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Large Long-Range F−F Indirect Spin−Spin Coupling Constants. Prediction of Measurable F−F Couplings over a Few Nanometers

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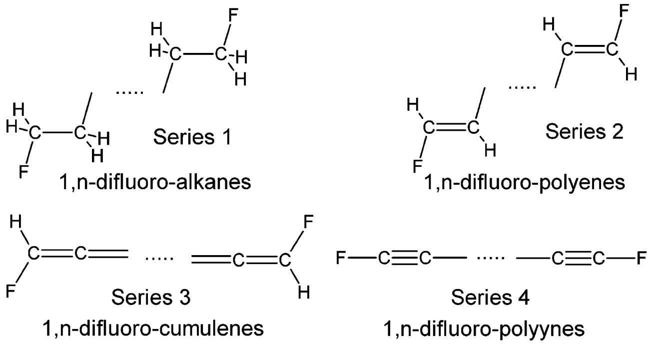
Large long-range indirect nuclear spin coupling constants are of great interest for quantum computers. But they are rarely observed and are usually considered very small, unless the coupled nuclear spins are proximate in space. Looking for counterexamples, we have calculated F−F couplings in four different series of acyclic hydrocarbons (alkanes, conjugated polyenes, conjugated polyynes, and cumulenes) where the coupled fluorine nuclei are separated by up to 11 bonds or 1.4 nm. The calculations were carried out at the level of the second-order polarization propagator approximation using locally dense basis sets. This approach has, in recent years, been shown to be particularly successful in reproducing indirect nuclear spin−spin couplings in organic molecules. We find that the F−F couplings in saturated alkanes diminish very quickly with the number of bonds between the coupled fluorine atoms, whereas in the conjugated polyenes and in particular polyynes the F−F couplings can be transmitted over much longer distances. We predict that the F−F coupling over 9 bonds or 1.1 nm is 12 Hz in (1*E*,3*E*,5*E*,7*E*)-1,8-difluoroocta-1,3,5,7-tetraene and the coupling over 11 bonds or 1.4 nm is 7 Hz in difluorodecapentayne. Analyzing the four Ramsey contributions, we find that the F−F couplings in the polyenes are dominated by the spin−dipolar term, which is known to be favored by π-electronic systems, whereas in the case of the polyynes the orbital paramagnetic terms make the largest contributions, although the spin−dipolar and the Fermi contact contributions are also significant.

Introduction

The search for a quantum computer has been the motivation for many research projects in recent years. Some years ago it was proposed to use nuclear magnetic resonance (NMR) of molecules in solution at room temperature for quantum computations.[1] Many groups took up this idea, and several quantum algorithms have been realized using NMR in solution.[2] In these nuclear magnetic resonance quantum computers (NMR-QC), nuclear spins of molecules take the role of quantum bits which are coupled to each other by indirect, i.e., electron-mediated, nuclear spin−spin coupling constants, *J*. One of the difficulties in this approach is the need for nonvanishing long-range indirect nuclear spin−spin coupling constants in molecules of reasonable size.[1] Often, nuclear spins of fluorine atoms are used as quantum bits in NMR-QC experiments.[3]

Unusually large F−F couplings are found in unsaturated compounds. Peralta et al.[4] have reported that the $^4J_{\mathrm{F-F}}$ couplings in some 1,8-difluoronaphthalenes remain appreciable due to a through-space transmission which occurs thanks to the proximity in space of fluorine substituents and the overlap of their lone pairs. Schaefer et al.,[5] on the other hand, have reported a $^9J_{\mathrm{F-F}}$ coupling of 1.3 Hz in fluorinated derivatives of biphenyl, which was assigned to the conjugative effect between the two phenyl rings.[6] Other examples are the $^5J_{\mathrm{F-F}}$ couplings in 1,4-difluorobenzene and 1,1,4,4-tetrafluorobuta-1,3-diene,[7] where the through-bond coupling is favored by π-conjugation. Recent calculations show that, for both saturated and unsaturated compounds, the F−F couplings are dominated by noncontact contributions.[8,9] F−F couplings in conjugated systems are therefore good candidates for nonvanishing long-range indirect nuclear spin−spin couplings.

CHART 1: Structures of the Model Compounds in the Four Series



To test this hypothesis, we have calculated $^{n+1}J_{\mathrm{F-F}}$ couplings in four series of molecules: (1) 1,*n*-difluoroalkanes, (2) conjugated 1,*n*-difluoropolyenes, (3) 1,*n*-difluorocumulenes, and (4) conjugated 1,*n*-difluoropolyynes (Chart 1).

Experimental fluorine−fluorine couplings are known for 1,2-difluoroethane,[10,11] (*E*)-1,2-difluoroethene,[11−14] 1,1,4,4-tetrafluorobuta-1,3-diene,[15] and difluoroethyne.[16] Several other compounds have been synthesized, but their F−F couplings have not been measured yet: 1,4-difluorobutane,[17] 1,5-difluorohexane,[17] (1*E*,3*E*)-1,4-difluorobuta-1,3-diene,[18] 1,3-difluoropropa-1,2-diene,[19] difluorobutadiyne,[20] and difluorohexatriyne.[21] Substituted conjugated 1,*n*-difluoropolyenes such as derivatives of,

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e.g., (1*E*,3*E*,5*E*)-1,6-difluorohexa-1,3,5-triene[22] and (1*E*,3*E*,5*E*,7*E*)-1,8-difluoroocta-1,3,5,7-tetraene have also been synthesized, but their F−F couplings were not reported either. The longer members of series 3 are probably not stable without further stabilizing substituents. However, the purpose of the present study is not to predict the F−F couplings of a particular molecule but to investigate whether large long-range couplings are, in principle, possible and what kind of electronic system is necessary for that. Therefore, we have calculated the F−F couplings for all molecules in series 1, 2, and 3 without any other substituents.

In particular, we have studied the importance of the four Ramsey contributions, orbital diamagnetic (OD), orbital paramagnetic (OP), spin−dipolar (SD), and Fermi contact (FC), and their dependence on the length of the coupling pathway. The calculations have been carried out at the level of the second-order polarization propagator approximation (SOPPA)[23−25] using locally dense basis sets.[26] In recent years, SOPPA has been shown to give very reliable one-bond and long-range spin−spin coupling constants not only in small molecules[9,24−32] but also in a wide range of carbocyclic compounds.[33]

One should also note the growing interest in the chemistry and NMR spectroscopy of fluorinated organic compounds due to their important biological activity. Furthermore, fluorine has been incorporated into α-helices,[34] proteins,[35] and bioactive small molecules[36] as NMR probes for aggregation, microenvironmental structure, and binding site interactions.

Methods of Calculation

The usual way of describing the different nonrelativistic contributions to the total indirect nuclear spin−spin coupling constants is by splitting them up into four terms, first suggested by Ramsey:[37]

$$ {}^{n}J_{M-N} = {}^{n}J^{\mathrm{OD}}_{M-N} + {}^{n}J^{\mathrm{OP}}_{M-N} + {}^{n}J^{\mathrm{SD}}_{M-N} + {}^{n}J^{\mathrm{FC}}_{M-N} \qquad (1) $$

where the orbital diamagnetic (OD) contribution is a ground-state average value,

$$ {}^{n}J^{\mathrm{OD}}_{M-N} = \frac{1}{3}\frac{\gamma_M\gamma_N}{h}\left(\frac{\mu_0}{4\pi}\right)^2\frac{e^2\hbar^2}{m_{\mathrm{e}}}\sum_{\alpha=x,y,z}\left\langle\Psi_0\left|\sum_i\frac{\vec{r}_{iM}\cdot\vec{r}_{iN}-(\vec{r}_{iN})_\alpha(\vec{r}_{iM})_\alpha}{|r_{iM}|^3\,|r_{iN}|^3}\right|\Psi_0\right\rangle \qquad (2) $$

although it can also be expressed in a form which involves excited states.[38]

The last three contributions can be expressed as sums over excited states as

$$ {}^{n}J^{A}_{M-N} = \sum_{\alpha=x,y,z}\frac{2}{3}\frac{\gamma_M\gamma_N}{h}\sum_{n\neq 0}\frac{\langle\Psi_0|(\hat{\vec{O}}^{\mathrm{A}}_M)_\alpha|\Psi_n\rangle\,\langle\Psi_n|(\hat{\vec{O}}^{\mathrm{A}}_N)_\alpha|\Psi_0\rangle}{E_0-E_n} \qquad (3) $$

where A = OP, SD, and FC, with the following explicit operator expressions:

$$ (\hat{\vec{O}}^{\mathrm{OP}}_M)_\alpha = \frac{\mu_0}{4\pi}\frac{e\hbar}{m_{\mathrm{e}}}\sum_i\frac{(\vec{l}_{iM})_\alpha}{|r_{iM}|^3} \qquad (4) $$

$$ (\hat{\vec{O}}^{\mathrm{FC}}_M)_\alpha = \frac{\mu_0 g_e e\hbar}{3m_{\mathrm{e}}}\sum_i(\vec{s}_i)_\alpha\delta(\vec{r}_{iM}) \qquad (5) $$

$$ (\hat{\vec{O}}^{\mathrm{SD}}_M)_\alpha = \frac{\mu_0}{4\pi}\frac{g_{\mathrm{e}}e\hbar}{2m_{\mathrm{e}}}\sum_i\frac{3(\vec{s}_i\cdot\vec{r}_{iM})(\vec{r}_{iM})_\alpha-\vec{r}^{\,2}_{iM}(\vec{s}_i)_\alpha}{|r_{iM}|^5} \qquad (6) $$

The magnetogyric ratio of nucleus M is γ_M, $\vec{r}_{iM} = \vec{r}_i - \vec{R}_M$ is the difference of the position vectors of electron i and nucleus M, $\vec{s}_i$ is the electron i spin operator, $\vec{l}_{iM} = \vec{l}_i(\vec{R}_M)$ is the orbital angular momentum operator of electron i with respect to the position of nucleus M (in SI units), $\delta(x)$ is the Dirac delta function, and all other symbols in eqs 1−6 have their usual meaning.[39]

The coupling is transmitted by two basic mechanisms: (a) the interaction of the nuclear spins with the spins of the electrons expressed in the Fermi contact (FC) and spin−dipolar (SD) contributions and (b) the interaction of the nuclear spins with the orbital angular momentum of the electrons, which gives rise to the orbital paramagnetic (OP) and orbital diamagnetic (OD) contributions. Due to the interaction with the electron spin, the FC and SD terms arise from admixtures of excited triplet states $|\Psi_n\rangle$ to the singlet ground state $|\Psi_0\rangle$, whereas the OP term involves excited states $|\Psi_n\rangle$ of the same spin symmetry as the ground state $|\Psi_0\rangle$. Using polarization propagator[40,41] or linear response function methods,[42] all contributions to the coupling constants can be evaluated without explicit calculation of the excited states involved.[43] The response of the electronic framework considered at the SOPPA level[23,25] is defined by considering the corresponding singlet or triplet double excitations added to single excitations considered at the level of the random phase approximation (RPA).[44−46] Further details on propagator polarization schemes based on the Møller−Plesset perturbation theory (MP)[47] can be found elsewhere.[23,25,46] Replacement of the MP2 correlation coefficient in the SOPPA equations with the coupled cluster single and double (CCSD) amplitudes yields the SOPPA(CCSD) scheme.[48]

In the present work we have calculated the four contributions to ${}^{n}J_{\mathrm{F-F}}$ with $n = 3$, 5, 7, 9, and 11 (the number of bonds between the coupled fluorine nuclei) within the series of 1,(n − 1)-difluoroalkanes (series 1), conjugated 1,(n − 1)-difluoropolyenes (series 2), 1,(n − 1)-difluorocumulenes (series 3), and conjugated 1,(n − 1)-difluoropolyynes (series 4) at both the SOPPA and SOPPA(CCSD) levels of theory (see Table 1 and Figure 1).

Locally dense basis sets (LDBS)[26] were employed in order to keep the size of the basis sets within the current limitations of the SOPPA implementation in the Dalton program. The aug-cc-pVTZ-J basis set[31,49] was used for fluorine, which ensures the proper cusp behavior of the wave function at the position of the fluorine nuclei, whereas the cc-pVDZ basis set[50] was employed for carbon and hydrogen. In the following we report only the SOPPA results because at the SOPPA(CCSD) level we obtained similar results for all calculated couplings.

In the calculation of the spin−spin couplings, a local version of the Dalton 1.2 program package[51] was used, whereas the molecular geometries were optimized with the Gaussian 98[52] program package at the MP2/6-31G** level of approximation using the very tight optimization option. Geometrical parameters are available on request.

Results and Discussion

General Trends in the Series. In Table 1 and Figure 1, the total F−F coupling constants for series 1, 2, and 4 are shown as a function of the number of bonds, n, between the coupled fluorine atoms. For all the series, the total values of ${}^{n}J_{\mathrm{F-F}}$ follow the same pattern. They start, at $n = 3$, with a large negative

TABLE 1: Trans $^nJ_{F-F}$ Couplings (in Hertz) Calculated at the SOPPA Level Using Locally Dense Basis Sets[a]

n	D(F−F) (nm)	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J	exptl
			1,(n − 1)-Difluoroalkane[b]				
3	0.355	−1.52	−39.97	15.02	−9.88	−36.34	−30[10,c]
5	0.607	−0.71	−0.20	1.70	4.39	5.18	
7	0.861	−0.38	0.49	0.22	0.43	0.76	
			1,(n − 1)-Difluoropolyene[d]				
3	0.354	−1.76	−141.39	23.14	−9.51	−129.52	−132.70,[12] −131.88, −132.43[14] (−130.20, −133.79)[13,e]
5	0.601	−0.76	16.73	25.15	7.28	48.40	35.7[15,f]
7	0.847	−0.40	−2.75	12.89	3.61	13.35	
9	1.094	−0.24	0.68	9.46	2.40	12.29	
			1,(n − 1)-Difluorocumulene[g]				
5	0.583	−0.70	−59.33	39.36	32.35	11.69	
7	0.829	−0.35	−40.63	h	h		
9	1.079	−0.20	−28.95	i	i		
11	1.332	−0.13	−21.68	i	i		
			1,(n − 1)-Difluoropolyyne[j]				
3	0.380	−1.74	−73.68	24.11	7.63	−43.67	2.1[16]
5	0.640	−0.70	47.36	26.67	7.23	80.55	
7	0.899	−0.36	15.42	11.14	3.69	29.89	
9	1.158	−0.22	7.22	5.60	2.02	14.62	
11	1.418	−0.14	3.42	2.92	1.15	7.34	

[a] Basis set: aug-cc-pVTZ-J[31,49] on F; cc-pVDZ[50] on C and H. [b] 1,2-Difluorethane, 1,4-difluorobutane, and 1,6-difluorohexane. [c] Estimated. [d] (1E)-1,2-Difluoroethene, (1E,3E)-1,4-difluorobuta-1,3-diene, (1E,3E,5E)-1,6-difluorohexa-1,3,5-triene, and (1E,3E,5E,7E)-1,8-difluoroocta-1,3,5,7-tetraene. [e] Range of couplings measured for various solvents. [f] In 1,1,4,4-tetrafluorobuta-1,3-diene. [g] (1E)-1,4-Difluorobuta-1,2,3-triene, (1E)-1,6-difluorohexa-1,2,3,4,5-pentaene, (1E)-1,8-difluoroocta-1,2,3,4,5,6,7-heptaene, and (1E)-1,10-difluorodeca-1,2,3,4,5,6,7,8,9-nonaene. [h] Triplet quasi-instability.[i] Triplet instability. [j] Difluoroethyne, difluorobutadiyne, difluorohexatriyne, difluorooctatetrayne, and difluorodecapentayne.

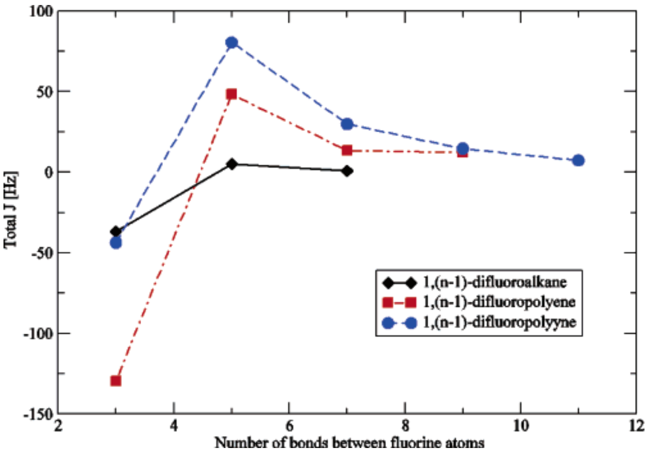

Figure 1. Total indirect nuclear spin−spin coupling constants, $^nJ_{F-F}$, at the SOPPA level for 1,(n − 1)-difluoroalkanes, conjugated 1,(n − 1)-difluoropolyenes, and conjugated 1,(n − 1)-difluoropolyynes.

value, in agreement with the experimental values for *trans*-1,2-difluoroethane,[10] $^3J_{F-F} = -30$ Hz (estimated), and for (E)-1,2-difluoroethene,[11−14] where $^3J_{F-F}$ is in the range between −130.20 and −133.79 Hz, depending on the solvent and the type of measurement. From $n = 3$ to $n = 5$, the total couplings rise to a positive value, and for all larger values of n the total couplings stay positive but fall off asymptotically. In the saturated compounds, the couplings decrease very rapidly. The F−F coupling over seven bonds or 0.86 nm in 1,6-difluorohexane is already less than 1 Hz, whereas the corresponding $^7J_{F-F}$ values in (1E,3E,5E)-1,6-difluorohexa-1,3,5-triene and difluorohexatriyne are ∼13.5 and ∼30 Hz, respectively. For the difluoropolyynes we predict a sizable F−F coupling constant ($^{11}J_{F-F} = 7.3$ Hz) over a distance of 1.4 nm, and the corresponding couplings in the polyene series are only slightly smaller. Connecting the F atoms with a conjugated π-electronic system is obviously a very efficient way of transmitting the F−F spin−spin coupling over large distances. The even larger coupling in the polyynes with two orthogonal π-electronic systems indicates that the fluorine atoms couple via their two orthogonal lone pairs to the π-electronic system.

Although we are not aware of an experimental value for any of the five or more bond couplings, we can at least compare with the value for $^5J_{F-F} = 35.7$ Hz in 1,1,4,4-tetrafluorobuta-1,3-diene.[15] These results support our previous findings[9] that SOPPA calculations with locally dense basis sets are capable of reproducing fluorine−fluorine couplings in organic molecules. We are therefore puzzled by the apparently large disagreement between our calculated value for $^3J_{F-F} = -43.67$ Hz and the only available experimental result ($^3J_{F-F} = 2.1$ Hz) for difluoroethyne[16] measured at low temperature. Earlier semiempirical calculations[53] predict $^3J_{F-F} = -85.4$ Hz, which supports our results. One might wonder whether the assignment of the spectrum was correct.

Triplet Instabilities and Quasi-instabilities. The expression “triplet instability” (or quasi-instability)[54] describes the situation in which the triplet principal propagator[55] or Hessian matrix of a restricted wave function has at least one negative (or positive but very small) eigenvalue, which means that at least one of the triplet excitation energies of the molecule is negative (or positive but very small).[56e,59] This problem arises typically for restricted Hartree−Fock or semiempirical wave functions[56,57] and in particular for molecules with π-electronic systems.[25,28,31,32,58] In this way, the theoretically calculated electronic response of such a molecule will be described incorrectly, and the triplet contributions to the coupling constant, i.e., Fermi contact and spin−dipolar contributions, will be either too large or too small, depending on the sign of the transition moments.

However, this problem can easily be detected by calculating the few lowest eigenvalues of the Hessian matrix, i.e., the few lowest triplet excitation energies. Triplet instabilities or quasi-instabilities can be overcome (a) by removing or adding electron correlation[25,28,31,32,56e,57] or (b) by eliminating one or both of the two two-electron integrals of the corresponding matrix

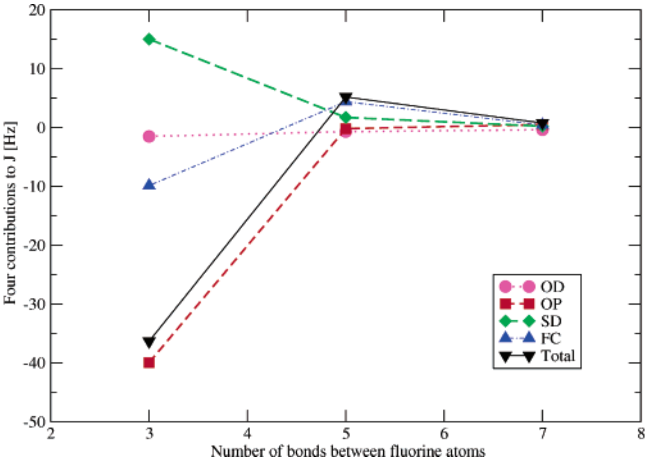

Figure 2. Total indirect nuclear spin−spin coupling constants and the four contributions to ${}^{n}J_{\mathrm{F-F}}$ at the SOPPA level for 1,(n − 1)-difluoroalkanes.

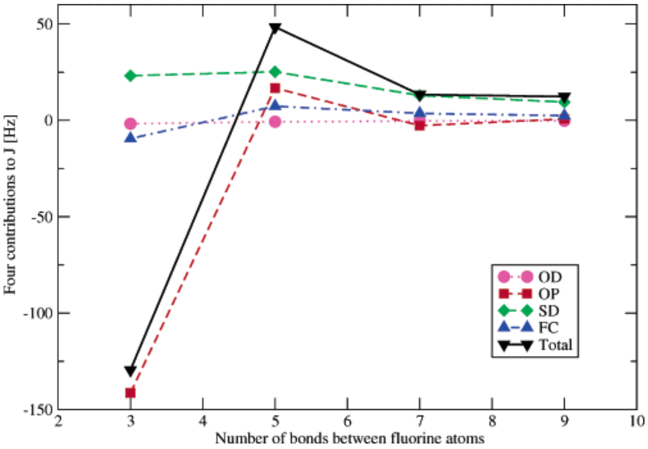

Figure 3. Total indirect nuclear spin−spin coupling constants and the four contributions to ${}^{n}J_{\mathrm{F-F}}$ at the SOPPA level for conjugated 1,(n − 1)-difluoropolyenes.

element[59] in an RPA calculation. Some cases were reported where these problems still remain at the correlated SOPPA level.[25,28]

For series 3, we find a triplet quasi-instability for (1*E*)-1,6-difluorohexa-1,2,3,4,5-pentaene and triplet instabilities for (1*E*)-1,8-difluoroocta-1,2,3,4,5,6,7-heptaene and (1*E*)-1,10-difluorodeca-1,2,3,4,5,6,7,8,9-nonaene at the RPA, SOPPA, and SOPPA(CCSD) levels. The corresponding results are therefore not included in Table 1.

Trends of the Four Contributions. In Table 1 and Figures 2−4, the four Ramsey contributions to the couplings are shown as a function of the number of bonds between the coupled fluorine atoms. Overall we notice that the orbital diamagnetic term is always negative and is almost independent of the type of molecule but decreases monotonically with the length of the molecules. Nothing general can be said about the sign of the orbital paramagnetic contribution. The spin−dipolar term, on the other hand, is always positive. The Fermi contact contribution is also positive in all molecules except 1,2-difluoroethane and (*E*)-1,2-difluoroethene. This behavior does not agree with the Dirac vector model.[60] This model, though basic, is still a useful tool for understanding *J* couplings and predicts that the coupling between two identical atoms (with the same magnetogyric ratio) has the same (opposite) sign for couplings over an odd (even) number of bonds. Hence, the Dirac vector model sequence is followed only by the Fermi contact term in the polyyne series.

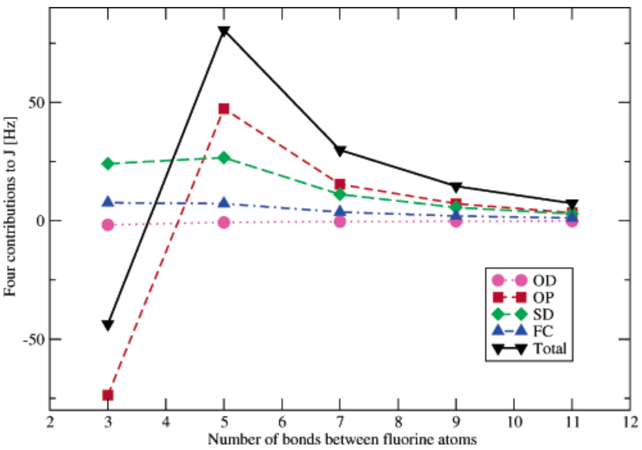

Figure 4. Total indirect nuclear spin−spin coupling constants and the four contributions to ${}^{n}J_{\mathrm{F-F}}$ at the SOPPA level for conjugated 1,(n − 1)-difluoropolyynes.

The vicinal couplings ${}^{3}J_{\mathrm{F-F}}$ are dominated by a large and negative orbital paramagnetic term in all series. The spin−dipolar term is positive and much less important, and the Fermi contact term is even smaller. This distinguishes clearly the fluorine−fluorine couplings from the corresponding proton−proton couplings in the unsubstituted molecules, where the main contribution is the Fermi contact term.[32,61] The OP contribution in (*E*)-1,2-difluoroethene is almost twice as large as that in difluoroethyne and is about 3.5 times the OP term in 1,2-difluoroethane. It is very interesting to note that the Fermi contact term has different signs in 1,2-difluoroethene and difluoroethyne.

The most interesting changes in the couplings are observed when going from the vicinal to the five-bond couplings. In the alkanes, all four terms become much smaller and the FC term changes sign. In the case of the polyenes and polyynes, the OP term changes dramatically. It increases from a large negative value to a reasonable large positive value by $\Delta J^{\mathrm{OP}}_{\mathrm{F-F}} = 158.12$ and 121.04 Hz, respectively. The SD term, on the other hand, increases slightly when the single, double, or triple bond is replaced by two conjugated π-bonds. This shows clearly that the noncontact OP and SD contributions are most influenced by changes in the π-electronic system and benefit most from a conjugate π-system, as reported previously[7] for 1,4-difluorobenzene and 1,1,4,4-tetrafluorobuta-1,3-diene.

In the longer alkanes, we observed the usual pattern: the FC term is larger than the SD term and both die off quickly with increasing length of the coupling pathway. The OP term, on the other hand, oscillates. The spin−dipolar contribution shows the same trend in the conjugated polyenes and polyynes. In both series, the SD term is about 3−4 times the corresponding FC term, with an increasing (decreasing) factor along the series of polyenes (polyynes). In the conjugated polyenes, the SD term is also the largest contribution, as the OP term exhibits an oscillatory behavior and even changes sign along the series. In the conjugated polyynes, on the other hand, the OP term is the largest contribution and dies off monotonically. The OD term is negligible for both series. The largest OP terms are found for the cumulenes. Furthermore, the OP term decreases only slowly with the number of bonds in the cumulenes.

Although the Fermi contact contribution is always less important than the spin−dipolar and orbital paramagnetic contributions in the conjugated systems, it is remarkable that both triplet properties, i.e., the FC and SD terms, change much less along the two series than the orbital paramagnetic contribution. Consequently, there is still a nonvanishing Fermi contact interaction over 1.4 nm in difluorodecapentayne. Furthermore, the FC term is almost the same in difluoroethyne and difluorobutadiyne. This shows that the spin polarization due to the contact interaction between the fluorine nucleus and the s-electrons around this nucleus can also be transmitted over long distances through the π-system.

Concluding Remarks

We have calculated all four Ramsey contributions to the indirect F−F couplings for some 1,*n*-difluoroalkanes, conjugated 1,*n*-difluoropolyenes, conjugated 1,*n*-difluoropolyynes, and 1,*n*-difluorocumulenes at the ab initio SOPPA level using locally dense basis sets. The agreement with the few measured F−F couplings in these molecules is quite good, apart from difluoroethyne. For this molecule we find a large disagreement between our results and earlier calculations and the published value from a single measurement.

Analyzing the four Ramsey contributions to the F−F couplings, we can draw the following conclusions:

(1) The total three-bond couplings are negative in all series and are dominated by a negative orbital paramagnetic term, whereas the total couplings in all longer molecules are positive.

(2) The absolute values of the couplings decrease along the series, with the exception of difluorobutadiyne, where $|^5J_{\mathrm{F-F}}|$ is almost twice as large as $|^3J_{\mathrm{F-F}}|$ in difluoroethyne due to the change in sign of the orbital paramagnetic term.

(3) The couplings die off very quickly with the number of bonds in the saturated 1,*n*-difluoroalkanes. In the conjugated polyenes and polyynes, the F−F couplings can be transmitted over much longer distances. For difluorodecapentayne we predict a F−F coupling of ~7 Hz over a distance of 1.4 nm or 11 bonds.

(4) The F−F couplings in molecules with conjugated π-systems are dominated by the noncontact OP and SD contributions. In both cases, the overall behavior of the OP and SD contributions is similar, though they have different relative values. In the polyynes, the OP term is always larger but also decreases faster than the SD term. In the conjugated polyenes, on the other hand, the spin−dipolar term is the dominating contribution. This feature is completely unusual for other types of couplings. In 1,4-difluorobuta-1,3-diene the OP term is still larger than the FC term, whereas in the longer molecules of this series the FC term is more important than the OP term. In general, also the Fermi contact term is still important for couplings over a nanometer or 11 bonds.

(5) We find triplet instabilities or quasi-instabilities for the longer 1,*n*-difluorocumulenes.

But our most important conclusion is that there should be measurable couplings between fluorine nuclear spins separated by distances of a few nanometers. Our results suggest that one could find F−F coupling constants of a few hertz in 1,*n*-difluoropolyens or 1,*n*-difluoropolyynes over even longer distances. From the asymptotic behavior of the calculated couplings in the 1,*n*-difluoropolyynes, we can estimate couplings of $J_{\mathrm{F-F}} \approx 3.6$ Hz over 13 bonds or a distance of ~1.6 nm and of $J_{\mathrm{F-F}} \approx 1.8$ Hz over 15 bonds or a distance of ~2 nm.

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References and Notes

(1) (a) Gershenfeld, N. A.; Chuang, I. L. *Science* **1997**, *275*, 350−356. (b) Warren, W. S. *Science* **1997**, *277*, 1688−1689. (c) Gershenfeld, N. A.; Chuang, I. L. *Science* **1997**, 1689−1690.

(2) For example: (a) Chuang, I. L.; Gershenfeld, N.; Kubinec, M. *Phys. Rev. Lett.* **1998**, *80*, 3408−3411. (b) Jones, J. A.; Mosca, M. *J. Chem. Phys.* **1998**, *109*, 1648−1653.

(3) For example: Tei, M.; Mizuno, Y.; Manmoto, Y.; Sawae, R.; Takarabe, K. *Int. J. Quantum Chem.* **2003**, *95*, 554−557.

(4) (a) Peralta, J. E.; Contreras, R. H.; Snyder, J. P. *J. Chem. Soc., Chem. Commun.* **2000**, *20*, 2025−2026. (b) Peralta, J. E.; Barone, V.; Contreras, R. H.; Zaccari, D. G.; Snyder, J. P. *J. Am. Chem. Soc.* **2001**, *123*, 9162−9163.

(5) Schaefer, T.; Peeling, J.; Penner, G. H. *Can. J. Chem.* **1986**, *64*, 2162.

(6) Contreras, R. H.; Peralta, J. E. *Prog. NMR Spectrosc.* **2000**, *37* (4), 321−425.

(7) Peruchena, N. M.; Aucar, G. A.; Contreras, R. H. *J. Mol. Struct. (THEOCHEM)* **1990**, *210*, 205−210.

(8) (a) Shtarev, A. B.; Pinkhassik, E.; Levin, M. D.; Stibor, I.; Michl, J. *J. Am. Chem. Soc*. **2001**, *123*, 3484. (b) Bryce, D. L.; Wasylishen, R. E. *J. Mol. Struct*. **2002**, *602*−*603*, 463−472. (c) Barone, V.; Peralta, J. E.; Contreras, R. H.; Snyder, J. P. *J. Phys. Chem. A* **2002**, *106*, 5607−5612.

(9) Barone, V.; Provasi, P. F.; Peralta, J. E.; Snyder, J. P.; Sauer, S. P. A.; Contreras, R. H. *J. Phys. Chem. A* **2003**, *107*, 4748−4754.

(10) Abraham, R. J.; Kemp, R. H. *J. Chem. Soc. B* **1971**, 1240−1245.

(11) Weigert, F. J. *J. Fluorine Chem.* **1990**, *46*, 375−384.

(12) Kanazawa, Y.; Baldeschwieler, J. D.; Craig, N. C. *J. Mol. Spectrosc.* **1965**, *16*, 325−348.

(13) Ihrig, A. M.; Smith, S. L. *J. Am. Chem. Soc.* **1972**, *94*, 34−41.

(14) den Otter, G. J.; MacLean, C. *Chem. Phys.* **1974**, *3*, 119−124.

(15) Servis, K. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 1339−1344.

(16) Bürger, H.; Sommer, S. *J. Chem. Soc., Chem. Commun.* **1991**, *7*, 456−458.

(17) (a) Hoffmann, F. W. *J. Org. Chem.* **1949**, *14*, 105−110. (b) Katritzky, A. R.; Chermprapai, A.; Patel, R. C. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2901−2903.

(18) Craig, N. C.; Neese, C. F.; Nguyen, T. N.; Oertel, C. M.; Pedraza, L.; Chaka, A. M. *J. Phys. Chem. A* **1999**, *103*, 6726−6739.

(19) (a)Zens, A. P.; Ellis, P. D.; Ditchfield, R. *J. Am. Chem. Soc.* **1974**, *96*, 1309−1312. (b) Bunegar, M. J.; Fields, R.; Haszeldine, R. N. *J. Fluorine Chem.* **1980**, *15*, 497−510.

(20) (a) Bieri, G.; Heilbronner, E.; Stadelmann, J. P.; Vogt, J.; von Niessen, W. *J. Am. Chem. Soc.* **1977**, *99*, 6832−6838. (b) Bieri, G.; Stadelmann, J. P.; Thommen, F.; Vogt, J. *Helv. Chim. Acta* **1978**, *61*, 357−360. (c) Bieri, G.; Schmelzer, A.; Åsbrink, L.; Jonsson, M. *Chem. Phys.* **1980**, *49*, 213−224.

(21) (a) Sato, T.; Arulmozhiraja, S.; Niino, H.; Sasaki, S.; Matsuura, T.; Yabe, A. *J. Am. Chem. Soc.* **2002**, *124*, 4512−4521. (b) Caraiman, D.; Koyanagi, G. K.; Cunje, A.; Hopkinson, A. C.; Bohme, D. K. *Organometallics* **2002**, *21*, 4293−4296. (c) Sato, T.; Niino, H.; Yabe, A. *J. Am. Chem. Soc.* **2003**, *125*, 11936−11941.

(22) (a) Dědek, V.; Chvátal, Z. *J. Fluorine Chem.* **1986**, *31*, 363−379. (b) Shevchenko, I.; Andrushko, V.; Lork, E.; Röschenthaler, G.-V. *Eur. J. Inorg. Chem.* **2003**, 54−56.

(23) (a) Nielsen, E. S.; Jørgensen, P.; Oddershede, J. *J. Chem. Phys.* **1980**, *73*, 6238−6246. (b) Packer, M. J.; Dalskov, E. K.; Enevoldsen, T.; Jensen, H. J. Aa.; Oddershede J. *J. Chem. Phys.* **1996**, *105*, 5886−5900. (c) Bak, K. L.; Koch, H.; Oddershede, J.; Christiansen, O.; Sauer S. P. A. *J. Chem. Phys.* **2000**, *112*, 4173−4185.

(24) Geertsen, J.; Oddershede, J. *Chem. Phys.* **1984**, *90*, 301−311.

(25) Enevoldsen, T.; Oddershede, J.; Sauer, S. P. A. *Theor. Chem. Acc.* **1998**, *100*, 275−284.

(26) Provasi, P. F.; Aucar, G. A.; Sauer, S. P. A. *J. Chem. Phys.* **2000**, *112*, 6201−6208.

(27) (a) Oddershede, J.; Jørgensen, P.; Beebe, N. H. F. *Chem. Phys.* **1997**, *25*, 451−458. (b) Geertsen, J.; Oddershede, J. *Chem. Phys.* **1986**, *104*, 67−72. (c) Geertsen, J. *Chem. Phys. Lett.* **1987**, *134*, 400−402. (d) Geertsen, J.; Oddershede, J.; Scuseria, G. *Int. J. Quantum Chem. Symp.* **1987**, *21*, 475−485. (e) Geertsen, J.; Oddershede, J.; Scuseria, G. *J. Chem. Phys.* **1987**, *87*, 2138−2142. (f) Oddershede, J.; Geertsen, J.; Scuseria, G. *J. Phys. Chem.* **1988**, *92*, 3056−3059. (g) Geertsen, J.; Oddershede, J.; Raynes, W. T.; Scuseria, G. *J. Magn. Reson.* **1991**, *93*, 458−471. (h) Geertsen, J.; Oddershede, J.; Raynes, W. T.; Marvin, T. L. *Mol. Phys.* **1994**, *82*, 29−50. (i) Kirpekar, S.; Enevoldsen, T.; J.; Oddershede, J.; Raynes, W. T. *Mol. Phys.* **1997**, *91*, 897−907.

(28) Scuseria, G.; Geertsen, J.; Oddershede, J. *J. Chem. Phys.* **1989**, *90*, 2338−2343.

(29) (a) Scuseria, G. *Chem. Phys. Lett.* **1986**, *127*, 236−241. (b) Bagno, A.; Saielli, G.; Scorrano, G. *Chem. Eur. J.* **2002**, *8*, 2047−2056. (c) Ruden, T. A.; Lutnæs, O. B.; Helgaker, T.; Ruud, K. *J. Chem. Phys.* **2003**, *118*,

9572−9581. (d) Bagno, A.; Casella, G.; Saielli, G.; Scorrano, G. *Int. J. Mol. Sci.* **2003**, *4*, 193−202. (e) Giribet, C. G.; de Azua, M. C. R.; Vizioli, C. V.; Cavasotto, C. N. *Int. J. Mol. Sci.* **2003**, *4*, 203−217. (f) Grayson, M. *Int. J. Mol. Sci.* **2003**, *4*, 218−230.

(30) (a) Wigglesworth, R. D.; Raynes, W. T.; Sauer, S. P. A.; Oddershede, J. *Mol. Phys.* **1997**, *92*, 77−88. (b) Wigglesworth, R. D.; Raynes, W. T.; Sauer, S. P. A.; Oddershede, J. *Mol. Phys.* **1998**, *94*, 851−862. (c) Sauer, S. P. A.; Møller, C. K.; Koch, H.; Paidarová, I.; Špirko, V. *Chem. Phys*. **1998**, *238*, 385−399. (d) Kirpekar, S.; Sauer, S. P. A. *Theor. Chem. Acc.* **1999**, *103*, 146−153. (e) Wigglesworth, R. D.; Raynes, W. T.; Kirpekar, S.; Oddershede, J.; Sauer, S. P. A. *J. Chem. Phys.* **2000**, *112*, 3735−3746. (f) Wigglesworth, R. D.; Raynes, W. T.; Kirpekar, S.; Oddershede, J.; Sauer, S. P. A. *J. Chem. Phys.* **2001**, *114*, 9192. (g) Sauer, S. P. A.; Raynes, W. T. *J. Chem. Phys.* **2000**, *113*, 3121−3129. (h) Sauer, S. P. A.; Raynes, W. T. *J. Chem. Phys.* **2001**, *114*, 9193. (i) Grayson, M.; Sauer, S. P. A. *Mol. Phys.* **2000**, *98*, 1981−1990. (j) Sauer, S. P. A.; Raynes, W. T.; Nicholls, R. A. *J. Chem. Phys.* **2001**, *115*, 5994−6006.

(31) Provasi, P. F.; Aucar, G. A.; Sauer, S. P. A. *Int. J. Mol. Sci.* **2003**, *4*, 231−248.

(32) Provasi, P. F.; Aucar, G. A.; Sauer, S. P. A. *J. Chem. Phys.* **2001**, *115*, 1324−1334.

(33) (a) Krivdin, L. B.; Sauer, S. P. A.; Peralta, J. E.; Contreras, R. H. *Magn. Reson. Chem*. **2002**, *40*, 187−194. (b) Krivdin, L. B. *Magn. Reson. Chem*. **2003**, *41*, 91−101. (c) Krivdin, L. B. *Magn. Reson. Chem*. **2003**, *41*, 157−168. (d) Krivdin, L. B. *Magn. Reson. Chem*. **2003**, *41*, 417−430. (e) Krivdin, L. B. *Magn. Reson. Chem*. **2003**, *41*, 885−901. (f) Krivdin, L. B. *Magn. Reson. Chem*. **2004**, *42*, 1−13. (g) Krivdin, L. B. *Magn. Reson. Chem*., in press. (h) Sauer, S. P. A.; Krivdin, L. B. *Magn. Reson. Chem*., in press.

(34) (a) Bilgiçer, B.; Fichera, A.; Kumar, K. *J. Am. Chem. Soc.* **2001**, *123*, 4393−4399. (b) Bilgiçer, B.; Xing, X.; Kumar, K. *J. Am. Chem. Soc.* **2001**, *123*, 11815−11816.

(35) (a) Duewel, H. S.; Daub, E.; Robinson, V.; Honek, J. F. *Biochemistry* **2001**, *40*, 13167−13176. (b) Feeney, J.; McCormick, J. E.; Dauer, C. J.; Birdsall, B.; Moody, C. M.; Starkmann, B. A.; Young, D. W.; Francis, P.; Havlin, R. H.; Arnold, W. D.; Oldfield, E. *J. Am. Chem. Soc.* **1996**, *118*, 870−8706.

(36) (a) Kitteringham, N. R.; O'Neill, P. M. Metabolism of fluorine-containing drugs. Park, B. K., Ed. *Annu. Rev. Pharmacol. Toxicol.* **2001**, *41*, 443−470. (b) Colmenares, L. U.; Zou, X.; Liu, J.; Asato, A. E.; Liu, R. S. H. *J. Am. Chem. Soc.* **1999**, *121*, 5803−5804. (c) Kim, H. W.; Rossi, P.; Schoemaker, R. K.; DiMagno, S. G. *J. Am. Chem. Soc.* **1998**, *120*, 9082−9083. (d) *Biomedical Frontiers of Fluorine Chemistry*; Ojima, I., McCarthy, J. R., Welch, J. T., Eds.; ACS Symposium Series 639; American Chemical Society: Washington, DC, 1996.

(37) Ramsey, N. F. *Phys. Rev.* **1953**, *91*, 303−307.

(38) Sauer, S. P. A. *J. Chem. Phys.* **1993**, *98*, 9220−9221.

(39) Mills, I.; Cvitaš, T.; Homann, K.; Kallay, N.; Kuchitsu K. *Quantities, Units and Symbols in Physical Chemistry*; Blackwell Scientific Publications: Oxford, 1993.

(40) Linderberg. J.; Öhrn, Y. *Propagators in Quantum Chemistry*; Academic Press: London, 1973.

(41) Jørgensen. J.; Simons, J. *Second Quantization-Based Methods in Quantum Chemistry*; Academic Press: New York, 1981.

(42) Olsen, J.; Jørgensen, P. *J. Chem. Phys.* **1985**, *82*, 3235−3264.

(43) Sauer, S. P. A.; Packer, M. J. In *Computational Molecular Spectroscopy*; Bunker, P. R., Jensen, P., Eds.; Wiley: London, 2000; pp 221−252.

(44) McLachlan, A. D.; Ball, M. A. *Rev. Mod. Phys.* **1964**, *36*, 844−855.

(45) Rowe, D. J. *Rev. Mod. Phys.* **1968**, *40*, 153−166.

(46) Oddershede, J.; Jørgensen, P.; Yeager, D. L. *Comput. Phys. Rep.* **1984**, *2*, 33−92.

(47) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618−622. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1−19.

(48) Sauer, S. P. A. *J. Phys. B* **1997**, *30*, 3773−3780.

(49) The aug-cc-pVTZ-J basis set can be downloaded from http://fyskem.ki.ku.dk/sauer/basissets

(50) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(51) Helgaker, T.; Jensen, H. J. A.; Jørgensen, P.; Olsen, J.; Ruud, K.; Ågren, H.; Auer, A. A.; Bak, K. L.; Bakken, V.; Christiansen, O.; Coriani, S.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Fernandez, B.; Hättig, C.; Hald, K. Halkier, A.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Pedersen, T. B.; Ruden, T. A.; Sanchez, A.; Saue, T.; Sauer, S. P. A.; Schimmelpfennig, B.; Sylvester-Hvid, K. O.; Taylor, P. R.; Vahtras, O. *DALTON, an electronic structure program, Release 1.2*; 2001, http://www.kjemi.uio.no/software/dalton/dalton.html

(52) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(53) Hirao, K.; Nakatsuji, H.; Kato, H.; Yonezawa, T. *J. Am. Chem. Soc.* **1972**, *94*, 4078−4087.

(54) (a) Čižek, J.; Paldus, J. J. *Chem. Phys.* **1967**, *47*, 3976−3985. (b) Chambaud, G.; Levy, B.; Millie, P. *Theor. Chim. Acta* **1978**, *48*, 103−118.

(55) Oddershede, J. *Adv. Quantum Chem.* **1978**, *2*, 275−352.

(56) (a) Scuseria, G. E.; Contreras, R. H. *Theor. Chim. Acta* **1981**, *59*, 437−450. (b) Scuseria, G. E.; Engelmann, A. R.; Contreras, R. H. *Theor. Chim. Acta* **1982**, *61*, 49−57. (c) Contreras, R. H.; Ruíz de Azúa, M. C.; Giribert, C. G.; Aucar, G. A.; Lobayan de Bonczok, R. *J. Mol. Struct. (THEOCHEM)* **1993**, *284*, 249−269. (d) Lobayan, R. M.; Aucar, G. A. *J. Mol. Struct. (THEOCHEM)* **1998**, *452*, 1−11. (e) Lobayan, R. M.; Aucar, G. A. *J. Mol. Struct. (THEOCHEM)* **1998**, *452*, 13−23.

(57) (a) Scuseria, G. E.; Contreras, R. H. *Chem. Phys. Lett.* **1982**, *93*, 425−428. (b) Righini, R.; Giribert, C. G.; Ruíz de Azúa, M. C.; Contreras, R. H. *J. Mol. Struct. (THEOCHEM)* **1990**, *210*, 199−204. (c) Aucar, G. A.; Contreras, R. H. *J. Magn. Reson.* **1991**, *93*, 413−418.

(58) Gómez, C. A.; Provasi, P. F.; Aucar, G. A. *J. Mol. Struct. (THEOCHEM)* **2002**, *584*, 159−168.

(59) Gómez, C. A.; Provasi, P. F.; Aucar, G. A. *J. Mol. Struct. (THEOCHEM)* **2003**, *620*, 149−156.

(60) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983.

(61) Kaski, J.; Lantto, P.; Vaara, J.; Jokisari, J. *J. Am. Chem. Soc.* **1998**, *120*, 3993−4005.