Proximity Effects on Nuclear Spin–Spin Coupling Constants. 1. ¹J(CH) Couplings in the Vicinity of an Atom Bearing Lone Pairs

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Proximity effects on ¹J(CH) couplings are studied from a theoretical point of view in the following systems: CH₄/FH (**A**) and H₂O/HCN (**B**) which form dimers by hydrogen-bond interactions. ¹J(CH) couplings for different intermolecular distances are calculated for the C—H bond facing the atom bearing lone pairs. While in the former system, this coupling is increased owing to the proximity to the F atom; in the latter this coupling is decreased owing to the proximity to the O atom. These opposite trends are accompanied by slight shortening and lengthening, respectively, of the corresponding C—H bond lengths. As part of this work, measurements of ¹J(CH) couplings in 9-(1,3-dioxolan-2-yl)-1,2,3,4-tetrafluorotriptycene (**I**) and 1-formyl-2-hydroxy-8-fluoronaphthalene (**II**) and ¹J(NH) in *o*-fluorobenzamide (**III**), showing proximity effects as those described above are carried out. These results suggest that ¹J(XH) couplings are adequate probes to distinguish two different types of X—H···Y hydrogen bonds.

Introduction

The orientational effect of a lone pair on coupling constants is a very well-known phenomenon, and many trends have been observed in experimental data.[1,2] They provide interesting information on molecular structures. From a theoretical point of view, the CLOPPA method[3] (contributions from localized orbitals within the polarization propagator approach) permits insight into the factors defining some of these trends.[4–6] In particular, this approach allowed a clear distinction between proximity effects and through-space transmission[7,8] of the second-order terms that contribute to spin–spin coupling constants. When a moiety is close to the bonds connecting the coupled nuclei, its proximity modifies the electronic distribution around those bonds, affecting the magnitude of the coupling constant under consideration. Such proximity also affects the coupling constant since virtual transitions take place between orbitals belonging to the coupling pathway and the proximate moiety. The first of these can be considered an effect operating through the ground state wave function, and the second an effect described by the second-order perturbation theory.

In methylenedioxybenzene, the proximity of an aromatic C—H bond *cis* to the oxygen lone pair was found to increase by several hertz the corresponding ¹J(CH) coupling through a modification in the ground state wave function.[5] Recently, Afonin et al.[9] speculated that the increase in a ¹J(CH) coupling corresponding to a C—H bond proximate to an F atom is a probe that shows the existence of a hydrogen bond of type F···H—C. Satonaka

et al.[10] arrived at similar conclusions regarding the increase in the ¹J(CH) coupling of a formyl C—H bond proximate to a carbonyl oxygen. In this case the hydrogen bond is of type C=O···H—C=O. These results suggest that coupling constants can be adequate probes for study of hydrogen bonds, especially if a detailed knowledge of proximity effects on spin–spin coupling constants is achieved.

In order to obtain insight into these effects, in this series of papers different systems will be studied with different approaches. In this first one theoretical calculations as well as a few measurements are carried out. Theoretically, the following two systems are considered using the supermolecule approach: CH₄/FH (**A**) and H₂O/HCN (**B**). The latter was studied by Turi and Dannenberg[11a] from a theoretical point of view and by Fillery-Travis et al.[11b] and by Gutowsky et al.[11c] from experimental points of view.

Measurements were carried out in compounds where for chemical reasons one can expect that by far the largest contributions to substituent effects on ¹J(XH) couplings come from a proximity effect. These molecules were designed and synthesized to include molecular constraints aimed at facilitating the sought-after effects and are necessarily more complex than the systems treated theoretically. The following couplings were measured: ¹J(CH) couplings in 9-(1,3-dioxolan-2-yl)-1,2,3,4-tetrafluoro-triptycene (**I**) and 1-formyl-2-hydroxy-8-fluoronaphthalene (**II**) and ¹J(NH) coupling in *o*-fluorobenzamide (**III**). **I** is highly hindered, and two rotamers, *ap* and *sc*, are separately observed at room temperature;[13] while in **Ia**, the C(9)—H bond is placed in *sc* orientation with respect to the F atom, and in **Ib**, it is placed *ap* (see Scheme 1). In **II**, the formyl C—H bond is brought in close proximity to the peri F atom owing to the intramolecular

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I

II   III
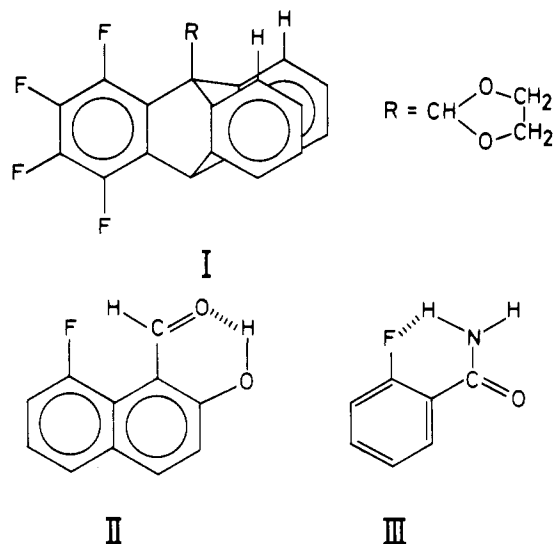
C=O···H—O hydrogen bond.[12] In **III**, an intramolecular hydrogen bond of type F···H—N is known.[14]

Calculations presented in this paper show that, if a C—H bond in the proximity of an atom bearing lone pairs is slightly shortened, an increase in the corresponding ^1J(CH) coupling is observed, and if it is slightly lengthened, a decrease in that coupling is observed. As such changes in the ^1J(CH) coupling are found to originate in the Fermi contact term, it can be expected that an increase in the bond strength takes place in the former, while a weakening of the bond strength is expected in the latter. An increase in the ^1J(CH) coupling and a slight shortening of the corresponding C—H bond is observed in the molecular system **A**. Similar shortening of a C—H bond involved in an intramolecular hydrogen bond was reported recently by Popelier and Bader.[15] In system **B** the proximity to the oxygen lone pairs yields a slight lengthening of the C—H bond and a concomitant decrease in the Fermi contact contribution to the ^1J(CH) coupling is calculated.

Methods of Calculation

Optimized geometries were obtained with the Gaussian 92 program[16] using different basis sets as described in each case. Coupling constants were calculated with the SYSMO program (System Modena)[17–19] which allows their calculation using the equation of motion method (EOM)[20] with the random phase approximation.[21] In this work this program was modified in order to allow calculations at the MECI level (mono-excited configuration interaction).[22] This modification was introduced to be able to calculate the Fermi contact term of the ^1J(CH) coupling in HCN, overcoming the nonsinglet instability problem.[8]

Experimental Section

Nuclear magnetic resonance spectra were recorded for dilute solutions in deuterochloroform using a Bruker AM-300 spectrometer operating at 75.48 MHz (^{13}C) and 30.42 MHz (^{15}N), as reported in earlier papers.[12–14] The fully coupled ^{13}C spectra of **I** and **II** were taken with digital resolutions of 0.07 and 0.6 Hz, respectively, while the fully coupled ^{15}N spectrum of **III** was taken with digital resolution of 0.4 Hz.

Results and Discussion

Calculations. When the geometry of system **A** is optimized, a bonding structure displayed in Figure 1 is obtained. Actually, this bonding structure corresponds to a saddle point of the potential hypersurface. The fully optimized structure seems to correspond to a van der Waals complex with the F—H direction pointing toward the C atom in much the same way as in the CH_4/H_2O

d(FH$_1$)=2.685Å
d(CH$_1$)=1.0891Å
α =121.2°
β =170.7°
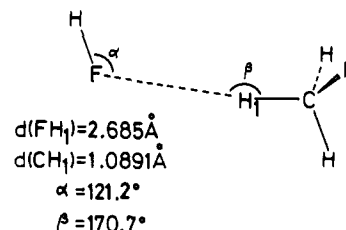
Figure 1. Equilibrium geometry of dimer **A**. It was obtained with an MP2(frozen core)/D95++(d,p) basis set.
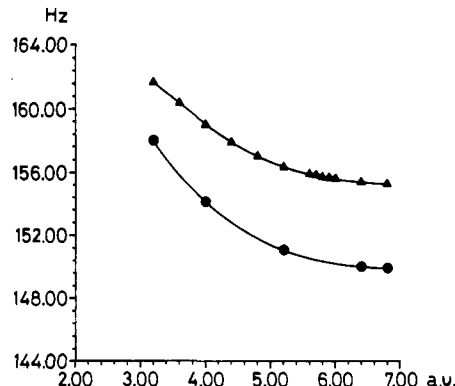
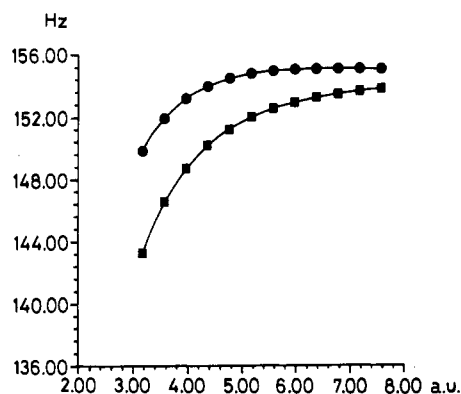**Figure 2.** ^1J(CH) coupling vs the intermolecular F···H distance in **A** corresponding to the C—H bond facing the F atom. They are calculated at the RPA level using two different basis sets: (▲) (9s5p/5s/9s5p) contracted to [4s2p/2s/5s2p]; (●) (11s7p2d/5s2p/11s7p2d) contracted to [6s4p1d/3s1p/5s3p1d].

SCHEME 1
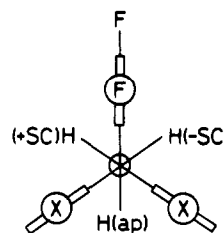
system recently reported by Szczesniak et al.[23] The basis set employed in its optimization is D95++(d,p) at the MP2 (frozen core) level of approximation. It is worthy of noting that the H—C bond facing the F atom is slightly shorter than the other three (1.0891 Å vs 1.0900, 1.0898, and 1.0901 Å). The almost linear arrangement F···H—C suggests that the main attractive interaction defining the dimerization is the hydrogen-bond one. Such shortening of a C(sp^3)—H bond involved in a hydrogen bond is in agreement with results obtained recently by Popelier and Bader[15] when the geometry is optimized to study intramolecular hydrogen bonds of type C=O···H—CH$_2$. This trend is also in line with the observations that the vibrational frequencies of the formyl C—H bond in o-nitrobenzaldehyde are very large, probably as a result of the C—H···O=N interaction.[24]

For the molecular system **A**, the Fermi contact term (FC) of the ^1J(CH) coupling corresponding to the C—H bond facing the F atom vs the intermolecular F···H distance, calculated with two different basis sets, is displayed in Figure 2. These basis sets are (9s5p/5s/9s5p) contracted to [4s2p/2s/5s2p] and (11s7p2d/5s2p/11s7p2d) contracted to [6s4p1d/3s1p/5s3p1d].[25] The FC term is calculated at the RPA level. The relative orientation of both molecules is shown in Scheme 2a. Calculations were carried out by keeping fixed the intramolecular geometries at the values given by the standard model of Pople and Gordon.[26] Although the actual calculated couplings depend on the basis set, the same trend is observed in both cases. The FC term increases when the intermolecular distance is decreased. For all distances displayed in Figure 2 a repulsive interaction between the molecules is calculated and is seen to increase with decreasing intermolecular

Figure 3. $^1J(CH)$ couplings *vs* the intermolecular F···H distance in **A** corresponding to the C—H bonds which do not face the F atom. They are calculated at the RPA level using the following basis set: (9s5p/5s/9s5p) contracted to [4s2p/2s/5s2p]. (■): It corresponds to the in-plane C—H bond (see Scheme 2a). (●): It corresponds to the out-of-plane C—H bonds (see Scheme 2a).

SCHEME 2

a

b
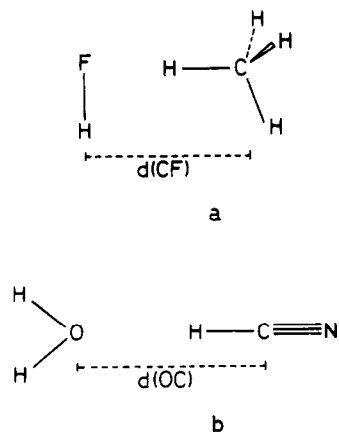
TABLE 1: Calculation of the Lengthening of the C—H Bond in HCN upon Dimerization in System B[a]

wave function	C—H bond length (Å)		
	system B[b]	monomer	diff
HF/6-31G(d,p)	1.067	1.059	0.008
HF/D95++(d,p)	1.068	1.061	0.007
MP2/6-31G(d,p)	1.073	1.064	0.009
MP2/D95++(d,p)	1.076	1.068	0.008

[a] Geometry optimizations were carried out with different ground state wave functions for the HCN monomer and for the 1:1 HCN···H_2O complex in system **B**. [b] Taken from ref 11a.

distance. The magnitude of the $^1J(CH)$ coupling is somewhat exaggerated, as it is well-known to occur for methane using basis sets like those employed here.[27]

The opposite trend is observed for the FC terms of $^1J(CH)$ couplings for the other three C—H bonds, i.e. an increase with increasing intermolecular distance. These trends are displayed in Figure 3. A larger sensitivity is observed for that corresponding to the in-plane C—H bond (see Scheme 2a).

The equilibrium geometry of dimer **B** was obtained from ref 11a. It is shown in Scheme 2b. In order to assess the oxygen lone pair proximity effect on the C—H bond length, the structure of the HCN monomer was optimized using four different quality ground state wave functions, which are those used in ref 11a to obtain the equilibrium geometry of dimer **B**. The corresponding C—H bond lengths in the monomer and the dimer are compared in Table 1. It is observed that the dimerization yields a slight lengthening of the C—H bond. It is worth noting that this trend is opposite to that observed in dimer **A**. This lengthening is notably insensitive to the quality of the ground state wave function.
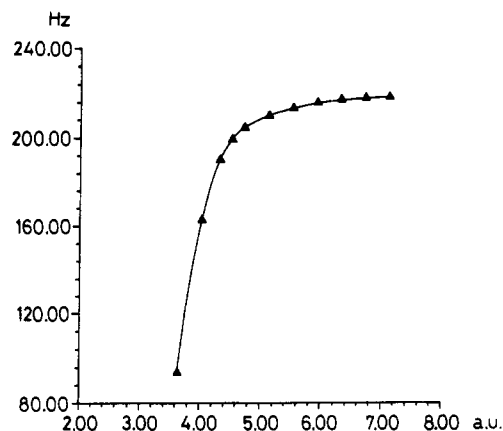
Figure 4. $^1J(CH)$ coupling *vs* the intermolecular O···C distance in **B**. Calculations were carried out at the MECI level using the 6-31G basis set.

TABLE 2: Experimental Values for sc-$^1J(CH)$ and ap-$^1J(CH)$ in I, $formyl$-$^1J(CH)$ in II, and $^1J(^{15}NH)$ in III, with the Last Two Compared, Respectively, with the Corresponding Values in Salicylaldehyde and in Benzamide

compound	coupling	exp (Hz)
I	sc-$^1J(CH)$	168.2
I	ap-$^1J(CH)$	164.5
II	$formyl$-$^1J(CH)$	186.1
salicylaldehyde	$formyl$-$^1J(CH)$	177.7[a]
		177.06[b]
III	$^1J(NH)$	89.8[c]
benzamide	$^1J(NH)$	93.0[d]

[a] Taken from ref 28a. [b] Taken from ref 28b. [c] Sign not determined. Only one $^1J(^{15}NH)$ coupling was observed. [d] Average value of cis-$^1J(NH)$ = 98.2 Hz and $trans$-$^1J(NH)$ = 87.8 Hz (taken from ref 30a).

For the molecular system **B**, the FC term of the $^1J(CH)$ coupling vs the O···C distance (see Scheme 2b) is displayed in Figure 4. In order to avoid the nonsinglet Hartree–Fock instability problem present in *ab initio* calculations of coupling constants in unsaturated compounds, the MECI approximation[22] was employed for all calculations shown in Figure 4. They were carried out using the intramolecular geometrical data obtained for the dimer equilibrium geometry,[11a] and the 6-31G basis set was employed. Therefore, the calculated trend originates only in an electronic effect and not in a possible change in the lengthening of the C—H bond for different intermolecular distances. It is observed that this coupling decreases when the intermolecular distance, is decreased. This trend is followed well up to an O···H distance shorter than a typical O—H bond length, in spite of the increase in the repulsion energy between both monomers.

It is important to point out that MECI calculations were also carried out for system **A**, and trends similar to those depicted in Figures 2 and 3 were obtained. They are not shown here. However, the magnitudes of the respective couplings were smaller.

Measurements. The ap and sc rotamers observed at room temperature in compound I[13] provide two $^1J(CH)$ couplings corresponding to $C(sp^3)$—H bonds which differ mainly in orientation with respect to the F atom placed at ring position 1. In the ap isomer the C—H bond is furthest from the fluorine, and in the sc isomer the C—H vector is 60° to the C—F direction. Therefore, they constitute adequate examples to verify the trend found in system **A**. These couplings are shown in Table 2, where the formyl $^1J(CH)$ coupling in II and the $^1J(NH)$ couplings in III are also displayed and compared, respectively, with the formyl $^1J(CH)$ coupling in salicylaldehyde and with the $^1J(NH)$ couplings in benzamide. The following features of data shown in this table are worthy of comment. In I, the $^1J(CH)$ corresponding to an sc orientation with respect to the F atom is 3.7 Hz larger than that with an ap orientation, paralleling the trend found in system **A**. In II, the formyl $^1J(CH)$ coupling is *ca.* 9 Hz larger than that

in salicylaldehyde.[28] This increase can safely be ascribed to a proximity effect owing to the closeness between the C—H bond and the F atom. This indicates that this C(sp^2)—H bond shows a proximity effect similar to that described above for system **A**.

The ^{15}N spectrum of 2-fluorobenzamide (**III**) at 300 K is a triplet of doublets with ^1J(NH) = 89.8 Hz. Either the two contributing J(NH) values were essentially equal or rapid rotation had permitted the observation of only an average value, and so the measurement was repeated at 243 K with the same result. This value is in good agreement with those reported by Fritz, Winkler, and Küng[29] but through oversight not recognized in our earlier paper.[14] In benzamide the two ^1J(NH) values are respectively 87.8 and 98.2 Hz for solutions in DMSO,[30a] and the average of these two, 93.0 Hz, is significantly larger than the value observed for **III**. Similarly, reduced magnitudes of one-bond couplings have been found for pentafluoro- and 2,6-difluorobenzamides, 90.7 and 90.6 Hz, respectively for solutions in CH$_2$Cl$_2$.[30b] Therefore, the hydrogen bond in **III** yields an effect on the ^1J(NH) coupling for the N—H bond involved in it which is similar to that described in system **B**.

Concluding Remarks

The proximity of a C—H bond to an atom bearing lone pairs may yield either an increase or a decrease in the corresponding ^1J(CH) coupling. While in the first case a slight shortening of the C—H bond length is calculated, in the second case a slight lengthening of that C—H bond length is obtained.

A shortening of the length of a C—H bond in the proximity of a lone pair was reported in several cases: for instance, in the methyl C—H bonds in α-picoline,[31] in a C—H bond in a *syn*-periplanar arrangement with respect to an oxygen lone pair,[32] and in an intramolecular hydrogen bond between an O atom and a methyl C—H bond.[15] In the present study the molecular system **A** reproduces this behavior, and it is observed that between the two molecules FH and CH$_4$ an attractive interaction between the F atom and one of the C—H bonds takes place. Following Popelier and Bader,[15] it can be said that a hydrogen-bonding interaction takes place. These conclusions are in agreement with results reported by Afonin et al.,[9] who rationalized an increase in a ^1J[C(sp^2)—H] coupling as originating in a hydrogen-bond interaction with a proximate F atom, and with those reported by Satonaka et al.,[10] who rationalized a similar increase in a formyl ^1J(CH) coupling as originating in a hydrogen bond of type O=C—H···O=C.

In the molecular system **B**, a hydrogen bond of type O···H—C takes place,[11] and this interaction yields a slight lengthening of the C—H bond. It is found that the corresponding ^1J(CH) coupling is smaller the shorter is the intermolecular distance. This trend seems to indicate that the corresponding hydrogen bond presents a certain covalent character. This possibility was discussed recently by Blake et al.[33] In the present case, support for this rationalization can be found in the following facts. It is known that an increase in the coordination number of an atom reduces the one-bond couplings involving it.[2] The only exceptions known to this rule are those where the additional coordination takes place through a p-type orbital. Obviously, this cannot be the case for an H atom. Therefore the decrease in the ^1J(CH) coupling seems to work like an increase in the coordination of the H atom. One dramatic example of a two-coordinated H atom is that of a two-electron C—H—C bond reported recently by McMurry et al.,[34] where they measured ^1J(CH) = 47 Hz and they calculated its equilibrium bond length as *ca.* 1.27 Å. This peculiar 2-center, 2-electron C—H—C bond was recently confirmed theoretically by Cioslowski.[35]

References and Notes

(1) Gil, V. M. S.; von Philipsborn, W. *Magn. Reson. Chem.* **1989**, *27*, 409.

(2) Jameson, C. J. In *Multinuclear NMR*; Mason, J.; Ed.; Plenum: New York, 1987; Chapter 4.

(3) Diz, A. C.; Giribet, C. G.; Ruiz de Azúa, M. C.; Contreras, R. H. *Int. J. Quantum Chem.* **1990**, *37*, 663.

(4) Contreras, R. H.; Aucar, G. A.; Giribet, C. G.; Ruiz de Azúa, M. C.; Cavasotto, C. N.; Krivdin, L. B. *J. Mol. Struct. THEOCHEM.* **1990**, *210*, 175.

(5) Biekofsky, R. R.; Pomilio, A. B.; Contreras, R. H. *J. Mol. Struct. THEOCHEM.* **1990**, *210*, 211.

(6) Contreras, R. H.; Ruiz de Azúa, M. C.; Giribet, C. G.; Aucar, G. A.; Lobayan, R. *J. Mol. Struct. THEOCHEM.* **1993**, *284*, 249.

(7) Cavasotto, C. N.; Giribet, C. G.; Ruiz de Azúa, M. C.; Contreras, R. H. *J. Comput. Chem.* **1991**, *12*, 141.

(8) Contreras, R. H.; Facelli, J. C. *Ann. Reps. NMR Spectrosc.* **1993**, *27*, 255.

(9) (a) Afonin, A. V.; Andriyankov, M. A. *Zh. Org. Khim.* **1988**, *24*, 1034. (b) Afonin, A. V.; Sigalov, M. V.; Korustova, S. E.; Aliev, I. A.; Vashchenko, A. V.; Trofimov, B. A. *Magn. Reson. Chem.* **1990**, *28*, 580.

(10) (a) Satonaka, H.; Abe, K.; Hirota, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 953. (b) Satonaka, H.; Abe, K.; Hirota, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2031.

(11) (a) Turi, L.; Dannenberg, J. J. *J. Phys. Chem.* **1993**, *97*, 7899. (b) Fillery-Travis, A. J.; Legon, A. C.; Willoughby, L. C. *Proc. R. Soc. London A* **1984**, *396*, 405. (c) Gutowsky, H. S.; Germann, T. S.; Augsburger, J. D.; Dykstra, C. E. *J. Chem. Phys.* **1992**, *96*, 405.

(12) Rae, I. D.; Staffa, A.; Diz, A. C.; Giribet, C. G.; Ruiz de Azúa, M. C.; Contreras, R. H. *Aust. J. Chem.* **1988**, *40*, 1923.

(13) Rae, I. D.; Weigold, J. A.; Contreras, R. H.; Yamamoto, G. *Magn. Reson. Chem.* **1992**, *30*, 1047.

(14) Rae, I. D.; Weigold, J. A.; Contreras, R. H.; Biekofsky, R. R. *Magn. Reson. Chem.* **1993**, *31*, 836.

(15) Popelier, P. L. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1992**, *189*, 542. There is disagreement in the literature whether the type of interaction reported in this reference should be called "hydrogen bonding" or not (different definitions of hydrogen-bonding interactions were recently listed in: Aakeroy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, 397). Obviously, this is a matter of semantics. The terminology used in Popelier and Bader's paper is used in the present work, although other authors may prefer a different description.

(16) Program Gaussian 92, Revision E.2. Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1992.

(17) Lazzeretti, P.; Zanasi, R. *J. Chem. Phys.* **1982**, *77*, 2448.

(18) Lazzeretti, P. *Int. J. Quantum Chem.* **1979**, *15*, 181.

(19) Lazzeretti, P. *J. Chem. Phys.* **1979**, *71*, 2514.

(20) McCurdy, C. V., Jr.; Rescigno, T. N.; Yaeger, D. L.; McKoy, V. In *Methods of Electron Structure Theory*; Schaefer, H. F., III, Eds.; Plenum: New York, 1977; Vol. 3, p 339.

(21) Oddershede, J. *Adv. Quantum Chem.* **1978**, *11*, 275.

(22) Geertsen, J.; Oddershede, J. *J. Chem. Phys.* **1984**, *90*, 301.

(23) Szczesniak, M. M.; Chalasinski, G.; Cybulski, S. M.; Cieplak, P. *J. Chem. Phys.* **1993**, *98*, 3078.

(24) Pinchas, S. *Anal Chem.* **1957**, *29*, 334; *J. Phys. Chem.* **1963**, *67*, 1862.

(25) van Duijneveldt, F. B. *IBM Res. Rep.* **1971**, RJ945.

(26) Pople, J. A.; Gordon, M. *J. Am. Chem. Soc.* **1967**, *89*, 4253.

(27) Lazzeretti, P.; Zanasi, R. *J. Chem. Phys.* **1982**, *77*, 2448.

(28) (a) Schaeffer, C. D., Jr.; Yoder, C. H. *J. Org. Chem.* **1971**, *36*, 2201. (b) Äyräs, R.; Laatikainen, R.; Lötjönen, S. *Org. Magn. Reson.* **1980**, *13*, 387.

(29) Fritz, H.; Winkler, T.; Küng, W. *Helv. Chim. Acta* **1975**, *58*, 1822.

(30) (a) Kaplan, L. M.; Galat, W. F.; Shokol, W. A.; Tirov, E. W. *Zh. Obsch. Khim.* **1981**, *51*, 621. (b) Resvukhin, A. I.; Furin, G. A.; Jakobsen, G. G. *Izv. Akad. Nauk. USSR, Ser. Khim.* **1981**, 2512.

(31) Tufró, M. F.; Contreras, R. H.; Facelli, J. C. *J. Mol. Struct. THEOCHEM.* **1992**, *254*, 271.

(32) Angellotti, T.; Krisko, M.; O'Connor, T.; Seriani, A. S. *J. Am. Chem. Soc.* **1987**, *109*, 4464.

(33) Blake, P. R.; Park, J. B.; Adams, M. W. W.; Summers, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 4931.

(34) McMurry, J. E.; Leckta, T.; Hodge, C. N. *J. Am. Chem. Soc.* **1989**, *111*, 8867.

(35) Cioslowski, J. *J. Am. Chem. Soc.* **1993**, *115*, 5177.