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NMR Shielding Tensors and Indirect Spin–Spin Coupling Tensors in HCN, HNC, CH_3CN, and CH_3NC Molecules

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The shielding and indirect spin–spin coupling tensors are calculated for HCN, HNC, CH_3CN, and CH_3NC, using large atomic basis sets and multiconfiguration wavefunctions that contain the most important correlation effects. The isotropic and anisotropic components of the tensors are compared with experimental data. Deviations between the calculated and experimental results appear to be largely due to vibrational and solvent effects. © 1995 Academic Press, Inc.

INTRODUCTION

Significant progress has been made during the past few years in ab initio studies of shielding tensors and indirect spin–spin coupling tensors. The requirements for reliable shielding and spin–spin coupling tensor calculations are very different. For the shielding, theoretical methods must be used which yield gauge origin-independent results. Self-consistent-field (SCF) calculations often give qualitatively correct shielding tensors. Electron correlation effects are required to obtain accurate results, in particular for molecules with double bonds or lone pairs. Various methods that differ in the treatment of the correlation effect have recently successfully been applied to a variety of molecular systems (*1–3*). In contrast, the calculation of spin–spin coupling tensors is notoriously unreliable within the SCF approximation. This is due to the fact that SCF wavefunctions are often unstable with respect to triplet perturbations. Neither the Fermi contact nor the spin–dipole contribution to the spin–spin couplings can therefore be described in this approximation. Recent progress in the use of correlated wavefunctions (*4–6*) has improved spectacularly the accuracy of ab initio results.

In this work, we use ab initio multiconfiguration self-consistent-field (MCSCF) wavefunctions to calculate the shielding tensors and indirect spin–spin coupling tensors in HCN, HNC, CH_3CN, and CH_3NC. The approach is the same as the one we used in recent works (*7–9*), where NMR parameters were calculated successfully for similar molecular systems. In this study we extend our discussion to the anisotropies of both the shielding and the spin–spin coupling tensors, as some experimental data are available for these quantities.

THEORY AND COMPUTATIONAL DETAILS

The theory of NMR shielding tensors and indirect spin–spin coupling tensors is well known; see, for example, Refs. (*10–13*). We only outline the basic ideas here to emphasize some fundamental aspects of this work.

Both the shielding tensor $\boldsymbol{\sigma}(X)$ and the spin–spin coupling tensor $\mathbf{J}(XY)$ are second-order molecular properties. The shielding tensor is determined by considering the terms in the perturbation expansion proportional to the external magnetic field and the magnetic moment of nucleus X. The spin–spin coupling tensor describes the contributions that are bilinear in nuclear magnetic moments of X and Y. The contributions to $\boldsymbol{\sigma}(X)$ and $\mathbf{J}(XY)$ consist of response and average value terms. The response terms can be calculated from second-order perturbation theory and can be represented as the linear response functions $\langle\langle \mathbf{A};\mathbf{B}\rangle\rangle_0$, where $\mathbf{A}$ and $\mathbf{B}$ denote the perturbation operators and subscript 0 indicates that the linear response function is taken at the zero frequency (*14*). When SCF wavefunctions are used, the $\langle\langle \mathbf{A};\mathbf{B}\rangle\rangle_0$ are given by the time-dependent Hartree–Fock (TDHF) approximation. This approximation is also known as the coupled Hartree–Fock (CHF) method or the random-phase approximation (RPA) (*15*). In this work, we use MCSCF wavefunctions to compute the linear response properties. This approach has recently been successfully applied in calculations of numerous molecular properties, including the NMR parameters (*1, 4, 7–9, 16, 17*).

For the shielding tensor, the operators $\mathbf{A}$ and $\mathbf{B}$ correspond to the angular momentum operator $\mathbf{L}$ and the orbital hyperfine operator (paramagnetic spin–orbit operator) $\mathbf{L}_X/r_X^3$, where the subscript X indicates that the operator is defined with respect to the nucleus X. For the spin–spin coupling constants, $\mathbf{A}$ and $\mathbf{B}$ represent the paramagnetic spin–orbit, spin–dipole, or Fermi-contact operators. Only the $\langle\langle \mathbf{A};\mathbf{A}\rangle\rangle_0$ terms contribute to the isotropic constants; the anisotropy depends also on the mixed spin–dipole–Fermi-contact term. The diamagnetic contribution to $\boldsymbol{\sigma}(X)$ and the diamagnetic spin–orbit contribution to $\mathbf{J}(XY)$ are

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calculated as average values of the terms in the total Hamiltonian bilinear in two perturbations.

The perturbation operators **A** and **B** are vectors and the resulting second-order property is a tensor. In NMR experiments in solution only the trace of the tensors $\boldsymbol{\sigma}$ and **J** is observed. In contrast, theoretical calculations give all tensor components straightforwardly, that is, nine independent numbers for each tensor. It does not appear likely that all these components may be measured experimentally in the near future, although progress has been made toward setting up specific NMR experiments to yield these quantities. In particular, experimental results are available which give information about the anisotropy and asymmetry of the tensor. In this work, we report only the isotropic average and the anisotropy. The definitions we use are $X_{Av} = (X_{11} + X_{22} + X_{33})/3$ and $\Delta X = X_{33} - (X_{11} + X_{22})/2$, where X is σ or J. We will not discuss the antisymmetric part of any tensors. Thus, the values of X_{ii} are determined by diagonalizing the symmetric part of the tensor $\boldsymbol{\sigma}$ or **J**, and we select as σ_{33} the component with the largest value, and as J_{33} the component with the largest absolute value. For axial tensors, this definition of $\Delta\sigma$ coincides with the recently proposed definition of span $\Omega = \sigma_{33} - \sigma_{11}$, where σ_{11} is the smallest tensor component (*18*). For the hydrogen atoms in the CH_3 group, the calculated span is 10–20% larger than $\Delta\sigma$. We will use the standard symbol $^nJ(XY)$ for the isotropic average of the coupling tensor through n bonds, and $^1J(C{\equiv}N)$ for the coupling across the triple bond. We omit the subscript "Av" in this case.

The approach we have taken and the approximations we have applied are similar to those used in our earlier calculations for HN_3 and CH_2N_2 molecules (*8, 9*). The CH_3CN and CH_3NC molecules are isoelectronic with CH_2N_2, so the computational limitations (basis sets, treatment of correlation effects) are similar for these systems. We outline here the main points of the computational technique and refer to (*8, 9*) for a more thorough discussion.

Two contracted Gaussian-type orbital (CGTO) basis sets, called basis III and IV in (*8, 9*), have been applied throughout this work. In the shielding-tensor calculations we have used London orbitals (*19*), also known as GIAOs (gauge invariant atomic orbitals) (*20, 21*). In basis III, the C and N atoms are described by a $[11s7p2d/7s6p2d]$ set, and for the H atoms a $[6s2p/4s2p]$ contraction is used. Basis IV has somewhat different contractions for s and p orbitals and more polarization functions. The contractions for C and N are $[11s7p3d1f/8s7p3d1f]$ and for H $[6s3p1d/5s3p1d]$ (see Ref. (*1*) for more details). For HCN and HNC we present the results obtained with the larger basis IV; for CH_3CN and CH_3NC mainly the smaller basis set values are given. Test calculations indicate that basis III is large enough to give results which are fairly saturated. For CH_3CN and CH_3NC basis IV has 210 functions, and a systematic calculation of all properties using this basis set becomes computationally too expensive. We have compared basis III and IV results (for various wavefunction approximations) for CH_3NC shielding tensors and Fermi-contact contributions to the spin–spin coupling tensors (largest term in most cases) and found only small differences.

For each molecule we have used SCF and two MCSCF wavefunctions. The SCF results are reported for the shielding tensors. However, the emphasis is on comparison of our correlated values and other theoretical and experimental results. For the spin–spin coupling, the SCF values are often meaningless, and only correlated results are discussed. The first functions for HCN and HNC are complete-active-space (CAS SCF) functions that include all the valence orbitals in the active space. The second MCSCF functions are RAS SCF (restricted-active-space SCF), in which additionally single and double excitations are considered in six more active orbitals. Hence, for these two molecules we include some effects of dynamic correlation. For CH_3CN and CH_3NC the first MCSCF functions are of the CAS SCF type and include in the active space the occupied valence SCF orbitals and two more orbitals. The second MCSCF functions are RASSCF functions which in addition allow single and double excitations into all the remaining valence shell orbitals. Thus, the RASSCF function provides an approximation to full valence CAS SCF. For each molecule, the configuration expansion for the first MCSCF function (CASSCF) includes less than 5000 determinants, and for the second (RASSCF) about 300,000 determinants. We shall discuss primarily the results obtained with the larger RASSCF functions.

The molecular geometries are taken from other ab initio studies and experiment: HCN (*22*), HNC (*23*), CH_3CN (*24*), and CH_3NC (*25*). We use the symbol C1 for the carbon atom of the CH_3 group, and C2 for the carbon atom in the C≡N bond.

RESULTS AND DISCUSSION FOR SHIELDING TENSORS

The calculated shielding tensors are listed in Table 1. Our SCF results are in good agreement with other SCF results; see Refs. (*23, 26–28*). For example, the differences between our values and those of Cybulski and Bishop (*23*) for HCN and HNC are on the order of 1 ppm (usually much smaller) for σ_{Av} and 2 ppm for $\Delta\sigma$. For CH_3CN the differences are larger, on the order of 10 ppm for C and N, as different geometries have been used. We used the geometry of Ref. (*24*), and our results and the results in Ref. (*24*) do not differ by more than 2 ppm. Finally, for CH_3NC our results agree very well with those of Ref (*28*). In summary, the GIAO basis sets are sufficiently large for results close to SCF basis set limit.

The triply bonded atoms show a systematic correlation correction: the σ_{Av} are larger than the corresponding SCF results, and the $\Delta\sigma$ are smaller. Our results for HCN and

TABLE 1
Calculated Nuclear Shielding Tensors, Average Values σ_{Av} and Anisotropies $\Delta\sigma$ (in ppm)

	H		C1		C2		N	
	σ_{Av}	$\Delta\sigma$	σ_{Av}	$\Delta\sigma$	σ_{Av}	$\Delta\sigma$	σ_{Av}	$\Delta\sigma$
				SCF				
HCN	29.21	14.71	—	—	71.06	309.70	−50.44	584.61
CH_3CN	30.35	10.21	190.99	17.97	61.76	351.12	−45.03	526.51
HNC	28.18	21.84	—	—	3.04	404.65	94.35	376.54
CH_3NC	28.81	8.71	165.17	43.36	1.68	388.15	87.29	412.76
				MCSCF				
HCN	29.31	14.87	—	—	86.76	287.31	2.63	506.35
CH_3CN	30.38	10.27	192.64	20.95	82.56	309.22	18.59	455.47
HNC	27.88	21.98	—	—	34.82	359.05	110.64	352.08
CH_3NC	28.99	8.76	169.90	42.81	38.99	339.08	106.94	371.26

HNC are in agreement with the MP2 values (*23*); for CH_3CN the MP2 correlation corrections are smaller (*24*). Since the correlation treatments in MCSCF and MP2 are very different, this suggests that the most important correlation effects have been properly described. A recent study indicates that higher-order perturbation corrections can significantly affect $\sigma(N)$ in HCN (*26*). The correlation corrections to $\sigma(N)$ in HCN and CH_3CN are more difficult to describe in MCSCF than for the other atoms. The differences between our two MCSCF results are on the order of 15 ppm. In contrast, for $\sigma(N)$ in HNC and CH_3NC and for all carbon atoms the differences are on the order of 5 ppm. It appears that further extensions of the active space would result in smaller changes in the shielding constants (*1*).

From a knowledge of property surfaces we may study the temperature dependence of the molecular properties, as the property values can be computed for the different rovibrational states (*5, 29, 30*). However, such a detailed study is not feasible for many-electron polyatomic molecules. We have considered here the effect of stretching the triple bond for HCN and HNC. An SCF study of shielding derivatives (*31*) suggests that this is the most important geometrical coordinate. Table 2 presents the results obtained for the shielding tensors. These show a very systematic trend where σ_{Av} decreases while $\Delta\sigma$ increases with the stretch of the C≡N bond.

We have calculated from the data in Table 2 the values of the properties, at R_e, the energy minima for the used wavefunctions. The minima for HCN and HNC are very close to our initial R values; hence the results for all the properties are practically the same as those given for R. The first derivatives of $\sigma(C)$ and $\sigma(N)$ in HCN are on the same order of magnitude as the SCF values given by Chesnut and Wright (*31*); the second derivatives are somewhat smaller. The SCF values of Ref. (*31*) indicate that the effects of C≡N bond stretch are similar in HCN and CH_3CN. It appears that the values at $R \pm 0.1$ in Table 2 give reasonable upper estimates of the rovibrational effects for the isotropic shielding constants and the anisotropies.

The comparison of calculated and experimental isotropic shielding constants involves many steps (*32*). The experimentally measured quantity is usually the chemical shift with respect to a reference compound, and conversion to the absolute shielding scale is required. The measured liquid (or low-density gas) value has to be modified to predict the isolated molecule result. The SCF calculations of Jackowski (*33, 34*) for $(CH_3CN)_n$, $n = 1,2,3$, indicate very large gas-to-liquid changes in the shielding, approximately −7 ppm for the C atom in the triple bond and 16 ppm for the N atom. These values are on the same order of magnitude as

TABLE 2
Dependence of the Calculated Shielding Tensors on the C≡N Bond Length

	H		C		N	
	σ_{Av}	$\Delta\sigma$	σ_{Av}	$\Delta\sigma$	σ_{Av}	$\Delta\sigma$
			HCN			
$R - 0.1$	29.48	14.69	95.27	277.56	21.41	480.57
R	29.31	14.87	86.76	287.31	2.63	506.35
$R + 0.1$	29.12	15.09	76.58	299.93	−16.76	533.39
			HNC			
$R - 0.1$	27.99	21.76	45.57	345.95	122.05	337.21
R	27.88	21.98	34.82	359.05	110.64	352.08
$R + 0.1$	27.74	22.24	24.49	371.94	96.77	370.95

Note. The values for σ_{Av} and $\Delta\sigma$ are in ppm, the C≡N bond length is in atomic units, $R = 2.18452$ a.u. in HCN, and $R = 2.20059$ a.u. in HNC.

the experimental estimates. Finally, the result for a single molecule derived from experiment refers to the rovibrationally averaged shielding, not to the value of the lowest rovibrational state or the geometry at the potential minimum. As indicated by the geometry dependence of Table 2, for both atoms in the C≡N bond this introduces another factor of uncertainty, on the order of 10 ppm.

Similar problems arise in the comparison of $\Delta\sigma$ with experiment. The SCF calculations (*33, 34*) suggest that the association effect in CH_3CN is small for the carbon atoms, but large for the nitrogen atom, for which the shielding anisotropy may be reduced by almost 30 ppm.

In Table 3, we compare our results with experiment. For HNC, since there are no experimental values, we have included a set of other ab initio results (*23*). Comparison of the calculated and experimental shielding for the triply bonded carbon atoms suggests that the σ_{Av} are too large, whereas the $\Delta\sigma$ appear to be ~20 ppm too small. This appears to be a systematic trend, although some deviations occur in the reported experimental shielding. Our MCSCF functions appear to overestimate the correlation corrections, and this explains some of the differences between theory and experiment. At the same time, these differences would diminish with the elongation of the triple bond, as shown in Table 2. This confirms the need for a systematic study of rovibrational effects.

RESULTS AND DISCUSSION FOR INDIRECT SPIN–SPIN COUPLING TENSORS

All the indirect spin–spin coupling tensors are given in hertz for the ^1H, ^{13}C, and ^{15}N isotopes. For a fixed molecular geometry the tensors for the other isotopes can be obtained from the magnetogyric ratios.

In Table 4 we compare our isotropic values with experiment. Many other experimental values have been reported for isotropic constants (see, e.g., (*55, 56*) and the references in Table 4). They have not been quoted, as the differences are usually negligible (on the order of 1% or smaller). No experimental data exist for HNC. We have therefore included another set of ab initio results in the table for this molecule.

The agreement between the calculated isotropic constants and experiment is in general satisfying. Our results for HCN

TABLE 3
Comparison of the Calculated Shielding Tensors with Experimental Data

	H		C1		C2		N	
	σ_{Av}	$\Delta\sigma$	σ_{Av}	$\Delta\sigma$	σ_{Av}	$\Delta\sigma$	σ_{Av}	$\Delta\sigma$
				HCN				
Calc.	29.31	14.87	—	—	86.76	287.31	2.63	506.35
Exp.	28.32[a]	—	—	—	82.1[b]	316.3 ± 1.2[c]	−20.4[e]	563[f]
						334 ± 20[d]		
				CH_3CN				
Calc.	30.38	10.27	192.64	20.95	82.56	309.22	18.59	455.47
Exp.	29.06[g]	2.1[h]	187.7[b]	22.9[h]	73.8[b]	324.6[h]	−9.1[e]	488 ± 8[k]
						378 ± 20[j]	0.6[e]	
						307 ± 4[j]		452 ± 10[j]
				HNC				
Calc.	27.88	21.98	—	—	34.82	359.05	110.64	352.08
Theor.[l]	27.97	23.09	—	—	33.17	362.15	107.51	357.27
				CH_3NC				
Calc.	28.99	8.76	169.90	42.81	38.99	339.08	106.94	371.26
Exp.	—	4.26 ± 0.01[m]	165.9[n]	52.4 ± 0.3[m]	34.5[n]	359 ± 5[m]	130[o]	360 ± 73[o]
							83.8[p]	

Note. We refer to the quoted works for a detailed description of the experimental conditions, analysis of error bars, and, in particular, conversion of chemical-shift data to absolute shielding, and numerous references to earlier results. We have attempted wherever possible to select the more recent experimental data or the data which are closer to the calculated values (for example, gas-phase rather than liquid-phase results). The following values should be used if it is necessary to convert chemical-shift data to absolute scale: σ(N) in CH_3NO_2 = −135.8, σ(C) in TMS = 192.7, and σ(H) in TMS = 31.03 ppm.

[a] Ref. (*35*); [b]Ref. (*36*); [c]Ref. (*37*); [d]Ref. (*38*); [e]Ref. (*39*); [f]Ref. (*40*); [g]Ref. (*41*); [h]Ref. (*42*); [i]Ref. (*43*); [j]Ref. (*44*); [k]Ref. (*45*); [l]Ref. (*23*); [m]Ref. (*46*); [n]Ref. (*47*); [o]Ref. (*48*); [p]Ref. (*49*).

TABLE 4
Isotropic Indirect Spin–Spin Coupling, J_{Av}, in Hertz

	HCN		CH_3CN		HNC		CH_3NC	
	This work	Other results	This work	Other results	This work	Other results	This work	Other results
^1J(C≡N)	−19.83	−18.5	−21.55	−17.8	−10.47	−15.46	−12.57	−8.88
^1J(CC)	—	—	71.97	58.0	—	—	—	—
^1J(CN)	—	—	—	—	—	—	−19.26	−10.7
^1J(CH)	249.27	267.3	142.43	135.73	—	—	143.50	145.2
^1J(NH)	—	—	—	—	−112.61	−113.65	—	—
^2J(CC)	—	—	—	—	—	—	−5.23	—
^2J(CN)	—	—	2.82	2.9	—	—	—	—
^2J(HC)	—	—	−15.46	−9.94	16.44	22.02	—	—
^2J(HN)	−6.44	−8.7	—	—	—	—	4.46	3.11
^2J(HH)	—	—	−22.91	−16.9	—	—	−19.05	—
^3J(HC)	—	—	—	—	—	—	2.63	2.72
^3J(HN)	—	—	−2.03	−1.63	—	—	—	—

Note. The quoted results are as follows: HCN experimental data from Ref. (*38*); CH_3CN experimental data from Ref. (*50*) (the error bars do not exceed 0.2 Hz), and ^2J(HH) from Ref. (*51*, p. 36); HNC ab initio results from Ref. (*52*); and CH_3NC experimental data from Ref. (*53*) for ^1J(CN) and ^1J(CH) and Ref. (*54*) for the other constants (recomputed from ^{14}N data when needed).

are also similar to the results of Galasso (*52*), who obtained for ^1J(C≡N), ^1J(CH), and ^2J(HN) −22.32, 243.70, and −8.32 Hz, respectively. For CH_3CN, all seven values of the larger RASSCF calculation fall between the smaller CASSCF calculation and experiment. The same trend has been observed for HN_3 and diazomethane (*9*). It suggests that both MCSCF functions underestimate the correlation effects. However, the results for CH_3NC do not follow this pattern. Some of the constants agree very well with experiment, while for ^1J(CN) the relative difference is larger than for any other constant.

There are only a few experimental results for the anisotropy of the indirect spin–spin couplings. In Table 5 we compare our results with some other available data. It is difficult to extract the anisotropy of the indirect spin–spin coupling tensor from experiment, and the early results appear to be unreliable (see the comments in (*46*)).

It should be stressed that an important contribution to the anisotropy comes from the mixed spin–dipole–Fermi-contact term. For example, in the CAS SCF calculation for HCN, we find Δ^1J(C≡N) and Δ^1J(CH) to be −49.32 and −70.17 Hz, in fair agreement with our best tabulated values. When we omit this mixed term we obtain −39.08 and +5.15 Hz, respectively, for these anisotropies.

The variation of the spin–spin coupling tensors with the C≡N bond length in HCN and HNC is shown in Table 6. The absolute values of the isotropic constants through this bond (that is, ^1J(C≡N), ^2J(HN) in HCN and ^{2}J(HC) in HNC) decrease with the bond stretch. Conversely, the absolute values of the other two isotropic constants and all the anisotropies increase with the bond length. These results are in agreement with the intuitive interpretation—as the triple bond is stretched, it becomes weaker and the molecular properties become more anisotropic.

CONCLUSIONS

All the parameters of the NMR effective Hamiltonian have been determined for HCN, HNC, CH_3CN, and CH_3NC using MCSCF wavefunctions. In general, good agreement is observed with experiment when available and with other accurate ab initio values. The calculated anisotropies of the

TABLE 5
Anisotropy of the Indirect Spin–Spin Coupling, ΔJ, in Hertz

	HCN	CH_3CN		HNC	CH_3NC	
	This work	This work	Other results	This work	This work	Other results
Δ^1J(C≡N)	−54.64	−50.70	—	−50.49	−47.06	−60.0 ± 3.9
Δ^1J(CC)	—	36.57	30 ± 33	—	—	—
Δ^1J(CN)	—	—	—	—	−17.04	−12.0 ± 2.4
Δ^1J(CH)	−63.34	−28.82	−50	—	−24.70	−108
Δ^1J(NH)	—	—	—	36.39	—	—
Δ^2J(CC)	—	—	—	—	11.64	—
Δ^2J(CN)	—	−7.66	−18 ± 7	—	—	—
Δ^2J(HC)	—	5.12	—	33.34	—	—
Δ^2J(HN)	−19.51	—	—	—	−1.91	—
Δ^2J(HH)	—	−18.97	—	—	−17.65	—
Δ^3J(HC)	—	—	—	—	5.21	—
Δ^3J(HN)	—	−4.30	—	—	—	—

Note. The quoted results are as follows: CH_3CN from Ref. (*42*) and from Ref. (*53*) for Δ^1J(CH); and CH_3NC from Ref. (*46*) (recomputed from ^{14}N data) and from Ref. (*53*) for Δ^1J(CH).

TABLE 6
Dependence of the Calculated Indirect Spin–Spin Coupling Tensors on the C≡N Bond Length

	HCN					
	CH		CN		NH	
	J_{Av}	ΔJ	J_{Av}	ΔJ	J_{Av}	ΔJ
$R-0.1$	240.93	−59.24	−27.47	−52.48	−9.47	−17.73
R	249.27	−63.34	−19.83	−54.64	−6.44	−19.51
$R+0.1$	256.51	−67.68	−12.47	−56.22	−3.87	−21.39
	HNC					
	NC		HC		HN	
	J_{Av}	ΔJ	J_{Av}	ΔJ	J_{Av}	ΔJ
$R-0.1$	−19.22	−48.38	24.13	31.07	−111.00	33.74
R	−10.47	−50.49	16.44	33.34	−112.61	36.39
$R+0.1$	−1.52	−52.62	10.09	35.57	−113.34	39.06

Note. J_{Av} and ΔJ are in Hz, the C≡N bond length is in atomic units, R = 2.18452 a.u. in HCN, and R = 2.20059 a.u. in HNC.

shieldings and spin–spin couplings are as reliable as the isotropic averages. Since similar wavefunctions have been used for a series of molecules (also, for four CH_2N_2 isomers and HN_3 isoelectronic with CH_3CN and CH_3NC (*8, 9*)), we are in a position to judge the overall accuracy of these calculations. With improvements of the calculations—increase of the size of the basis set, and better description of correlation—the accuracy of the results improved systematically. An important problem that remains to be solved is the analysis of the geometry dependence and solvent effects.

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