The global minimum on the Si_3H_6 potential energy surface is trisilacyclopropane. This is in contrast with the hydrocarbon analogues, for which propene is the global minimum on the C_3H_6 surface, and reflects the relative strengths of the Si–Si vs C–C π bonds,[10] as well as the smaller strain in the three-membered silicon ring.[21]

Acknowledgment. This work was supported by a grant from the Petroleum Research Fund, administered by the Americal Chemical Society, and by grants from the National Science Foundation (CHE83-09948) and the Air Force Office of Scientific Research (82-0190). The computer time made available by the North Dakota State University Computer Center and by the National Science Foundation at the San Diego Supercomputer Center is gratefully acknowledged.

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Magnetic Properties in Terms of Localized Quantities. 7. Application to Nitrogen NMR Shifts

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Received February 20, 1987

Abstract: Magnetic susceptibility and NMR chemical shift tensors for various classes of nitrogen-containing molecules are calculated by means of the IGLO method. The compounds studied are the amines $NH_m(CH_3)_{3-m}$ (m = 0, 1, 2, 3), $C_6H_5NH_2$, the three-membered ring aziridine ($(CH_2)_2NH$), the nitriles CH_3CN and C_6H_5CN, the isonitrile CH_3NC, diazomethane (CH_2NN), hydrazine (N_2H_4), and some diazenes RN=NR (R = H, CH_3). Generally the agreement between theory and experiment is good, with the exception of nitrogen atoms in NN multiple bonds. It is found that the calculated NMR chemical shifts of nitrogens involved in NN double bonds are too paramagnetic, even in the limit of near Hartree–Fock quality of the basis sets. Because of the large magnitude of the deviations between theory and experiment, gas-to-liquid shifts or asymmetry effects cannot explain the differences. We conclude that correlation effects, which are neglected in the IGLO method as well as in any other theory of coupled Hartree–Fock type, are likely to play an important role in the calculation of NMR shifts for nitrogen atoms involved in NN multiple bonds.

I. Introduction

Nitrogen NMR spectroscopy is becoming more and more an indispensable tool for the identification of bioorganic molecules and the investigation of their reaction mechanisms. The experimental difficulties due to quadrupolar nuclei (^{14}N) or low abundance (^{15}N) have been overcome by the advent of new techniques.[1,2]

On the theoretical side, however, only very few ab inito methods are capable of calculating magnetic properties of molecules having more than a few first-row atoms. Conventional coupled Hartree–Fock or finite perturbation methods, though applicable in principle, cannot be used because of the computational problems connected with the choice of a single gauge origin describing the external magnetic field. Therefore only methods that use local gauge origins, i.e., Ditchfield's GIAO,[3] Hansen and Bouman's LORG,[4] and our IGLO approach,[5] are expected to give results of reasonable accuracy when they are applied to large molecules.

We have shown that the IGLO method (IGLO stands for individual gauge for localized molecular orbitals) provides detailed and reliable information on magnetic susceptibility and chemical shift tensors of small- to medium-sized molecules.[6] It has been used to assign the principal axes of chemical shift tensors in highly strained hydrocarbons[7] and to answer some unresolved questions in carbocation chemistry,[8] and recently it has been applied successfully to compounds containing silicon and phosphorus[9] and to a number of boranes and carboranes.[10]

In this paper we present calculations on second-order properties of some representative nitrogen compounds, covering approximately the whole range of nitrogen NMR shifts. In our calculations we cannot distinguish ^{15}N from ^{14}N NMR shifts. Experimentally the primary isotope effect is of the order of 0.1 ppm[1,2] and hence negligible for our purposes.

Due to the lone-pair electrons at nitrogen, its NMR chemical shifts are somewhat more difficult to calculate than are those for carbon. In order to check the convergency of the calculated properties when enlarging the basis we performed calculations with rather large basis sets. Experiences from these basis saturation tests are used in the accompanying paper on five- and six-membered heterocycles,[11] where we could not afford such large bases.

This paper is organized as follows: In section II we briefly describe the IGLO ansatz, sign conventions, basis sets and geometries used, and the problem of referencing relative chemical shifts. In section III magnetic susceptibility tensors are given, and in sections IV and V nitrogen and carbon chemical shifts are discussed. Our conclusions are summarized in section VI.

II. Computational Method and Reference Standards

The IGLO method for the ab initio calculation of second-order magnetic properties is essentially of coupled Hartree–Fock (CHF)

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0002-7863/87/1509-5950$01.50/0

Table I. Magnetic Susceptibilities[a,b]

no.	molecule	expt	DZ	II	III	χ_{11}	χ_{22}	χ_{33}	χ^d	χ^p	χ^{nl}
1	NH_3	18.0[c]	17.3	17.4	17.5	17.9	17.9	16.7	14.4	2.3	0.8
2	NH_2CH_3		31.0	27.4	26.5	31.4	24.1	24.1	26.0	1.2	−0.7
3	$NH(CH_3)_2$		45.2	38.9	37.3	39.5	37.3	35.1	37.9	0.7	−1.3
4	$N(CH_3)_3$		54.5	47.8		50.9	50.8	41.6	49.7	0.2	−2.1
5	$(CH_2)_2NH$	*d*	43.6	38.9	38.1	45.0	36.4	32.9	35.0	2.7	0.4
6	CH_3CN	27.6[e]	33.7	31.4	29.9	36.3	26.8	26.8	32.4	−2.2	−0.2
7	CH_3NC	27.6[f]	31.7	28.8	27.4	36.1	23.1	23.1	32.0	−3.2	−1.4
8	*trans*-HNNH		−1.2	3.1	2.9	17.1	6.6	−15.0	20.8	−13.2	−4.7
9	*cis*-HNNH		2.0	4.4	3.7	15.1	4.0	−8.0	20.8	−12.3	−4.8
10	*trans*-CH_3NNCH_3		24.7	26.5		39.8	31.1	8.6	45.2	−13.5	−5.3
11	*cis*-CH_3NNCH_3		28.4	27.5		43.7	30.0	8.8	45.2	−12.6	−5.1
12	CH_2NN		29.0	25.4	22.4	23.2	22.9	21.1	33.1	−9.4	−1.3
13	$C_6H_5NH_2$	63.0[h]	85.5	76.2		112.4	61.3	54.8	86.2	−8.1	−1.8
14	C_6H_5CN	65.2[i]	88.3	79.8		119.0	63.4	56.9	92.7	−12.5	−0.5
15	N_2H_4		27.3	25.5	24.9	31.6	21.9	21.2	24.4	1.1	−0.6

[a] Units are ppm cgs/mol (diamagnetic contributions are positive); principal values χ_{ii} (i = 1, 2, 3), χ^d, χ^p, and χ^{nl} are given for the largest basis set used. [b] For the definitions of the anisotropies $\Delta\chi_1$ and $\Delta\chi_2$, see text; calculated anisotropies are given in parentheses, following the experimental ones. [c] Reference 24, gas-phase value; $\Delta\chi = -1.3$[g] (−1.2). [d] Reference 25; $\Delta\chi_1 = -16.5 \pm 0.7$ (−15.55), $\Delta\chi_2 = -4.6 \pm 0.85$ (−5.14). [e] Reference 26; $\Delta\chi = 10.5 \pm 0.5$ (9.53). [f] Reference 26; $\Delta\chi = 13.5 \pm 0.7$ (13.0). [g] Reference 25. [h] Reference 28, p 175. [i] Reference 28, p 143.

type. Its formalism has been described elsewhere in detail,[5] so we can restrict ourselves to a summary of its main features.

Our approach consists in solving the CHF equations for localized MOs with individual gauge origins for the occupied MOs. Each origin is chosen as the centroid of charge of its MO. With this choice both dia- and paramagnetic contributions to χ and σ become small in magnitude, and we avoid the computation of a small number χ (or σ) as a difference of two artificially large quantities χ^d and χ^p (or σ^d and σ^p). Using localized MOs together with individual origins of the vector potential permits the determination of the magnetic susceptibility and of the NMR shielding tensors of all atoms in a molecule with comparable accuracy in a single calculation.

There is, of course, a price to pay for these achievements. As we need individual first-order perturbation operators for each occupied MO, the IGLO formalism is somewhat more complicated than a conventional CHF scheme with canonical MOs and a common gauge origin. Nevertheless, the computational effort of an IGLO calculation is at most twice that of a standard SCF calculation with the same basis.

From its definition as the mixed second derivative of the energy E with respect to the nuclear moment $\mu(K)$ and the external magnetic field B, it is obvious that the shielding tensor $\sigma(K)$ of a nucleus K is nonsymmetric in general; i.e., it has nine independent components.

$$\sigma(K)_{\alpha\beta} = \left(\frac{\partial^2 E}{\partial\mu(K)_\alpha \partial B_\beta} \right)_{\mu(K)_\alpha = B_\beta = 0} : \qquad \alpha, \beta = x, y, z$$

The antisymmetric part of the σ tensor should influence the NMR spectrum only to second order.[12-15] If measurable at all, antisymmetry effcts should show up in those cases where the difference between the off-diagonal elements, $\sigma_{\alpha\beta} - \sigma_{\beta\alpha}$, is of the order of several hundred ppm. Some of the molecules of this study are possible candidates, and we will comment on their antisymmetric behavior in section IV.

The absolute shieldings obtained from the calculations describe the screening effects of the electrons on the nuclei; i.e., they are referenced with respect to the naked nuclei. Shielding (diamagnetic) MO contributions are positive, and deshielding (paramagnetic) ones negative.

In order to compare the calculated absolute shielding data more easily with the experimental data, which are referenced to some common standard, we have to convert them to the respective relative scale. This can be done without difficulty for ^1H, ^{13}C, and ^{29}Si, where we have calculated the absolute shieldings of tetramethylsilane (TMS) with bases DZ and II. Following the usual convention, relative shifts of the reference molecules, calculated with the corresponding basis sets, are set to zero, low-field signals with respect to the reference are positive and high-field signals are negative.

In mapping our absolute nitrogen shielding data to a relative shift scale, we decided to choose the ammonia molecule in its r_z geometry[16] as our reference. Because of its smallness we can afford rather large basis sets in the calculations of its magnetic properties. Although this establishes a relative nitrogen scale, comparison with experiment is not facilitated very much. It is well-known that ammonia exhibits a very large gas-to-liquid shift (−20 ppm at 300 K) that is strongly temperature dependent (−23 ppm at 195.5 K) mainly due to the large nonlinear temperature dependence of the NMR shifts in the liquid.[17,20]

Thus it is necessary to extrapolate measured NMR shifts to zero pressure and to $T = 0$ K; otherwise it appears to be rather difficult to compare our data with those obtained experimentally, and it is not surprising that the agreement between theory and experiment is not as good as for the carbon shifts.

A more detailed discussion of the influence of geometry variations on NMR chemical shifts in ammonia and some other molecules containing first- and second-row atoms will be given elsewhere.[9] Nitrogen-specific difficulties as to the comparison of experimental with calculated shifts are discussed in section IV.

For magnetic susceptibilities χ, given in "ppm cgs"/mol, the sign convention is such that diamagnetic contributions are positive and paramagnetic ones negative. Susceptibility anisotropies $\Delta\chi_1$ and $\Delta\chi_2$ are defined as $\chi_{11} - (\chi_{22} + \chi_{33})/2$ and $\chi_{22} - (\chi_{11} + \chi_{33})/2$. For linear and pseudolinear molecules $\Delta\chi$ is defined as $\Delta\chi = \chi_\parallel - \chi_\perp$. The anisotropies $\Delta\sigma$ are defined analogously.

Three different Huzinaga Gaussian lobe basis sets[19] have been used: (i) basis DZ: C or N, 7s3p contracted to [4111,21]; H, 3s contracted to [21]; Si, 10s6p contracted to [511111,3111]; (ii) basis II: C or N, 9s5p1d contracted to [51111,2111,1], d exponent 1.0; H, 5s1p contracted to [311,1], p exponent 0.65; Si, 11s7p2d contracted to [5 6*1,2 5*1,1 1], d exponents 1.4 and 0.35; (iii) basis III: C or N, 11s7p2d contracted to [41111111,211111,11], d exponents 1.40 and 0.35; H, 6s2p contracted to [3111,11] p exponents 1.30 and 0.33.

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III. Susceptibilities

In Table I magnetic susceptibilities are listed. Calculations with different basis sets are compared to experimental data, if available. For the respective largest basis the principal values are given, and the relative importance of diamagnetic, paramagnetic, and nonlocal contributions to χ is shown. We emphasize that none of the contributions alone can be compared with experiment directly—only their sum adds to the measurable quantity χ.

Although DZ calculations give rather meaningful results, especially if one compares them with data from conventional CHF calculations, there is a considerable improvement obtained with basis II. Enlarging the basis even further still leads to slight changes in χ.

It is well-known that experimental susceptibilities measured in the gas phase are more diamagnetic than in the liquid state. Ammonia is the only molecule for which experimental gas-phase data for χ are available, and our calculations seem to converge to that value. The small anisotropy $\Delta\chi$, and its unusual sign, is nicely reproduced by the calculation. For ammonia and *trans*-diazene **8** we have calculated the magnetic properties using larger basis sets than basis III. An 11s7p4d basis for N (cf. Table IV) led to the following IGLO data for χ and $\Delta\chi$ for ammonia (in ppm cgs/mol, CHF(0) values in parentheses): 17.42 (17.44) and −1.11 (−1.07), which are in good agreement with each other and with the observed gas-phase values.

For the other molecules of Table I, experimental liquid-state data are given, and our calculated values are too diamagnetic in these cases. Substituting methyl groups for hydrogen in ammonia or in the diazenes **8** and **9** leads to an increased susceptibility by about 10–12 ppm cgs/mol per CH_3 unit. This is in accord with our findings in hydrocarbons.[6a] As far as experimental anisotropies are available for the other molecules, the agreement between theory and experiment is good.

According to our calculations the diazenes **8** and **9** are almost paramagnetic. Here, and in the 1,2-dimethyldiazenes **10** and **11**, the nonlocal contributions are larger by a factor of up to 10 than they are normally.

With the exception of the nitrile group, we shall not comment on orbital contributions to χ. The contribution $\chi(C{\equiv}N)$ of the cyano group to the bulk susceptibility can be estimated by the Haberditzl scheme,[28,29] as 13.1 ± 0.5 ppm cgs/mol. According to Stolze and Sutter,[30] the local χ-tensor elements directed along the C≡N bond, in the molecular plane, and perpendicular to it are 21.0 ± 1.9, 13.0 ± 2.1, and 12.7 ± 2.0 ppm cgs/mol, in good agreement with 18.3, 12.6, and 12.6 ppm cgs/mol for acetonitrile and with 18.0, 13.2, and 12.2 ppm cgs/mol for benzonitrile from our IGLO calculations with basis II. For HCN we find 17.8, 12.4, and 12.4 ppm cgs/mol[6b] with a slightly larger basis set.

IV. Nitrogen Chemical Shifts

Our calculated NMR shielding tensors correspond to single molecules at a fixed geometry—mainly r_e or r_z—whereas the bulk of experimental data refer to measurements in the liquid state.[1,2,31,32] Depending on experimental conditions, considerably differing nitrogen NMR data are obtained. Due to its lone-pair electrons, temperature and solvent shifts are much more pronounced for nitrogen than for carbon.

Table II. Nitrogen NMR Shifts[a]

molecule	IGLO DZ	IGLO II	IGLO III	expt
methylamine (**2**)	−6.2	8.5	9.0	1.3[b]
dimethylamine (**3**)	−14.7	16.1	18.0	6.7
trimethylamine (**4**)	−54.3	−15.9		13.0[b]
aziridine (**5**)	−12.7	−11.9	−16.0	−11.4,[b] −8.5[c]
methyl cyanide (**6**)	263.7	285.1	295.2	239.5
methyl isocyanide (**7**)	101.9	152.8	168.1	162.0
trans-diazene[d] (**8**)	780.8	731.0	719.9	
trans-diazene[e] (**8**)	755.5	710.3	700.4	
cis-diazene (**9**)	631.3	641.6	646.2	
trans-dimethyldiazene (**10**)	789.7	726.2		
cis-dimethyldiazene (**11**)	651.5	638.3		
diazomethane (**12**)				
$H_2C\mathit{N}N$	189.4	247.0	267.7	286
$H_2CN\mathit{N}$	557.3	559.5	557.9	397
aniline (**13**)	24.5	45.1		56.5
benzonitrile (**14**)	270.0	298.8		258.7
hydrazine (**15**)	40.9	49.9	49.8	45.4

[a] Relative shifts in ppm; theoretical data are referenced to NH_3 in its r_z geometry, experimental ones to liquid ammonia. [b] Reference 1. [c] Reference 31. [d] Experimental geometry, ref 5. [e] Theoretical geometry, ref 37.

For this reason it would be helpful to have experimental gas-phase NMR data for nitrogen to compare our calculations with. Attempts to establish an absolute nitrogen NMR scale,[17] based on investigations of ammonia[33] and a few other molecules[18,34] in the gas phase revealed not only appreciable gas-to-liquid shifts of the NMR signals but also rather strong variations with temperature. The latter are mainly due to the nonlinear temperature dependence of the nitrogen NMR signals in the liquids, while $\sigma_0(T)$, the shielding in the limit of zero pressure, does not change much ($d\sigma_0/dT = 0.00651$ ppm/K for ammonia; $320 \leq T \leq 380$ K).

In addition, the signs of the observed shifts due to intermolecular interactions differ for different classes of nitrogen atoms. The ammonia type of behavior, i.e., a downfield shift of the liquid-state signal with respect to the gas-phase value, is expected to be shown by the pyrrole nitrogens in azoles, whereas azines and the pyridine-type nitrogens in azoles should exhibit upfield shifts like pyridine or HCN, for example.[18]

In Table II we compare calculated nitrogen shifts with experimental data. As discussed before, the latter can only serve as rough estimates of the "true" gas-phase signals in the zero-pressure limit.

Acetonitrile (**6**) may serve as an example for the difficulties arising while comparing calculated and measured data. At the first glance, IGLO calculation (basis III) and experiment differ by about 45 ppm (cf. Table II). This difference is reduced to 15 ppm when we take into account the experimental gas-to-liquid shifts of −20 ppm and +10 ppm observed for ammonia and acetonitrile at 300 K.[17,18] At lower temperatures (near 200 K) this difference is reduced further by an additional 4–5 ppm,[18,20] and we think that we would find an even better agreement if we could compare our data to NMR experiments extrapolated to 0 K. The same arguments lead us to expect that the observed difference of about 40 ppm (basis II) in the NMR shifts of benzonitrile (**14**) will be reduced by approximately 30 ppm.

Experimental nitrogen chemical shift anisotropies are available for acetonitrile from liquid crystal[41] and solid-state[40] investigations

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Table III. Principal Values of Nitrogen Shielding Tensors[a,b]

molecule	σ_{11}	σ_{22}	σ_{33}
ammonia (**1**)	260	260	228
	268	268	230
methylamine (**2**)	266	246	211
	274	252	215
dimethylamine (**3**)	280	211	208
	286	215	212
trimethylamine (**4**)	287	287	222
aziridine (**5**)	341	252	187
	351	269	195
methyl cyanide[c] (**6**)	317	−213	−213
	302	−211	−211
methyl isocyanide[c] (**7**)	380	−46	−46
	362	−50	−50
trans-diazene (**8**)	186	−362	−1370
	188	−270	−1310
cis-diazene (**9**)	168	−427	−918
	175	−420	−926
trans-dimethyldiazene (**10**)	184	−262	−1353
cis-dimethyldiazene (**11**)	191	−407	−951
diazomethane (**12**)			
$\mathrm{H_2C}\mathit{N}\mathrm{N}$	386	−158	−222
	372	−173	−235
$\mathrm{H_2CN}\mathit{N}$	−5	−319	−608
	4	−321	−590
aniline (**13**)	263	176	173
benzonitrile (**14**)	247	−181	−216
hydrazine (**15**)	255	175	167
	264	182	172

[a] Absolute shieldings in ppm; data obtained with basis II and basis III are shown in consecutive lines. [b] For principal axes, see text. [c] For a discussion of the experimental anisotropies, see text.

and for methyl isocyanide.[38] The solid-state anisotropy $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} = 488 \pm 8$ ppm agrees somewhat better with our value of 512 ppm (basis III; cf. Table III) than the 452 ± 10 ppm obtained from liquid crystal measurements. In methyl isocyanide we get an anisotropy of 412 ppm (basis III), which is within the experimental error bars of 360 ± 73 ppm. In view of the differing experimental data, and of the discussion above we can hardly expect a better agreement with our calculations.

Similar to our observations for the central carbon atom of the methyl-substituted methanes with the DZ basis, we calculate the central nitrogen in the series methyl-, dimethyl-, and trimethylamine to be shielded too much. The corrections obtained with basis II are 15, 31, and 38 ppm, while basis III additionally changes the data of basis II by 0.5, 2, and (probably) 3 ppm for molecules **2** **3**, and **4**. We note that inclusion of gas-to-liquid shifts in ammonia and trimethylamine[18] will increase the difference by about 15 ppm.

The diazenes **8**–**11** deserve special interest because of their calculated extreme low-field shifts. Experimentally, too, substituted diazenes constitute the low-field end of the nitrogen NMR shift scale, especially (trimethylsilyl)methyldiazene (δ(NC) = 650 ppm, δ(NSi) = 680 ppm). We find practically no difference between the unsubstituted molecules **8** and **9** and the 1,2-dimethyl-substituted molecules **10** and **11**. This makes a cautious comparison with our calculated data for *trans*-HN = $\mathrm{NSiH_3}$ less dubious (δ(NH) = 950 ppm, δ(NSi) = 1025 ppm, basis II). Although it might be that substituents could change the calculated shifts drastically, we consider them to be much too paramagnetic.

Ther exists another theoretical calculation of the NMR data for **8** and **9**[35] using SOS-Cl,[36] which gives paramagnetic shifts about 50–70 ppm smaller than those obtained by IGLO at identical geometries. This is not too astonishing, since a conventional CHF-type theory with a single origin of the vector potential and small basis sets should lead to an unbalanced description of dia- and paramagnetic terms for σ, resulting in chemical shifts that are too diamagnetic in general.

Table IV. Relative Nitrogen Shifts in *trans*-Diazene[a]

basis set	IGLO	CHF(0)	CHF(N)
DZ	753	713	692
6-31G**	634	642	630
DZ**[b]	589	590	579
6-31G**[c]	649	651	647
II	710.3	704.9	703.9
III	700.4	698.6	697.4
IV[d]	697.9	697.4	695.5

[a] Theoretical geometry from ref 37; shifts in ppm relative to NH_3 in its r_z geometry, calculated with the respective basis set and method. [b] One set of d functions (η = 1.0) and p functions (η = 0.65) added to N and H, respectively. [c] N basis totally decoupled. [d] s and p functions for N as in basis III, plus four sets of d functions (η = 0.15, 0.50, 1.65, 5.50); basis for H as in basis III. The absolute shielding values (ppm) obtained with this basis are as follows: $\sigma(NH_3)$, 257.9 (IGLO), 257.0 (CHF(N)); σ(HNNH), −440.0 (IGLO), −440.4 (CHF(0)), −438.5 (CHF(N)).

For the sake of illustration we list relative nitrogen shifts for *trans*-diazene obtained with seven different basis sets for IGLO and for CHF with the common origin of the vector potential located at the center of mass [CHF(0)] and at one nitrogen atom [CHF(N)] (Table IV). Besides the energy, the difference between NMR chemical shifts of one atom, calculated with different origins for the common origin of the vector potential, $\sigma(0) - \sigma(N)$ for instance, is a measure of the completeness of the basis sets.

For small molecules like **8** or **9**, $\sigma(0) - \sigma(N)$ is not that large, but it is clear from Table IV that bases 6-31G** or DZ** are far from being complete even with respect to gauge transformations of this limited type. Basis sets II, III, and IV give results that are almost gauge invariant and that agree with the IGLO calculations. This means that the nitrogen shifts for **8** in the Hartree–Fock limit are much too paramagnetic. Results obtained with smaller basis sets like 6-31G** or DZ** are completely unreliable. Thus, the "better" NMR data of ref 35 are due to the insufficient basis set used.

The differences between near Hartree–Fock basis set results for molecules **8**–**11** and experimental data on substituted diazenes appear to be too large to be solely due to gas-to-liquid shifts or temperature effects. A possible second source of deviations between theory and experiment, namely, the influence of the asymmetry of the σ tensor, can be excluded, too. Asymmetry effects should play a role in those cases where both the anisotropy and the difference between the off-diagonal components of σ are large. Although the difference $\sigma_{11} - \sigma_{33}$ for **8** is about 1500 ppm and $\sigma_{xy} - \sigma_{yx}$ = 166 ppm, the line positions change only by 7 ppm to low field for σ_{22} and to high field for σ_{33} in the asymmetric case, leading to a decrease in the anisotropy by approximately 14 ppm, i.e., <1%. The trace $\bar{\sigma}$ of the shielding tensor either from the solution of the symmetric or from the unsymmetric eigenvalue problem are, of course, identical.

We conclude that it is essential to include electron correlation in connection with large basis sets in order to arrive at a correct description of the nitrogen NMR shieldings in these cases. In our previous papers, probably with the exception of molecules containing PP double bonds,[9] effects of electron correlation entered only indirectly via optimized molecular geometries into the calculation of magnetic properties. With the nitrogen atoms of the diazenes and the terminal nitrogen in diazomethane, we have apparently found a type of binding that deserves the direct inclusion of electron correlation.

In view of these findings we shall have to reinvestigate the central nitrogen of the NNO molecule, the NMR shifts of which did not agree with the measurements of Jameson et al.,[17] although they compared rather well with spin-rotation data.[6b] Probably neglecting electron correlation in our calculation is not justified for this molecule, too.

From the orbital contributions to σ(N) (Table V) it is clear that the nitrogen lone pair in amines is in no way exceptional or different from NH or NC bonds. In molecules with nitrogen

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Table V. Anisotropies of the MO Contributions to σ(N)[a,b]

molecule	σ(MO)	σ_{11}	σ_{22}	σ_{33}	MO
ammonia (**1**)	0	−12	−12	25	lp
	4	12	12	−11	N—H
methylamine (**2**)	−7	−8	−2	−11	lp
	6	14	−4	8	N—H
	1	12	15	−25	N—C
dimethylamine (**3**)	−9	2	24	−53	lp
	5	14	−6	7	N—H
	1	12	−19	8	N—C
trimethylamine (**4**)	11	4	4	24	lp
	6	13	14	−10	N—C
aziridine (**5**)	−2	35	−11	−29	lp
	0	23	10	−33	N—H
	13	24	9	6	N—C
methyl cyanide (**6**)	−124	30	−201	−201	lp
	−126	51	−214	−215	N≡C
	−21	2	−32	−32	C—C
methyl isocyanide (**7**)	−55	21	−93	−93	CH_3—N
	−48	114	−128	−128	N≡C
	−35	4	−54	−54	lp(C)
trans-diazene[c] (**8**)	−329	−35	21	−974	lp(N_1)
	−43	−20	9	−117	lp(N_2)
	−131	10	−248	−157	N_1—H
	−3	−1	−22	13	N_2—H
	−191	−4	−257	−313	N=N
trans-diazene[d] (**8**)	−341	−35	20	−1009	lp(N_1)
	−44	−19	9	−121	lp(N_2)
	−133	10	−249	−159	N_1—H
	−3	−0	−22	14	N_2—H
	−198	−5	−257	−332	N=N
cis-diazene[c] (**9**)	−272	−49	40	−805	lp(N_1)
	−9	2	−59	30	lp(N_2)
	−159	4	−236	−245	N_1—H
	−16	−12	9	−46	N_2—H
	−177	−8	−393	−130	N=N
cis-diazene[d] (**9**)	−259	−55	40	−761	lp(N_1)
	−14	3	−69	25	lp(N_2)
	−156	6	−254	−219	N_1—H
	−17	−14	11	−47	N_2—H
	−184	−8	−390	−154	N=N
trans-dimethyldiazene (**10**)	−339	−20	19	−1016	lp(N_1)
	−37	−15	11	−107	lp(N_2)
	−136	0	−251	−157	N_1—C
	−2	−1	−21	17	N_2—C
	−192	−9	−240	−326	N=N
cis-dimethyldiazene (**11**)	−253	−27	39	−772	lp(N_1)
	−8	0	−56	32	lp(N_2)
	−165	1	−228	−268	N_1—C
	−16	−11	8	−44	N_2—C
	−173	−7	−394	−118	N=N
diazomethane (**12**)					
$H_2C\mathit{N}N$	−7	42	20	−84	4e3c[e]
	−97	65	−222	−135	N=N
	−34	3	−67	−39	lp(N_2)
	−92	24	−112	−187	N—C
$H_2CN\mathit{N}$	−292	−44	17	−848	4e3c[e]
	−152	−142	−287	−24	N=N
	−70	−3	−239	32	lp(N_2)
	−25	−39	−40	2	N—C
aniline (**13**)	−6	9	14	−41	lp
	0	−1	−10	11	N—H
	−16	18	−34	−31	N—C
benzonitrile (**14**)	−120	30	−185	−206	lp
	−143	−9	−204	−216	N≡C
	−18	2	−28	−28	C—C
hydrazine (**15**)	−29	−12	−81	7	lp(N_1)
	2	2	3	−0	lp(N_2)
	1	14	12	−22	N—N
	−5	5	4	−24	N—H

[a] Absolute shielding, projected to the principal axes of σ(N), in ppm; basis II. [b] For the orientation of the principal axes, see text. [c] Theoretical geometry from ref 37. [d] Experimental geometry. [e] 4e3c means four-electron, three-center bond.

Table VI, Carbon NMR Shifts[a]

molecule	DZ	II	III[b]	expt	
				c	*d*
methylamine (**2**)	26.7	26.6	25.9	28.3	
dimethylamine (**3**)	33.8	33.8	33.7	38.2	
trimethylamine (**4**)	55.0	55.0		47.6	
aziridine (**5**)	14.1	12.2	11.7	18.2	
methyl cyanide (**6**)					
CH_3	6.8	0.5	−1.0	0.3	
CN	133.3	122.3	123.8	117.7	
methyl isocyanide (**7**)					
CH_3	27.1	24.1	23.0	26.8	29.3
NC	196.0	188.1	186.0	158.2	158.5
trans-dimethyldiazene (**10**)	53.5	51.7			
cis-dimethyldiazene (**11**)	57.4	52.7			
diazomethane (**12**)	52.7	28.6	23.4	23.1	
aniline (**13**)					
C1	150.0	153.2		146.7	148.7
C2	113.0	113.5		115.1	114.4
C3	137.6	137.1		129.3	129.1
C4	120.3	119.6		118.5	116.3
benzonitrile (**14**)					
C1	115.4	115.0		112.8	109.4
C2	136.6	136.3		132.1	129.8
C3	131.8	132.2		129.2	126.9
C4	137.0	137.6		132.8	129.8
CN	129.3	116.0		119.5	115.9

[a] In ppm relative to TMS. [b] Converted to the TMS scale, assuming $\sigma(CH_4) - \sigma(TMS) = 5.7$ ppm for basis III. [c] Reference 21. [d] Reference 22.

atoms involved in multiple bonds, however, the anisotropy of the nitrogen lone pair governs the orientation of the principal axis systems; the next important contributions come from CN triple and NN double bonds, followed by N_1H bonds, which are not different from N_1C bond contributions.

The contribution from the nitrogen 1s AO is strongly shielding (236.0 ppm), isotropic, and almost independent of the basis set used and is not shown in the tables. Functional groups show only slightly varying isotropic contributions to σ(N) in different molecules. They even do not differ much for different basis sets, provided the latter are chosen reasonably large (i.e., basis II or larger). In hydrogen cyanide,[6b] acetonitrile (**6**), and benzonitrile (**14**) the nitrile group has a deshielding effect of approximately 255 ppm on nitrogen, although the magnitudes of the principal components of the constituting MOs (the CN triple bond and the nitrogen lone pair) differ considerably.

For the diazenes the most shielding principal component σ_{11} of σ(N) is perpendicular to the molecular plane, and the least shielding one approximately along the NH or NC bond. These observations hold true for aziridine, too. In acetonitrile, benzonitrile, and methyl isocyanide σ_{11} is along the C_3 and C_2 axes, and so behaves the central nitrogen of diazomethane. For the terminal N, however, the C_2 axis corresponds to the least shielding component σ_{33}, and σ_{11} is in the molecular plane, perpendicular to σ_{33}.

Taking care of the precautions mentioned at the beginning of this section, general trends for nitrogen NMR shifts can be seen from Tables II–V. For molecules without NN multiple bonds calculated and experimental shifts are in good agreement. Terminal nitrogens, the lone-pair electrons of which are more easily involved in interactions with their neighbors, are calculated to be more deshielded than what is found experimentally; e.g., isonitriles are described better than nitriles. These deviations, which are in a range of about 40 ppm, can be explained for most of the molecules in this study by gas-to-liquid shifts of the NMR signals. For different types of nitrogen atoms the latter are observed to show different signs, varying from approximately −25 to +15 ppm.

Nitrogen atoms involved in NN multiple bonds are found to be considerably more shielded in experiment than in our calculations.

V. Carbon Chemical Shifts

Compared to the shifts for nitrogen, calculated carbon NMR shifts (Table VI) do not cause severe problems. The agreement between theory and experiment is already good for DZ basis sets and improved further by using basis sets II and III. This statement is in line with our findings in previous investigations and explicitly

Table VII. Principal Values of Carbon Shielding Tensors[a,b]

molecule	σ_{11}	σ_{22}	σ_{33}
methylamine (**2**)	193	154	152
	189	150	147
dimethylamine (**3**)	194	144	138
	190	139	134
trimethylamine (**4**)	200	125	89
aziridine (**5**)	217	179	145
	213	176	140
methyl cyanide (**6**)			
CN	297	−43	−43
	296	−52	−52
	(283)[c]	(−28)[c]	(−28)[c]
CH_3	206	185	185
	199	184	184
	(196)[c]	(191)[c]	(191)[c]
methyl isocyanide (**7**)			
NC	259	−123	−123
	260	−127	−127
CH_3	200	153	153
	194	151	151
trans-dimethyldiazene (**10**)	180	122	122
cis-dimethyldiazene (**11**)	160	150	110
diazomethane (**12**)	215	166	111
	210	163	121
aniline (**13**)			
C1	169	19	−69
C2	180	76	−19
C3	189	45	−67
C4	192	66	−38
benzonitrile (**14**)			
C1	183	86	−35
	(170 ± 4)[d]	(89 ± 7)[d]	(−18 ± 2)[d]
C2	188	43	−62
	(179 ± 4)[d]	(13 ± 2)[d]	(−9 ± 4)[d]
C3	193	47	−58
	(179 ± 3)[d]	(15 ± 2)[d]	(−2 ± 3)[d]
C4	193	41	−69
	(184 ± 7)[d]	(35 ± 11)[d]	(−39 ± 4)[d]
CN	311	−35	−46
	(281 ± 5)[d]	(−20 ± 9)[d]	(−38 ± 14)[d]

[a] Absolute shieldings in ppm; data computed with bases II and III are shown in consecutive lines, followed by experimental data in parentheses, if available. The latter have been converted to the absolute scale, using σ(TMS) = 192.7 ppm (IGLO, basis II). [b] For the orientation of the principal axes and a discussion of the experimental anisotropies, see text. [c] Reference 27. [d] Reference 23.

includes molecules with CN multiple bonds. Although the trace of σ(C) does not change much in going from basis II to basis III, the principal values of σ do change. In general, the large basis leads to smaller anisotropies $\Delta\sigma$ that are closer to experimental ones.

Anisotropies are much more sensitive to changes in the basis sets, and the available experimental data, mainly from liquid crystals, lead to values for $\Delta\sigma$ that are smaller than those from our calculations. Low-temperature crystalline data seem to agree somewhat better with our results, at least for strained hydrocarbons.[7] In acetonitrile we find $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} = 348$ ppm (basis III) for $^{13}C{\equiv}N$; liquid crystal data are 307 ± 4 ppm[41] and 311 ± 30 ppm,[27] and the experimental value of 204 ± 3 ppm[40] seems to be in error.

The principal axes of σ cannot be obtained from experiment except in those cases where they are completely defined by symmetry. One example is the carbon atoms C_2 and C_3 of benzonitrile (**14**). The in-plane components σ_{ii} (ii = aa, bb) are given along the CH bond and perpendicular to it in ref 12, although these directions are not required by symmetry to be the principal axes. As far as the σ_{ii} are concerned, the deviations between IGLO and experiment are larger for these two atoms than for the others, but our calculation reveals that the assumptions about the directions of σ_{aa} and σ_{bb} are correct to within 1°. To have a closer look at the deviations we would like to have another experimental set of data on **14**, preferentially from investigations in the solid state.

VI. Conclusions

We have applied the IGLO method to various classes of nitrogen-containing molecules. Keeping in mind that we calculate magnetic properties of single molecules at a fixed geometry, while experimentally additional shielding or deshielding effects due to intermolecular interactions of different types cannot be avoided—a fact that is especially important for the nitrogen lone-pair electrons—susceptibilities as well as carbon and nitrogen NMR chemical shifts are rather close to the experiment. When experimental gas-phase NMR data are available, we find excellent agreement with our calculations. It is somewhat better for the trace of the respective property than for the principal components of the tensors.

Contrary to carbon atoms, where basis sets of double-ζ quality give satisfactory results, triple-ζ bases plus polarization functions are necessary for nitrogen.

There is one important exception. NMR chemical shifts of those nitrogen atoms that are involved in an NN multiple bond, in diazenes, for example, are calculated to be much too paramagnetic, even in the limit of very large basis sets. In order to arrive at a correct description of the nitrogen shifts in these cases, we think that correlation must be taken into account. We plan to develop a method that includes electron correlation effects, based on a localized description like IGLO.

Nevertheless, the influence of solvent effects on NMR parameters, which is of great importance in hydrogen-bonded systems like ammonia, water, or hydrogen fluoride, can be handled by coupled Hartree–Fock type methods and will be discussed in a forthcoming paper.[39]

Acknowledgment. The author is grateful to Ulrich Fleischer and Prof. W. Kutzelnigg for valuable discussions and for critically reading the manuscript. The computations were done at the Cyber 205 vector computer of the Ruhr-Universität Bochum.

Registry No. **1**, 7664-41-7; **2**, 74-89-5; **3**, 124-40-3; **4**, 75-50-3; **5**, 151-56-4; **6**, 75-05-8; **7**, 593-75-9; **8**, 15626-43-4; **9**, 15626-42-3; **10**, 4143-41-3; **11**, 4143-42-4; **12**, 334-88-3; **13**, 62-53-3; **14**, 100-47-0; **15**, 302-01-2.