated from $\delta = 9.27$ ppm in tetra-*tert*-butyltetrahedrane and an observed low-field shift of ~ 25 ppm caused by a *tert*-butyl group. ^f M. Hesse, H. Meier, and B. Zeh, "Spektroskopische Methoden in der organischen Chemie", Georg Thieme Verlag, Stuttgart, 1979. ^g P. C. Lauterbur, private communication, quoted in ref a. ^h K. Jackowski and W. T. Raynes, *J. Chem. Res. Synop.*, 66 (1977). ⁱ B. R. Appleman and B. P. Dailey, *Adv. Magn. Reson.*, **7**, 231 (1974). ^k B. Tiffon and J. P. Doucet, *Can. J. Chem.*, **54**, 2045 (1976). ^l D. Cans, B. Tiffon, and J. E. Pubeois, *Tetrahedron Lett.*, 2075 (1976). ^m H. Spiess and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961). ⁿ G. R. Somaya, *J. Magn. Reson.*, **33**, 559 (1979). ^o R. A. Demarco, W. B. Fox, W. B. Mouiz, and S. A. Sojka, *J. Magn. Reson.*, **18**, 522 (1975). ^p I. D. Gay, J. F. Kriz, *J. Phys. Chem.*, **82**, 319 (1978); using liquid-phase data from ref c.

Table IV. Absolute Chemical Shifts (σ) for CH₄ and H₂CO as well as Relative Shifts (δ) for H₂CO Obtained with Different Basis Sets

	basis	DZ	I	II	V	exptl
H	σ CH ₄	32.55	31.14	31.06	31.22	30.611 ^a
	σ H ₂ CO	21.89	21.78	21.77	21.95	18.3 \pm 2 ^b
	δ	10.66	9.36	9.29	9.27	
C	σ CH ₄	212.3	209.2	196.7	193.7	197.35 ^c
	σ H ₂ CO	18.6	11.8	-3.8	-10.4	-1 \pm 10 ^d
	δ	193.7	197.4	200.5	204.1	

^a W. T. Raynes in "Nuclear Magnetic Resonance", R. K. Harris, Ed., The Chemical Society, London, 1978, Vol. 7, p 1. ^b S. G. Kukolich, *J. Am. Chem. Soc.*, **97**, 5704 (1975). ^c K. Jackowski and W. T. Raynes, *Mol. Phys.*, **34**, 465 (1977). ^d P. C. Lauterbur (private communication, quoted by D. B. Neumann and J. W. Moskowitz, *J. Chem. Phys.*, **50**, 2216 (1969)).

basis sets I and II were used as well. In some cases we have also performed traditional coupled Hartree-Fock (CHF) calculations in a DZ basis with a common origin that was chosen as the center of mass for χ , the respective nucleus for $\sigma(^{13}\text{C})$ or the closest C atom for $\sigma(^1\text{H})$.

We have further used the ab initio increment system described in section 6, mainly for molecules with more than six C atoms. The results are found in the tables under the heading IGLO INC.

The data for the susceptibilities are collected in Table I. The DZ values are roughly 20% larger than their experimental counterparts while the corresponding "error" is only about 10% for the results with basis sets I or II. The results of traditional CHF calculations are far off, except for methane.

It is understandable why the DZ IGLO calculations overestimate the absolute values of susceptibilities $|\chi|$ and why extension

Table V. Magnetic Properties of Benzene (Units as in Tables I-III)

	CHF ^a		IGLO		exp
	H	198 CGF ^b CM	C	72 CGF(DZ) ^b	
χ		78.3		75.7	54.8 ^f
$\Delta\chi^c$		68.4		64.3	59.7
$\sigma(\text{H})$	34.0	20.5		23.9	23.7 ^g
$\Delta\sigma(\text{H})^c$	-2.8	-6.7		-5.1	-3.9 \pm 0.9 ^h
$\delta(\text{H})^d$				8.69	7.24 ^g
$\sigma(\text{C})$		56.1	65.9	87.6	66 \pm 10 ^f
$\Delta\sigma(\text{C})^c$		200.8	199.7 ^e	210.9	180 \pm 1, 177.8 ^h
$\sigma(\text{C})^d$				130.6	130.8 ⁱ

^a P. Lazzeretti and R. Zanasi, *J. Chem. Phys.*, **75**, 5019 (1981).

The headings H, C, and CM under CHF specify that the (common) gauge origins are at the position of the H or C nucleus or at the center of mass, respectively. ^b Number of contracted Gaussians used in the respective calculation. ^c Anisotropies are defined as $\Delta\chi = \chi_{\text{out-of-plane}} - \text{av } \chi_{\text{in-plane}}$. ^d Relative shifts are given with respect to methane. ^e This is not the value given in ref 9, but the one obtained from σ_{xx} , σ_{yy} , and σ_{zz} in their Table VI. ^f B. R. Appleman and B. P. Dailey, *Adv. Magn. Reson.*, **7**, 231 (1974). ^g J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 2, Pergamon Press, New York, 1968. ^h C. L. Khetrapal and A. C. Kunwar, *Adv. Magn. Reson.*, **9**, 301 (1977). ⁱ E. Breitmaier and W. Voelter, "13C NMR Spectroscopy", 2nd Ed., Verlag Chemie, Weinheim, 1978. ^k M. Linden, A. Höhener, and R. B. Ernst, *J. Magn. Reson.*, **35**, 379 (1979), measured at 14 K.

of the basis lowers $|\chi|$. The local diamagnetic contributions χ_d are rather insensitive to the quality of the basis, for H₂CO one gets for example $\chi_d = -20.88$, -20.55 , and 20.55 for basis sets DZ, I, and V, respectively,² while the paramagnetic contributions

Table VI. Orbital Contributions to $\sigma(\text{H})$ of Aliphatic Protons (IGLO, Double ζ)^a

molecule		orbital										
		C ₁ -H ₁	C ₁ -H ₂	C ₂ -H		C ₃ -H		C ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	C ₂ =C ₃	
				sp ³	sp ²	sp ³	sp ²					
CH ₄		27.02	1.84									
C ₂ H ₆		27.19	1.90	0.06				1.26				
C ₃ H ₈	C-1	27.41	1.86	0.11		0.00		1.42	-0.03			
	C-2	27.48	2.06	0.06				1.31				
<i>n</i> -C ₅ H ₁₂	C-1	26.88	1.78	0.09		0.08		1.37	0.05	-0.14		
	C-2	26.92	1.97	0.06		0.08		1.36 (C-2-C-2)	0.11	-0.20		
								1.16 (C-2-C-1)				
C(CH ₃) ₄	C-1	26.96	1.61	0.00		0.01		1.44	0.04			
propene		26.79	1.82		-0.12		-0.08	1.64			-0.10	
cyclopropane		26.34	1.85	0.14				1.59	0.71			
cyclopropene		27.01	1.62		-0.02			2.06			-0.14	
cyclobutene		26.65	1.71	0.12 cis	-0.15		-0.25	1.32 sp ³ sp ³	-0.08		+0.15	
				0.23 trans				1.59 sp ³ sp ²				
<i>cis</i> -2-butene	H ip	27.06	1.84		-0.19		-0.21	1.26			-0.02	
	H op	26.66	1.88 ip		-0.08		-0.07	1.89			-0.10	
			2.00 op								-0.22	
<i>trans</i> -2-butene	H ip	27.07	1.80		-0.20		0.11	1.44			-0.38	
	H op	26.72	1.79 ip		-0.09		-0.01	1.70			-0.20	
			1.97 op								0.02	
bicyclobutane	CH	24.50	0.29 C-3					1.19 C ₂ -3	0.79			
			0.05 C-2 _{eq}					1.06 C ₂ -2				
		0.19 C-2 _{ax}										
	CH _{2eq}	26.82	1.55	0.32		-0.18 _{eq}		1.15	0.13 ^b			
bicyclo[1.1.1]- pentane	CH	26.25	1.10	0.35		+0.12 _{ax}		1.30	0.00			
		27.88		0.07		-0.17 _{eq}		0.53	1.20 ^b			
tetrahedrane	CH	23.99		0.33		+0.25 _{ax}			0.25			
						-0.33 _{ax}			0.07			
								-0.24		1.17	0.26 syn	
								syn cis				
			+0.13					-0.05 anti				
			syn trans									
			-0.24									
			anti cis									
			-0.02									
			anti trans									
								0.55	0.33 ^b			

^a The numbering of the atoms is as follows: The proton considered (H₁) is bound to its carbon atom (C₁), whose next neighbors are C₂ and H₂, and so on. The carbon atoms are classified according to their hybridization (sp³, sp², sp) and, if necessary, as primary (C-1), secondary (C-2), or tertiary (C-3). In cases, where relative orientations are important, equatorial and axial atoms are denoted by the subscripts eq or ax, and ip or op stand for in plane vic. out of plane. ^b Actually C₂-C₂'.

χ_p vary much more with the basis; for H₂CO one gets $\chi_p = +6.33$, $+7.09$, $+7.77$ in the same order.

The reason for this variation of χ_p is that $-\chi_p$ is obtained from a Hylleraas type functional which is an upper bound to the exact $-\chi_p$ (for the same gauge); hence the computed χ_p can only be smaller than the exact χ_p and is the closer to it the larger the basis is.

Thus, increasing of the size of the basis leads (for diamagnetic molecules) usually to a lowering of $|\chi| = -\chi$; for H₂CO one gets, including the nonlocal contributions $|\chi| = 10.49$, 9.73 , and 8.71 for basis sets DZ, I, and V. Since polarization functions are important, it is astonishing how close the DZ values are to the experimental ones.

When comparing theoretical with experimental susceptibilities the following arguments should also be considered.

Nearly all experimental results have been obtained from liquids, while the theoretical ones should rather be compared with gas-phase values (extrapolated to 0 K) which are not available for most of the molecules studied here. From available data^{17,18} on other systems concerning the temperature dependence and the gas-liquid shift, one can conclude that the experimental gas-phase values at 0 K should be about 5% smaller than the values indicated in Table I as "experimental". This would reduce the average error

of the data calculated with basis I or II to 5%. The results of paper 2² of this series suggest that the use of large basis sets is likely to reduce the susceptibilities by about this amount.

Recently the results of a traditional CHF calculation with a very large basis (198 contracted Gaussians) has been published for benzene.¹⁹ Although the basis was 3 times larger than ours, the susceptibility is less accurate than that of our DZ IGLO calculation (see Table V).

5. Chemical shifts

In Tables II and III the calculated relative chemical shifts $\delta(\text{H})$ of protons and $\delta(\text{C})$ for carbon are compared with the corresponding experimental values and with those obtained from the ab initio increment system described in section 6. Our method furnishes of course absolute values of $\sigma(\text{H})$, i.e., for the shift with respect to a naked nucleus. The relative shifts (compared to CH₄ as standard) are more appropriate for a comparison with experiment since absolute experimental shifts are often rather inaccurate.

The absolute DZ shifts are usually somewhat too high (too shielding). The basis dependence of $\sigma(\text{C})$ and $\sigma(\text{H})$ for CH₄ and H₂CO has been studied in paper 2.² We summarize in Table IV the basis dependence of the absolute and the relative shifts for H₂CO. The best available values for the absolute shifts are those for basis V. Table IV then indicates that the DZ value for $\sigma(\text{H})$

(17) C. Barter, R. G. Meisenheimer, and D. P. Stevenson, *J. Chem. Phys.*, **64**, 1312 (1960).

(18) C. Guidotti, U. Lamanna, and M. Maestro, *Theor. Chim. Acta*, **26**, 147 (1972).

(19) P. Lazzeretti and R. Zanasi, *J. Chem. Phys.*, **75**, 5019 (1981).

Table VII. Orbital Contributions to $\sigma(C)$ of Olefinic Carbon Atoms (IGLO, DZ)^a

molecule	orbital									
	C ₁ =C ₂	C ₁ -C ₂	C ₂ -C ₃	=C ₁ -H	=C ₂ -H	-C ₂ -H		C ₃ -H		
						sp ²	sp ³	sp ²	sp ³	
C ₂ H ₄	-65.0			-22.3	-1.4					
propene										
CH ₂	-58.4		-2.8	-22.2	-2.2					
CH	-61.7	-28.5		-23.6	-2.2		-0.1		-0.1	
cyclopropene	-59.9	-31.1	+4.7	-18.2	-6.6		-0.0			
cyclobutene	-65.2	-26.7	-0.1 sp ³ -sp ³	-30.7	-4.6		0.3		+0.2	
			-2.4 sp ² -sp ³							
cis-2-butene	-60.3	-27.5	-3.4	-21.7	-2.0		-0.0		-0.1	
trans-2-butene	-60.4	-26.3	-3.0	-23.2	-2.1		-0.1		-0.1	

molecule	orbital												
	C ₁ =C ₂	C ₁ -C ₂	C ₂ =C ₃	C ₂ -C ₃	C ₃ =C ₄	C ₃ -C ₄	=C ₁ -H	=C ₂ -H	-C ₂ -H	=C ₃ -H	-C ₃ -H	=C ₄ -H	-C ₄ -H
2,3-dimethyl-1,3-butadiene													
C	-60.9	-27.2	-1.4	-1.4			-2.3 cis	0.1 ip	-0.1 cis		-0.4 ip		
C		-27.5					-2.3 trans	+0.1 op	-0.6 trans		+0.1 op		
CH ₃													
CH ₂	-58.5		-2.4	+0.1	-0.2		-20.7 cis				-0.3 ip	-0.1 cis	-0.2 ip
CH ₃			-2.6				-25.5 trans				±0.0 op	0.0 trans	+0.1 op
trans-1,3-butadiene													
CH	-62.8	-29.6	-1.6				-26.3	-2.5 trans	-1.0	-0.4 trans			
CH ₃								-2.6 cis		-0.9 cis			
CH ₂	-62.0		-2.6	0.0			-22.3 trans	-2.2			-0.3	-0.2 trans	0.1 cis
CH ₃							-24.6 cis						
2-methylpropene													
CH ₂	-62.3		-3.1				-23.5			-0.4 ip			
CH ₃										0.0 op			
C	-64.7	-27.3					-3.0	+0.1 ip					
CH ₃								-0.2 op					
cis-1-butene													
CH ₂	-58.8		-3.0		-0.1		-22.9 cis	-2.1			-0.1 op		
CH ₃							-19.9 trans						
CH	-62.1	-27.1					-24.9	-2.4 cis	-0.2 op				
CH ₃								-2.1 trans					

^a See footnote a of Table VI.

in H₂CO is essentially correct while that in CH₄ is too large (shielding) by ~1 ppm, but that with basis I or II the error is only ~0.1 ppm in either case.

Table II confirms that the relative proton shifts obtained by DZ-IGLO calculations differ from their experimental counterparts by ~0–2 ppm, while IGLO result with basis I or II are in error by only a few tenths of a part per million, except for unusual systems such as cyclopropene.

As for susceptibilities one should compare the calculated values with gas-phase data, reduced to 0 K and zero density. Even then the theoretical values ought to be averaged over zero-point vibrations and internal rotations (see ref 2 and there especially the discussion of HF and F₂). So perfect agreement with experimental results in liquid phase or in solution cannot be expected.

Since Me₄Si is included in our study (at least with DZ basis), we could have used it as reference, but we have preferred methane for the following reasons: (1) Most gas-phase measurements of ¹H and ¹³C NMR spectra have been carried out with CH₄ as internal reference. (2) While the temperature dependence of gas-phase ¹H resonances in CH₄ is virtually zero, it is rather large for Me₄Si.²⁰ The gas-to-liquid shifts, i.e., the downfield shifts, observed at infinite dilution of the solute, with respect to the gas-phase shift at 35 °C, are however rather large for both CH₄ (-0.13 to 0.58) and Me₄Si (-0.11 + 0.52) in a series of solvents.^{21–24} (3) The temperature dependence of the ¹³C signals

of Me₄Si seems to be more pronounced than that of CH₄— and somewhat curious.^{25–28} Again, the ¹³C resonances of both Me₄Si and CH₄ are subject to solvent effects.^{22–24} Even at infinite dilution, medium shifts of up to ±1.5 ppm in common NMR solvents have been observed for Me₄Si, and in the gas-phase one finds a pronounced density dependence of the ¹³C NMR signal of CH₄.²⁹

The absolute ¹³C shifts are (Table III) less accurate than the corresponding proton shifts (Table II). Table IV indicates that, if we take the results for basis V as "exact", those obtained with a DZ basis are too large (shielding) by ~20–30 ppm, those with basis I by ~15–20 and those with basis II by ~5–10 ppm. These errors in the absolute shifts cancel to some extent in the relative shifts, but not entirely, so that for some unusual molecules such as bicyclobutane, benzene, allene, or the fluorethanes surprisingly good agreement with experiment is obtained, while the largest

(23) D. Ziessow and M. Carroll, *Ber. Bunsenges. Phys. Chem.*, **76**, 61 (1972).

(24) F. H. Rummens and F. M. Mourits, *Can. J. Chem.*, **55**, 3021 (1977).

(25) H. J. Schneider, W. Freitag, and M. Schommer, *J. Magn. Reson.* **18**, 393 (1975).

(26) H. J. Schneider and W. Freitag, *J. Am. Chem. Soc.*, **98**, 478 (1976).

(27) The unusual curvature, described in ref 25 and 26 could not be reproduced by Günther;²⁸ he found a linear temperature dependence of the ¹³C resonance.

(28) U. Günther, G. Bergmann, W. Dietrich, to be published.

(29) K. Jackowski and W. T. Raynes, *Mol. Phys.*, **34**, 465 (1977).

(30) R. Ahlrichs, H. Lischka, B. Zurawski, and W. Kutzelnigg, *J. Chem. Phys.* **63**, 4685 (1975).

(20) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1174 (1961).

(21) W. T. Raynes and M. A. Raza, *Mol. Phys.*, **17**, 157.

(22) M. R. Bacon and G. E. Maciel, *J. Am. Chem. Soc.*, **95**, 2413 (1973).

Table VIII. Ab Initio Increment Systems for χ , $\delta(^1\text{H})$, and $\delta(^{13}\text{C})$ Simple Hydrocarbons^a

orbital	χ^b	$\sigma(\text{H})$	$\sigma(\text{C})$
1s(C ₁)	0.15	0.0	200.9
C ₁ -H ₁	sp ³ in CH ₄	4.48	-0.6
	sp ³ C-1	4.21	25.67
	C ₁ -C ₂ =C ₃ -C ₄ trans ^c		-3.5
	sp ³ C-2	4.09	25.67
	sp ² C-1	3.24	26.10
	sp ² C-2	3.24	26.50
	sp	3.35	23.80
C ₁ -H ₂	sp ^{3 d}		1.90
	sp ^{2 d}		-0.13
C ₂ -H			
	C ₁ -C ₂ sp ³	0.09	-0.3
	sp ²	-0.05	-1.4
	C ₁ =C ₂ H trans ^d	-0.25	
	H cis ^d	-0.12	
	X-C ₁ =C ₂		
	X = C(sp ^s) ^c		-2.7
	X = H, C(sp ²) ^c		-1.4
C ₃ -H	C ₁ ≡C ₂	0.35	-5.7
	C ₁ =C ₂ -C ₃ H	0.03	-0.5
	H cis ^d	-0.05	
	C ₁ -C ₂ =C ₃ H trans ^d	+0.05	
C ₁ -C ₂	sp ³ -sp ³	4.78	1.18
	sp ³ -sp ²	3.55	1.49
	=C ₃ -C ₄ trans ^c		-6.1
	=C ₃ -C ₄ cis ^c		-3.9
	sp ² -sp ³	3.55	-1.20
	sp ² -sp ²	2.26	-0.65
C ₂ -C ₃	sp ³ -sp ³		-0.08
	sp ² -sp ³ cis		-0.50
	sp ² -sp ³ trans		-0.65
	sp ² -sp ²		-0.37
C ₃ -C ₄	C ₂ -C ₃ -C ₄		-0.16
	C ₂ =C ₃ -C ₄ cis ^c		-0.3
	C ₂ =C ₃ -C ₄ trans ^c		-1.1
C ₁ =C ₂	C-1=C-2,3	1.21	57.5
	C-2,3=C-1	0.20	64.3
	C-1=C-1	0.44	73.1
	C-2,3=C-2,3	1.20	60.3
C ₂ =C ₃	else		-0.33
C=C			-0.10
C ₁ ≡C ₂		18.26	5.03

^a For notations, see footnote a of Table VI. ^b The susceptibility is a property of the molecule as a whole; therefore, the increments given for C-H, C-C, C=C, and C≡C apply for each bond of that type in a molecule, neglecting the subscripts. ^c For ¹³C increments only. ^d For ¹H increments only.

errors are found for "normal" systems like propane or neopentane. With basis I or II the agreement with experiment is usually improved considerably, so that the errors are then only a few parts per million, with the exception of the fluorinated methanes.

In order to understand the seemingly unsystematic errors of the DZ IGLO calculations, one must note that the error is different for the contributions of CH and CC bonds. While on going from DZ to basis II the contribution of an aliphatic CH bond is reduced by ~5 ppm, the corresponding reduction for the contribution of a CC bond is ~10 ppm. This leads to a total lowering for $\sigma(\text{C})$ in methane by $\sim 4 \times 5 = 20$ ppm, but to $(\sim 3 \times 5) + 10 = 25$ ppm for ethane or $\sim 4 \times 10 = 40$ ppm for the central atom in neopentane. This explains, at least qualitatively, the large errors in the relative shifts for propane and neopentane. The corresponding lowerings for C-C bonds in rings are more similar to those of CH bonds, and there is a more complete cancellation of errors. For olefinic or acetylenic CH or CC bonds the change from the DZ basis to basis I lowers $\sigma(\text{C})$ rather consistently by ~8 ppm, which amounts to total reductions of ~24 ppm for olefinic and ~16 ppm for acetylenic C atoms, so that the relative lowering is not very different from that in methane. Of course other contributions are also changed, and therefore the above argument can only be qualitative, but it illustrates somewhat the

Table IX. Variation of $\sigma(\text{H})$ and $\sigma(\text{C})$ in CH₄ with r_{CH} (IGLO, DZ)

$r_{\text{CH}}/\text{\AA}$	$\sigma(\text{C})$	$\sigma(\text{H})$	E_{SCF}
1.080	221.0	33.03	-40.13976
1.085 ^a	220.0	32.86	-40.13986
1.090	219.0	32.69	-40.13981
1.094 ^b	218.2	32.56	-40.13968
1.100	217.0	32.37	-40.13933

^a Theoretical r_e (DZ). ^b Experimental r_o .

Table X. Variation of $\sigma(\text{H})$ and $\sigma(\text{C})$ in Ethane as a Function of the Dihedral Angle $\angle\text{HCCH}$ (IGLO, Double ξ)

r_{CC}	r_{CH}	$\angle\text{HCH}$, deg	$\angle\text{HCCH}$, deg	$\sigma(\text{C})$	$\sigma(\text{H})$	E_{SCF}
1.529	1.085	107.7	60	215.6	32.97	79.11971 ^a
1.532	1.102	107.3	60	212.3	32.54	79.11884 ^b
			40	213.1	32.41	79.11773
			20	214.8	32.32	79.11551
			0	215.6	32.28	79.11439
1.570	1.102	107.0	0	214.0	32.27	79.11446 ^a

^a Optimized calculated geometry, ref 30. ^b Experimental gas-phase geometry, ref 16.

exceptional role of a C-C single bond. The localized MO of this bond is probably less spherically symmetric than other localized MO's, it has therefore stronger paramagnetic contributions and is more sensitive to changes in the basis.

Let us note that the only molecule in which we found the carbon nucleus to be significantly more shielding than in methane is tetrahydrofuran with $\delta(\text{C}) = -13.6$. Although one cannot compare this directly with the experimental value of -15 for tetra-*tert*-butyltetrahydrofuran, it is noteworthy that this value is negative as well.

In a recent CHF calculation of benzene with a very large basis,¹⁹ mentioned at the end of section 5, $\sigma(\text{C})$ and $\sigma(\text{H})$ have also been obtained. The results are compared with ours and with experiment in Table V. Our DZ values are certainly better for $\sigma(\text{H})$, while those of ref 9 are somewhat better for $\sigma(\text{C})$. Unfortunately a calculation with basis I or II is so far prohibitive.

Ab initio calculations of chemical shifts for molecules larger than benzene have so far only been possible with the GIAO method.³¹⁻³⁵

6. Transferability of Orbital Contributions and an ab Initio Increment System for Hydrocarbons

In paper 2² we have pointed out that the chemical shifts are obtained by the IGLO method directly as sums over contributions of the various localized orbitals. We have also shown some examples where the contributions of similar localized orbitals are transferable. The best candidates for such a transferability are obviously the hydrocarbons.

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Table XI. Anisotropies $\Delta\chi$ and $\Delta\sigma$ of Some Selected Molecules

molecule	$\Delta\chi$		$\Delta\sigma(\text{C})$		$\Delta\sigma(\text{H})$	
	IGLO	exp ^a	IGLO	exp	IGLO	exp
C ₂ H ₂	1.82	7.7 4.5	243.8	245 ± 20 ^b 253 ± 17 ^c	16.9	22 ± 2 ^{b,f}
C ₂ H ₄	5.07		37.4	7.5 ^d		
C ₂ H ₆	4.62	3.6 ^e	13.5		2.5	3.4 ± 1.3 ^f
CH ₃ F	6.62	8.2 ± 0.8	86.9	68 ± 15 ^a		
CH ₂ F ₂	-0.5	-1.6 ± 0.4	-25.8			
CHF ₃	-1.26	-1.2 ± 0.6	-13.8			
H ₂ CCF ₂	0.32	2.7 ± 0.4	165.2 CF ₂			
			81.8 CH ₂			
<i>cis</i> -HFC=CHF	-1.86	2.1 ± 0.3	113.9			
F ₂ CO	-1.37	3.5 ± 0.6	194.8			
H ₂ CCCH ₂	0.77		32.4 CH ₂			
			69.4 C			
H ₂ CCO	-1.27	-2.6 ± 0.5	56.3 CH ₂			
			219.1 CO			
H ₂ CNN	-2.11		76.5			

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In Table VI the contributions of the localized MO's to $\sigma(\text{H})$ for hydrogen atoms attached to carbon via an sp^3 -type bond are collected for a variety of hydrocarbons. One first notes that the contribution of the CH bond of the considered H to "its" C dominates by far (~ 27 ppm) and varies rather little between different molecules. One order of magnitude smaller are two more contributions, namely those of the bonds that have the C atom in common with the first C atom (~ 2 ppm for C₁H₂ and ~ 1.5 ppm for C₁C₂). All other contributions are smaller by again 1 order of magnitude, except for cyclic systems. On closer inspection one sees that the contribution of C₁H₁ is given by 27.15 ± 0.35 for open hydrocarbons while in cyclic or polycyclic systems the corresponding contribution can be significantly smaller (24 ppm in tetrahedrane) or larger (27.9 ppm in bicyclopentane).

One can make a similar list for olefinic or acetylenic protons, and for susceptibilities or for $\sigma(\text{C})$ as well (that for $\sigma(\text{C})$ for olefinic carbon atoms is given in Table VII), and extract an increment system as it is given in Table VIII that can then be used for hydrocarbons of arbitrary size.

Of course, the results obtained with such an ab initio increment system can hardly be better than the set of ab initio data from which it is constructed. The data in Tables VI and VII are based on calculations with a DZ basis. We have improved our increment systems by including as many data as possible that were obtained with basis I or II. This is why one finds for example in Table VIII the increment 25.67 for the C₁H₄ contributions to $\sigma(\text{H})$ of an aliphatic H rather than the 27.15 as suggested from DZ results.

We have then used this increment system to evaluate χ , $\delta(\text{H})$ at $\delta(\text{C})$ for some hydrocarbons.

The results are compared with experiment and with the direct ab initio calculations in Table I-III. The IGLO INC values are usually closer to experiment than the IGLO DZ values, but not so good as the IGLO results with basis I or II. For $\delta(\text{C})$ the increment system is not yet fully satisfactory; the errors vary generally between ~ 0 and ~ 10 ppm. We expect that in including more calculations with basis I or II the increment system can be improved.

Nevertheless, one should not expect too much from an ab initio increment system. It is necessarily limited due to the following reasons: (1) As seen from Tables VI and VII, the transferability is not perfect. (2) The orbital contributions to susceptibility and chemical shifts do not only depend on the surrounding of the bond but also on the local geometry. This is illustrated in Table IX for the CH bond length in methane and in Table X for the CC bond length and the dihedral angle in C₂H₆. One should have increments as functions of geometrical parameters. (3) Both χ and σ are tensorial quantities, the increments should be tensors as well, and the increment system should cover both the isotropic

parts and the anisotropies, but this would become rather complicated since the relative orientation of various parts of the molecule enters directly.

It is evident from Table VII that cyclic or polycyclic hydrocarbons cannot be described by this increment systems, unless one introduces extra increments for ring strain, which we have not cared to attempt.

In defining an ab initio increment system, we never had in mind to compete with existing empirical systems. We rather wanted to show that increments with a definite physical meaning can be defined and that on these lines a better understanding of trends in NMR spectra is possible.

7. Anisotropies

Our calculations yield directly the susceptibility or chemical shift tensors. We have, so far, only indicated the isotropic parts of these tensors, because this is what one usually measures. In paper 2² we have also documented the anisotropies for several small molecules, including H₂CO.

In this paper we can only give the anisotropies for a few selected systems (Table XI). Very large anisotropies arise if multiple bonds are present.

8. Conclusions

The IGLO method has been shown to be useful for the calculation of magnetic properties of molecules of medium size, while traditional methods have been limited to small molecules. Relatively small basis sets turn out to be sufficient, and even a double- ζ basis is acceptable (though not highly accurate). Both χ and σ are obtained in terms of orbital contributions that have a direct physical meaning. So a bridge over the gap between ab initio theory and qualitative understanding is built. The ab initio increment system proposed here should also be understood as a tool for a better understanding of the origin of variations in the chemical shift rather than as a recipe for reproducing experimental values (where it cannot compete with empirical increment systems).

In comparing experimental and theoretical values, it is important to remember that theory predicts values for isolated molecules and that solvent effects as well as gas-liquid shifts are often quite large. This is one of the reasons why perfect agreement cannot be expected. Another reason is that our calculations have been done for fixed geometries and definite conformations (except for CH₄ and C₂H₆ as documented in Tables IX and X), while experimental data are averaged over zero-point vibrations and other internal motions. We have further ignored effects of electron

correlation; however, there has not been any indication so far that these are of significant importance for χ or σ .

We have not cared too much about comparison with previous theoretical values. For the molecules of this study, except the smaller ones, previous ab initio calculations hardly exist. One may mention that our calculations are probably the first to give the right order of the proton shifts in propene (cf. ref 11).

Forthcoming applications of the present method will be devoted to (a) a study of the effect of hydrogen bonding on χ and σ , (b)

accurate calculations on some small molecules such as CO, CO₂, N₂, etc.⁴⁴ (c) carbonium ions, (d) chemical shifts of fluorine, and (e) chemical shifts of phosphorus.

Acknowledgment. The computations have been carried out at the INTERDATA (Perkin-Elmer) 8-32 minicomputer sponsored by the Deutsche Forschungsgemeinschaft.

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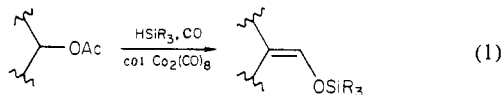
Communications to the Editor

Conversion of Alkyl Acetates to (Siloxymethylene)alkanes by Co₂(CO)₈-Catalyzed Reaction with a Hydrosilane and Carbon Monoxide

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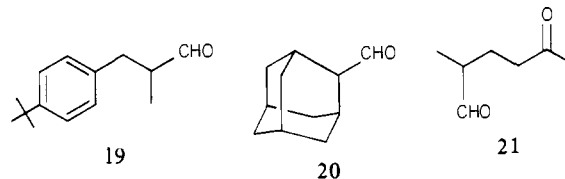
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In the study of the new Co₂(CO)₈-catalyzed reaction of aldehydes^{1a,b} and cyclic ethers^{1b,c} with hydrosilanes and carbon monoxide, we found a novel method of introducing various functional groups such as formyl, (trialkylsiloxy)methylene, and 1,2-bis(trialkylsiloxy)vinyl. It was suggested that tetracarbonyl(trialkylsilyl)cobalt [R₃SiCo(CO)₄ (**1**)], which was formed in situ by the reaction of Co₂(CO)₈ with hydrosilanes,² played a key role in these catalytic reactions of oxygenated compounds.³ The high affinity of the silicon in **1** for an oxygen atom would be the driving force for the cleavage of the carbon-oxygen bond in the oxygenated compounds to give intermediates having a carbon-cobalt bond. This line of thought has provided a new and promising methodology for the formation of carbon-transition metal bonds.^{3,4} Since it seemed plausible that the reaction of an alkyl acetate with **1** might give a tetracarbonylalkylcobalt, (vide infra, **2** → **22** → **23** in eq 4), it was anticipated that the catalytic reaction of an alkyl acetate with a hydrosilane and carbon monoxide in the presence of Co₂(CO)₈ (a precursor of **1**) might result in catalytic incorporation of carbon monoxide into the carbon atom bearing the acetoxy group. This is the case. In this paper, we describe the unprecedented transformation of alkyl acetates into [(trialkylsiloxy)methylene]alkanes (eq 1).⁵ This synthetically useful reaction is also applicable to lactones.



The representative results are given in Table I. A typical experimental procedure is illustrated below for the reaction of 2-adamantyl acetate (**4**, entry 6 in Table I). In a 100-mL stainless steel autoclave were placed 10 mmol of **4**, 30 mmol of HSiEt₂Me, 0.4 mmol of Co₂(CO)₈, and 20 mL of benzene.⁶ The autoclave

was charged with carbon monoxide to 50 atm at 25 °C and then heated with stirring in an oil bath at 200 °C for 6 h. Analysis of the reaction mixture by GLC showed it to contain 2-[(diethylmethylsiloxy)methylene]adamantane (**12**) in 95% yield. Distillation gave pure enol silyl ether **12**, bp 103–104 °C (0.25 mmHg), in 90% yield.⁷ Various cyclic and acyclic alkyl acetates (entries 1–7) underwent the incorporation of carbon monoxide to give (trialkylsiloxy)methylenated compounds **7–13** (enol silyl ethers). In all cases diethylmethylsilyl acetate was obtained as a byproduct.⁸ Trimethylsilane (HSiMe₃) and triethylsilane (HSiEt₃) can also be used in place of HSiEt₂Me⁹ and gave comparable product yields (entry 2). Since enol silyl ethers are known as extremely useful synthetic intermediates,¹⁰ all the products obtained in the present reaction are expected to be amenable to further synthetic elaboration. For example, treatment of **11** and **12** with KF in CH₃OH at 25 °C gave quantitatively aldehydes **19** and **20**, respectively.¹¹ The overall transformation of **3** and



(6) Toluene can also be used as a solvent.

(7) All new compounds were characterized by IR, NMR, and mass spectral data and elemental analyses. These data are given in the supplementary material. Characteristic spectral data include the following: ¹H NMR (CCl₄) δ 0.07–0.12 (s, C=COSiEt₂CH₃), 0.20–0.21 (COOSiEt₂CH₃), 5.93–6.12 (m, C=CHOSi); IR (neat) 1675–1685 cm⁻¹ (C=COSi); mass spectra, M⁺, M⁺ – 29 (M⁺ – Et).

(8) Diethylmethylsilyl acetate was identified by GLC with an authentic sample (Silicone OV-1, 3 mm × 6 m, 140 °C, the relative retention time to a standard, *n*-C₁₄H₃₀, was 0.18).

(9) HSiEt₂Me has an appropriate boiling point for handling with syringe (bp 77–78 °C). HSiMe₃ (bp 6.7 °C), HSiEt₂Me, and HSiEt₃ (bp 107–108 °C) are all commercially available (e.g., Petrarch Systems Co., PA).

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(11) Aldehyde **19** is important not only as a perfume component¹² but also as an intermediate for pharmacological active amines,¹³ and **20** has been reported to be somewhat difficult to prepare.¹⁴

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(5) A portion of this study has been presented at the 26th Symposium on Organometallic Chemistry, Kyoto, Japan, Oct 1979, abstr 151, and also described briefly in our first state of the art report.³