Analysis of the Electronic Origin of the $^{1}J_{CH}$ Spin−Spin Coupling Trend in 1-X-Cyclopropanes: Experimental and DFT Study

Álvaro Cunha Neto,[†] **Francisco P. dos Santos,**[†] **Rubén H. Contreras,**[‡] **Roberto Rittner,**[†] **and Cláudio F. Tormena***,[†]

Organic Chemistry Department, Chemistry Institute, University of Campinas, P.O. Box 6154, Campinas, São Paulo, Brazil 13084-971, and Department of Physics, FCEyN, University of Buenos Aires and CONICET, Buenos Aires, Argentina

Received: August 5, 2008; Revised Manuscript Received: September 22, 2008

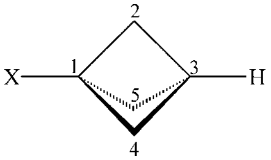
A conceptual analysis of the CLOPPA (Contributions from Localized Orbitals within the Polarization Propagator Approach) expressions that deconvolute NMR spin−spin coupling constants [Diz A. C.; Giribet C. G.; Ruiz de Azúa, M. C.; Contreras, R. H. *Int. J. Quantum Chem.* **1990**, *37*, 663.] into orbital contributions can provide an in-depth insight into the features of the electronic molecular structure that originate a given $^{1}J_{CH}$ experimental trend. In this work, several 1-X-cyclopropane derivatives are taken as model compounds to apply such ideas to rationalize substituent effects on the Fermi contact term of $^{1}J_{C1,H}$ spin−spin coupling. It is shown that in this type of coupling, its experimental trend, as measured in this work, cannot be accounted for with only the “bond” and the “other bond” contributions, requiring the inclusion of “other antibonding contributions”. Such effect is discussed in terms of hyperconjugative interactions.

Introduction

In order to get insight into molecular electronic features that originate trends in different types of NMR spin−spin coupling constants, SSCCs, several approaches were developed to decompose these spectroscopic parameters into contributions from localized molecular orbitals, LMOs. The pioneering of such approaches is the IPPP−CLOPPA one (Inner Projections of the Polarization Propagator[1]−Contributions from Localized Orbitals within the Polarization Propagator Approach.[2]) Afterward, other approaches were reported like two versions NJC[3] (Natural J-Coupling Analysis) and the **J**-**OC**-PSP approach by Cremer et al.[4]

If the formal CLOPPA expressions in terms of LMOs are carefully scrutinized, then several trends of SSCCs can be predicted without performing their actual calculations. One of the most interesting examples so far published is the correct description of the experimental X substituent effect on $^{1}J_{C3,H3}$ SSCCs in 1-X-bicyclo[1.1.1]pentantes (Scheme 1).[5]

SCHEME 1: 1-X-Bicyclo[1.1.1]pentanes (X = H, F, Cl, Br, CN, NH$_2$, and NO$_2$)



According to the Ramsey[6] study of the nucleus−electron magnetic interactions originating SSCCs, these spectroscopic parameters are described, within a nonrelativistic approach and for SSCCs measured in isotropic phase, by four terms, namely, Fermi Contact (FC), Spin−Dipolar (SD), Paramagnetic Spin−Orbit (PSO), and Diamagnetic Spin−Orbit (DSO), eq 1:

$$^{1}J_{CH} = {}^{FC}J_{CH} + {}^{SD}J_{CH} + {}^{PSO}J_{CH} + {}^{DSO}J_{CH} \qquad (1)$$

Although all four terms of eq 1 are considered within the CLOPPA approach,[2] this qualitative analysis becomes much easier when the experimental trend of SSCCs under consideration is largely dominated by the FC term. Within the CLOPPA approach, the FC term can be deconvoluted into LMOs as given in eq 2,

$$^{1}J^{FC}_{CH} = \sum_{ia,jb} {}^{1}J^{FC}_{ia,jb}(CH) \qquad (2)$$

where, occupied LMOs are labeled *i* and *j*, while vacant LMOs are labeled *a* and *b*. As shown previously,[2c,7] the LMO contributions to the FC term can be written as in eq 3,

$$^{1}J^{FC}_{ia,jb}(CH) = W_{ia,jb}[U_{ia,C}U_{jb,H} + U_{ia,H}U_{jb,C}] \qquad (3)$$

where $U_{ia,C}$ ($U_{jb,H}$) are the “perturbators”, i.e., the matrix elements of the FC operator between the occupied i (j) and vacant a (b) LMOs evaluated at the C (H) site of the coupling nuclei. These terms yield a measure of the strength of the i → a and j → b virtual excitations owing to the FC operator; and $W_{ia,jb}$ corresponds to the polarization propagator (PP) matrix elements and they give a measure of the electronic molecular system response to the presence of the nucleus−electron FC magnetic interaction, connecting two virtual excitations i → a and j → b. For the present purpose, it is very important to recall that the PP matrix elements decrease, in absolute value, when increasing the $\varepsilon_a-\varepsilon_i$ and $\varepsilon_b-\varepsilon_j$ energy gaps between these vacant and occupied LMOs involved in each virtual excitation.

Equations 2 and 3 are very useful when obtaining a qualitative description of a given type of SSCC trend along a series of compounds. It is observed that in some instances, such trends

---

* To whom correspondence should be addressed. E-mail: tormena@iqm.unicamp.br.

[†] Organic Chemistry Department, Chemistry Institute, University of Campinas.

[‡] Department of Physics, FCEyN, University of Buenos Aires and CONICET.

10.1021/jp8069805 CCC: $40.75

could be determined by either the "perturbators", the PP matrix, or both. In some cases, the PP behavior can rather easily be predicted if the following approximation is adopted: occupied LMOs are taken to be analogous to either bonding or lone-pair orbitals of the NBO approach of Weinhold et al.[8] (core orbitals are not considered since this is a qualitative approach and the participation of these occupied orbitals in the FC transmission is neglected in comparison with those involving valence orbitals). Using this approximation, the known trends of hyperconjugative interactions can be used to predict qualitatively a trend for a given SSCC along a series of compounds, resorting to the well-known theory of perturbed molecular orbitals.[9] With this idea in mind, the diagonal PP matrix elements in eq 3 are observed to decrease whenever there is an interaction increasing the energy gap between the i or j bonding and the a or b antibonding NBOs. It is important to recall that the PP matrix elements are largest for diagonal elements, followed by the "quasi" diagonal elements, i.e., either two bonds or two antibonding orbitals are equal to each other.

In previous works,[5] it was observed that the sum in eq 2 for the FC contribution to ${}^{1}J_{CH}$ SSCCs is largely dominated by the following two types of terms: (1) $i = j$ corresponds to the LMO localized on the σ_{CH} bond involving the coupling nuclei, and a = b corresponds to the vacant LMO localized at that σ_{CH} bond, i.e., this corresponds to a diagonal PP matrix. The corresponding term in eq 2 is dubbed the "bond contribution", ${}^{FC}J^{b}$.

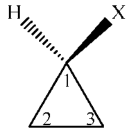
(2) Either i or j corresponds to the LMO on the σ_{CH} bond containing the coupling nuclei, and j or i corresponds to an occupied LMO on other σ_{CX} bond involving the C coupling nucleus; and a = b correspond to localized vacant MOs placed at that σ_{CH} bond containing the coupling nuclei. This contribution corresponds to a "quasi" diagonal PP matrix element. The corresponding term in eq 2 is dubbed "other bond contribution", ${}^{FC}J^{ob}$. However, it should be stressed that this term also involves the σ_{CH} bond and antibond orbitals containing the coupling nuclei.

For the FC term of ${}^{1}J_{CH}$ SSCCs, the ${}^{FC}J^{b}$ contribution is positive, whereas the ${}^{FC}J^{ob}$ one is negative, having the former a notable larger absolute value than the latter. The third most important term was dubbed "other antibonding orbital contributon", ${}^{FC}J^{oab}$ and it is analogous to J^{ob} but the roles of bonding and antibonding orbitals are interchanged. For this term, the PP matrix element is also "quasi" diagonal. The ${}^{FC}J^{oab}$ contribution to ${}^{1}J_{CH}$ is positive but its absolute value is usually notable smaller than those of ${}^{FC}J^{b}$ and ${}^{FC}J^{ob}$. The main question to be answered in the present work is about the general validity of the assertion made in the last sentence, i.e., are there cases where ${}^{FC}J^{oab}$ terms play an important role for defining an experimental trend of ${}^{1}J_{CH}$ SSCCs? Looking for compounds where such a trend could be verified, it is noteworthy that the σ_{C-H} bonding orbital containing the coupling nuclei should have an X substituent *geminal* to it. Other $\sigma^{*}_{C\text{-}X}$ antibonding orbitals corresponding to atoms bonded to the C carbon atom in σ_{C-H} should also play the role of "other antibonding orbitals" for the ${}^{1}J_{CH}$ SSCC under consideration. These conditions seem to be satisfied by 1-X-cyclopropanes (Scheme 2), and therefore, the set determined by X = H, Cl, Br, I, CN, COOH, CHO, NH_2 was chosen as a model series to assess the importance played by the ${}^{FC}J^{oab}$ term in defining the trend of ${}^{1}J_{C1H}$ SSCCs.

Experimental Details

Compounds are commercially available and were used without further purification. The NMR spectra were obtained on a Bruker Avance III 300 spectrometer equipped with an inverse 5 mm probe with z-gradient, operating at 300 and 75 MHz for ${}^{1}H$ and ${}^{13}C$, respectively. Samples were prepared as solutions of 20 mg of solute in 0.5 mL of $CDCl_3$. Spectra were taken at 300 K and were referenced to internal TMS. ${}^{1}J_{CH}$ SSCCs were determined using the coupled gHSQC pulse sequence.[10]

SCHEME 2: 1-X-Cyclopropanes



X
1 - H
2 - Cl
3 - Br
4 - I
5 - CN
6 - COOH
7 - CHO
8 - NH_2

TABLE 1: Theoretical and Experimental ${}^{1}J_{CH}$ SSCCs (Hz) for Compounds 1−8

	FC	total	experimental
1	163.0	165.2	162.0
2	195.0	196.3	192.7
3	194.2	195.8	192.6
4	189.7	191.2	189.0
5	175.4	177.5	178.5
6	172.3	174.4	169.6
7	170.4	172.5	168.7
8	171.3	173.2	172.0

Computational Approach

${}^{1}J_{CH}$ SSCCs were calculated using the CP-DFT methodology,[11] as implemented in the Gaussian03 package of programs.[12] Knowing the important role played by hyperconjugative interactions in the FC transmission, hyperconjugative interactions were evaluated using the Natural Bond Orbital (NBO)[13] method as it is implemented in the Gaussian03 program. In all calculations, the B3LYP hybrid functional was used, which consists of the hybrid Becke+Hartree−Fock exchange and the Lee−Yang−Parr correlation functional.[14] In geometry optimizations, the aug-cc-pVTZ basis set[15] was chosen. Calculations of all four terms of ${}^{1}J_{CH}$ (FC, SD, PSO, DSO) were carried out using the EPR-III basis set,[16] which is of a triple-ζ quality and includes diffuse and polarization functions. The s part of this basis set is enhanced to better reproduce the electronic density in the nuclear regions; this point is particularly important when calculating the FC term. For 1-I-cyclopropane (**4**), the aug-cc-pVTZ-PP[17] basis set was used for all calculations.

Results and Discussion

In Table 1, the theoretical (FC and total) and experimental ${}^{1}J_{C1H}$ SSCCs in 1-X-cyclopropanes (Scheme 2) are compared. It is observed that, as expected, the experimental trend is by far dominated by the FC term, and the whole trend is adequately reproduced at the level of approximation employed in this work (see Computational Approach).

In order to verify if the trend of the FC term displayed in Table 1 can be described resorting only to contributions ${}^{FC}J^{b}$ and ${}^{FC}J^{ob}$, in Table 2 the NBO occupancies of bonding and antibonding orbitals that, according to comments made in the Introduction, are expected to be important to influence the ${}^{FC}J^{b}$, ${}^{FC}J^{ob}$, and ${}^{FC}J^{oab}$ contributions to ${}^{1}J_{C1H}$ SSCCs in compounds **1** to **8**, eq 2 are collected. Data are presented as follows: from the occupancy of each bonding orbital is subtracted 2.000, i.e., the occupancy of an ideal bond and then such difference is

TABLE 2: Occupancies of Bonding and Antibonding Orbitales Relevant for J^b, J^{ob} and J^{oab} Contributions to $^1J_{C1H}$ SSCC in Compounds 1−8[a]

	σ_{C1-H}	σ^*_{C1-H}	$\sigma_{C1\text{-}X}$	$\sigma^*_{C1\text{-}X}$	σ_{C1-C}	σ^*_{C1-C}
1	−11	12	−11	12	−32	22
2	−13	28	−9	34	−32	40
3	−13	26	−12	37	−31	38
4	−15	22	−19	40	−31	36
5	−32	21	−11	30	−68	33
6	−18	17	−18	69	−75	30
7	−16	18	−12	61	−80	32
8	−12	38	−7	17	−41	35

[a] Occupancies for antibonding orbitals are given in 10−3, while those of bonding orbitals are obtained subtracting from the NBO calculated occupancies 2.000 (in 10−3).

TABLE 3: Sum of Occupancies of Bonding and Antibonding Orbitals That Are Relevant for the $^{FC}J^b$, $^{FC}J^{ob}$, and $^{FC}J^{oab}$ Contributions to $^1J_{C1H}$ in Compounds 1−8[a]

	$\lvert\sigma_{C1-H}\rvert + \sigma^*_{C1-H}$	$\sigma_{C1\text{-}X} + 2\sigma_{C1-C}$	$\sigma^*_{C1\text{-}X} + 2\sigma^*_{C1-C}$	s %	FC
1	23	−75	56	28	163.0
2	41	−73	114	28	195.0
3	39	−74	113	28	194.2
4	37	−91	112	30	189.7
5	53	−157	96	27	175.4
6	34	−169	128	29	172.2
7	34	−172	125	27	170.4
8	50	−89	87	27	171.3

[a] The s % character of the σ_{C1-H} is also shown.

expressed in 10^{-3} units. Occupancies of antibonding orbitals are given in 10^{-3} units. Although no linear relationship can be expected to connect occupancies with a given type of SSCC, in Table 3 the sum of occupancies that are considered to be adequate descriptors of how they affect such SSCCs are shown. Taking into account that delocalization interactions both from σ_{C1-H} and into σ^*_{C1-H} yield a decrease of the $^{FC}J^b$ term, the sum of their absolute values is shown in the first column of Table 3. Since delocalization interactions from "other bonds" yield a decrease of $^{FC}J^{ob}$, in the second column of the same Table 3 are shown the sum of the occupancies of the three "other bonds", and in the third column are displayed the sum of occupancies of the three "other antibonding orbitals". It is remarkable that the s% character of the σ_{C1-H} bond cannot account for the FC differences observed in Table 3; similar assertions hold for occupancies shown in the first and second columns. It is recalled that from the early work by Muller and Pritchard,[18] $^1J_{CH}$ SSCCs were related to the s% character of the corresponding σ_{C-H} bond; more recent attempts were reviewed briefly in ref 19. Therefore, the large increase in the FC term when going from compounds **1**−**4** seems to originate in data reported in the third column, which is equivalent to saying that in these cases, a relevant role is played by the $^{FC}J^{oab}$ term of eq 1. Similar assertions seems to hold for compounds **5**−**8**.

It is interesting to compare, Table 4, few substituent effects on $^1J_{C1H}$ SSCCs in the 1-X-cyclopropane series with the analogous substituted methanes (taken from refs 20 and 21). It is observed that for X = Cl, Br, I substituent effects on $^1J_{C1H}$ SSCC are larger for the halocyclopropane substrate than in halomethanes. This effect can easily be traced out to the large occupancies of the $\sigma^*_{C1\text{-}X}$ and σ^*_{C1-C} antibonding orbitals (it is recalled that there are two σ^*_{C1-C} antibonding orbitals) (see Table 1). These last two occupancies are large due to LP(*Hal*) → σ^*_{C1-C} interactions (*Hal* stands for halogen atom). Apparently, the CN substituent effect in methane is very large due to the strong $\sigma_{C-H} \rightarrow \pi^*$ hyperconjugative interactions of the methane σ_{C-H} bonds with any of both CN π-electronic systems. Such interactions yield a decrease of the absolute values of $^{FC}J^{ob}$ contributions, increasing $^1J_{CH}$. However, the σ_{C1-C} bonds in cyanocyclopropane (**5**) are expected to be less electron donors than the σ_{C-H} bonds in cyanomethane (acetonitrile). For this reason, it is expected that the CN substituent effect in the latter is expected to be larger than in the former. The difference of the NH_2 substituent effect on $^1J_{C1H}$ SSCC in cyclopropane and methane is only about 1 Hz, which is too small to attempt any qualitative rationalization.

TABLE 4: Comparison of Substituent Effects on $^1J_{CH}$ SSCC (in Hz) for Several Members of the 1-X-Cyclopropane Series (Table 1) with Analogous Values in Substituted Methanes CH_3−X

X	Cl	Br	I	CN	NH_2
1-X-cyclopropane	30.7	30.6	27.0	16.5	10
CH_3−X	25.0[a]	27.0[a]	26.0[a]	24[b]	11[b]

[a] Taken from ref 20. [b] Taken from ref 21.

Conclusions

Results presented in this work constitute a good example of the interesting potential of CLOPPA analytical expressions to be scrutinized for providing qualitative predictions of trends of $^1J_{CH}$ SSCCs in different series of compounds. This potential is notably enhanced if adequate approximations, based on physicochemical considerations, are included. In this work, this approach is applied to predict the kind of chemical surroundings that a σ_{C-H} bond should have for its corresponding $^1J_{CH}$ SSCC to be contributed by an $^{FC}J^{oab}$ term significant enough to define the experimental trend along a series of compounds. A point in case is a σ_{C-H} bond with a halogen atom bonded to the coupling C atom. In fact, the $\sigma^*_{C\text{-}Hal}$ antibonding orbital (where *Hal* stands for a halogen atom) is a very good electron acceptor. However, the halogen atom lone-pairs are very good electron donors. These facts are indicative that the $^{FC}J^{oab}$ term of such $^1J_{CH}$ SSCC should be important enough to define its trend for different halogen atoms. Similar conditions hold of other substituents undergoing strong hyperconjugative interactions into the antibonding orbitals playing the role of "other antibonds". This is observed for other substituents in 1-X-cyclopropane shown in Table 3.

Acknowledgment. The authors are grateful to FAPESP (Grant No. 06/03980-2, 05/59649-0) for the financial support of this work and for a fellowship (to A.C.N.) and a scholarship (to F.P.S.), and to CNPq for financial support and for fellowships (to R.R. and C.F.T). R.H.C. gratefully acknowledges financial support from CONICET (PIP 5119/05) and UBACYT(X222).

References and Notes

(1) (a) Oddershede, J.; Polarization Propagator Calculations. In *Advances in Quantum Chemistry*; Löwdin, P.-O., Ed.; Academic Press: New York, 1978, Vol. 11, p 275. (b) Engelmann, A. R.; Contreras, R. H. *Int. J. Quantum Chem.* **1983**, *23*, 1033.

(2) (a) Diz, A. C.; Giribet, C. G.; Ruiz de Azúa, M. C.; Contreras, R. H. *Int. J. Quantum Chem.* **1990**, *37*, 663. (b) Contreras, R. H.; Giribet, C. G.; Ruiz de Azúa, M. C.; Ferraro, M. B. *Electronic Origin of High Resolution NMR Parameters in Structure, Interactions, and Reactivity*; Fraga, S., Ed.; Elsevier: New York, 1992, Vol. 77B, Cap. 7, p 212; (c) Contreras, R. H.; Ruiz de Azúa, M. C.; Giribet, C. G.; Aucar, G. A.; Lobayan de Bonczok, R. *J. Mol. Struct. Theochem.* **1993**, *284*, 249. (d) González, J. A.; Aucar, G. A.; Ruiz de Azúa, M. C.; Contreras, R. H. *Int. J. Quantum Chem.* **1997**, *61*, 823.

(3) (a) Peralta, J. E.; Contreras, R. H.; Snyder, J. P. *J. Chem. Soc. Chem. Commun.* **2000**, 2025. (b) Barone, V.; Peralta, J. E.; Contreras, R. H.; Sosnin, A. V.; Krivdin, L. B. *Magn. Reson. Chem.* **2001**, *39*, 600. (c) Wilkens, S. J.; Westler, W. M.; Markley, J. L.; Weinhold, F. *J. Am. Chem. Soc.* **2001**, *123*, 12026.

(4) (a) Wu, A.; Gräfenstein, J.; Cremer, D. *J. Phys. Chem. A* **2003**, *107*, 7043. (b) Cremer, D.; Gräfenstein, J. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2791.

(5) Contreras, R. H.; Esteban, A. L.; Díez, E.; Della, E. W.; Lochert, I. J.; dos Santos, F. P.; Tormena, C. F. *J. Phys. Chem. A* **2006**, *110*, 4266.

(6) Ramsey, N. F. *Phys. Rev.* **1953**, *91*, 303.

(7) Giribet, C. G.; Ruiz de Azúa, M. C.; Contreras, R. H.; Lobayan de Bonczok, R.; Aucar, G. A.; Gomez, S. *J. Mol. Struct. THEOCHEM* **1993**, *300*, 467.

(8) (a) Reed, A. E; Curtiss, L. A; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Weinhold, F. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R, Ed.: Wiley: New York, 1998, Vol. 3, p. 1792.

(9) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975.

(10) (a) Palmer III, A. G.; Cavanagh, J.; Wright, P. E.; Rance, M. *J. Magn. Reson.* **1991**, *93*, 151. (b) Kay, L. E.; Keifer, P.; Saarinen, T. *J. Am. Chem. Soc.* **1992**, *114*, 10663. (c) Schleucher, J.; Schwendinger, M.; Sattler, M.; Schmidt, P.; Schedletzky, O.; Glaser, S. J.; Sorensen, O. W.; Griesinger, C. *J. Biomol. NMR* **1994**, *4*, 301.

(11) Sychrovský, V.; Gräfenstein, J.; Cremer, D. *J. Chem. Phys.* **2000**, *113*, 3530.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; *Gaussian 03 Revision C.02*, Gaussian, Inc., Wallingford CT, 2004.

(13) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. (*NBO 5.0G. Theoretical Chemistry Institute*, University of Wisconsin, Madison, WI, 2001);http://www.chem.wisc.edu/∼nbo5. Program was implemented in the Gaussian 03 package.

(14) (a) Becke, A. D. *Phys. Rev. A.* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(15) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358.

(16) Barone, V. *J. Chem. Phys.* **1994**, *101*, 6834.

(17) Peterson, K. A. *J. Chem. Phys.* **2003**, *119*, 11099.

(18) Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1959**, *31*, 768.

(19) Contreras, R. H.; Peralta, J. E.; Giribet, C. G.; Ruiz de Azúa, M. C.; Facelli, J. C. *Annu. Rep. NMR Spectrosc.* **2000**, *41*, 55.

(20) Lacey, M. J.; Macdonald, C. G.; Pross, A.; Shannon, J. S.; Sternhell, S. *Aust. J. Chem.* **1970**, *23*, 1421.

(21) Hu, Z.-M.; Zhan, C.-G. *Theo. Chim. Acta* **1993**, *84*, 521.

JP8069805