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ARTICLE

EPR and DFT Study of the Polycyclic Aromatic Radical Cations from Friedel-Crafts Alkylation Reactions

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Electron paramagnetic resonance and electron-nuclear double resonance methods were used to study the polycyclic aromatic radical cations produced in a Friedel-Crafts alkylating system, with *m*-xylene, or *p*-xylene and alkyl chloride. The results indicate that the observed electron paramagnetic resonance spectra are due to polycyclic aromatic radicals formed from the parent hydrocarbons. It is suggested that benzyl halides produced in the Friedel-Crafts alkylation reactions undergo Scholl self-condensation to give polycyclic aromatic hydrocarbons, which are converted into corresponding polycyclic aromatic radical cations in the presence of $AlCl_3$. The identification of observed two radicals 2,6-dimethylanthracene and 1,4,5,8-tetramethylanthracene were supported by density functional theory calculations using the B3LYP/6-31G(d,p)//B3LYP/6-31G(d) approach. The theoretical coupling constants support the experimental assignment of the observed radicals.

Key words: Electron paramagnetic resonance, Eelectron-nuclear double resonance, Density functional theory, Polycyclic aromatic radical cation

I. INTRODUCTION

It is well known that the Freidel-Crafts alkylation is a classic electrophilic aromatic substitution [1], and is a method used in the preparation of alky-substituted benzene. The catalyst usually used is aluminum chloride. Freidel-Crafts reactions, as we know them today, have grown with the Grignard method to be perhaps the most versatile and frequently used tools of organic chemistry, covering aromatic and aliphatic systems alike.

The aromatic radical cations, very important molecular species involved in many processes of physical, chemical, and biological interest, can be studied with electron paramagnetic resonance (EPR) spectroscopy. As already shown in previous studies [2], several novel polycyclic aromatic radical cations which are difficult to be prepared using other methods, have been observed from a Freidel-Crafts alkylation reaction with benzene, or substituted benzene, carried out in air-saturated systems without degassing the samples on a vacuum line. HCl gas evolved during the Freidel-Crafts alkylation reaction removes the dissolved oxygen in the solution, so that high-resolution EPR spectra are obtained. The results indicated that the benzyl halides produced in this alkylation reaction underwent Scholl condensation [3] to give polycyclic aromatic hydrocarbons, which were converted into the corresponding polycyclic aromatic radical cations in the presence of $AlCl_3$.

However, on reaction with alky-substituted benzenes the EPR pattern becomes extremely complex, and it has been shown that the type of radicals identified by EPR method depend on structure of the reactant. According to Ref.[4], the principal reactions of pure alkybenzene with $AlCl_3$ can involve dealkylation (dissociation) and alkylation, and either inter- and intra-molecular rearrangement. Sang *et al.* using EPR/ENDOR (electron nuclear double resonance), have investigated the reaction between *p*-xylene and Cl_2CHCH_3 in the presence of $AlCl_3$ [5]. They found that the radical cation examined was 2,6,9,10-tetramethylanthracene. This indicated the two methyl groups had broken away from the molecule in the presence of HCl during reaction.

EPR spectroscopy is the most important technique for the study of paramagnetic species. EPR emerged as the simplest and often most useful tool to detect, identify, and monitor the dynamic properties of free radicals in different conditions and environments [6]. The interaction between magnetic nuclei and unpaired electrons is represented by the hyperfine tensor, which can be factored into both an isotropic (Fermi) term and

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anisotropic (dipolar) term. The isotropic term, the so-called hyperfine coupling constant (hfcc) is a function of the Fermi contact interaction of the unpaired electron with a determined nucleus and strongly depends on the spin density at the nucleus position. On the other hand, the anisotropic term can be obtained from the classical expression of two interacting magnetic dipoles, and its value mainly depends on the overall spin distribution. EPR measurements performed in dilute fluid solutions under high-resolution conditions provide extremely precise isotropic hyperfine coupling constants for nuclei with both large and vanishing spin densities, unattainable with other techniques. Moreover, EPR can help to characterize the structure of paramagnetic species with unpaired electrons. Although EPR spectroscopy also provides rich information of the radical properties, its application in chemistry and biology is rather limited due to the difficulty of the interpretation of the hfcc and g values.

The ENDOR [6] technique has proven to be particularly useful for radicals [5] of polycyclic aromatic hydrocarbons having many overlapping lines and/or incompletely resolved EPR lines and for radicals in solid media in which these lines are broadened by hyperfine anisotropy. The ENDOR method overcomes the limited resolution of EPR spectroscopy by introducing additional selection rules. Furthermore, by detecting the nuclear magnetic resonance (NMR) transitions in the microwave range, the sensitivity is enhanced by orders of magnitude relative to pure NMR spectroscopy of radicals. The increase in resolution by ENDOR relative to EPR spectroscopy is due to a drastic decrease in the number of lines. It can readily be verified that any magnetic nucleus X or any set of n equivalent nuclei with a coupling constant a_{X} gives rise to a single pair of ENDOR signals, irrespective of the spin quantum number I and the g_n factor. The pair generally appears in a separate NMR frequency range characteristic of X. With each further set, the number of lines grows additively, not multiplicatively as in EPR. Independent of n and I, the total number of ENDOR lines for k sets is thus $2k$ and not $(2n_1I+1)$, $(2n_2I+1)\cdot\cdot(2n_kI+1)$. Therefore, this technique is particularly suited for an assignment of a complex hyperfine pattern, and the drastically improved resolving power compared to EPR spectroscopy makes ENDOR spectroscopy highly attractive for organic chemists and biochemists.

The assignment of the isotropic hfccs to different magnetic nuclei in each paramagnetic species is an important task for EPR spectroscopy. Theoretical predictions of radical hyperfine structures are serving an important role in the understanding of the properties of radicals and their reactions. Theoretical calculations are to provide valuable support for experimental results, and provide very important sources of information allowing us to obtain both the molecular geometry and the hfcc values. Many efforts have been devoted to the calculation of hyperfine coupling in order to carry out a correct assignment of the experimental data [7]. For this reason it has received a great deal of attention from theoretical chemists and EPR spectroscopists for many years [8-10]. Recently, density function theory (DFT) formalism can be used very efficiently to predict the hfcc at a reduced computational cost compared to the calculation of this property [11-13]. DFT procedure with a BLYP or B3LYP [14,15] functional is to be preferred when calculating hfcc of organic radicals [16-18].

The theoretical prediction of coupling constants of radicals produced in Friedel-Crafts alkylation is important, since the experimental spectra are often composed of many overlapping spectra. In addition to an unequivocal assignment of the absolute values $|a_{\mathrm{Xk}}|$, full information on the structure of a radical requires knowledge of the signs of its coupling constants, which is not directly available from an EPR spectrum. Experimental, theoretical, or combinations of both, make it possible to assign the hfcc and to determine their sign.

In this work, we report that comparison of experimental (EPR and ENDOR) and calculated hfcc provides important information for identifying the radicals formed, when alkyl aromatic (m-xylene, p-xylene) reacts with alkyl chloride as the solvent in the presence of excess aluminum chloride. This combination of experimental and computational techniques has enabled us to study the properties of radical cations and to assign the EPR spectra of radical cations produced from the Freidel-Crafts alkylation reaction. Studies of possible radical products in different reactants provide a better understanding of how the reactant affects which radicals are formed, and proposes a possible mechanism for radical formation.

II. EXPERIMENTS

A. Sample preparation

The sample tubes used in this work were Pyrex tubes with 4 mm in diameter. The samples were prepared directly in EPR tubes. As the mixture was heated gently, gases were released. The samples were not degassed on a vacuum line. During the Friedel-Crafts reaction the evolution of gases removes the dissolved oxygen in the solution. The sample was placed in the resonance cavity and its spectrum was recorded. The volume ratio of alkybenzene to alkyl chloride was 1:1.

B. EPR measurements

EPR spectra were obtained on a Varian E-115 spectrometer at the Lanzhou Institute of Chemical Physics operating at a microwave frequency of 9.5 GHz. The fields were calibrated with a Varian E-500 NMR gaussmeter, and the microwave frequency was measured with a frequency counter Model H/P 5342A. EPR spectra

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were recorded at room temperature. Computer simulations of isotropic spectrum were carried out with the EPR SimFonia program (Bruker).

C. ENDOR Spectrum

Under the control of Aspect Program, the ENDOR spectrum was recorded on a Bruker ER-2000 EPR spectrometer equipped with an EN810 ENDOR accessory. The parameters for ENDOR experiments are ES=5 MHz, ET=60 s, MD=40 kHz, RF=100-200 W (on 15 MHz). The ENDOR spectrum was obtained at 240-250 K.

D. Computational method

All calculations in this work were performed on isolated molecules using the Gaussian 03 package [19]. Starting geometries were optimized initially using the molecular mechanics method before using the UB3LYP functional in conjunction with the 6-31G(d) basis set, and these optimized structures were used for further calculations. The use of this relatively small basis set is justified by the number of geometry optimizations and by the fact that DFT methods are known to be weakly dependent on basis sets [20]. The hyperfine coupling constants were calculated using the unrestricted B3LYP hybrid density functional method and either 6-31G(d,p) or 6-31+G(d,p) basis set. Isotropic hyperfine coupling constants $a(i)$ are related to the spin densities at the corresponding nuclei by [21]

$$a_{\mathrm{iso}} = 0.28025\frac{8\pi}{3h}g_{\mathrm{e}}\beta_{\mathrm{e}}g_{\mathrm{N}}\beta_{\mathrm{N}}\rho(r_i) \qquad (1)$$

here, $\rho(r_i)$ is the spin density on the nucleus i, which is just $\rho(r_i)=|\Psi(r)|^2$, where $\Psi(r)$ is the molecular orbital containing the unpaired electron. g_{e} and g_{N} are the electron and nuclear g-factors, β_{e} and β_{N} are the Bohr and nuclear magnetons. The Gaussian 03 package reveals Mulliken atomic spin populations of a radical in Bohr magneton units (μ_{B}) (1 μ_{B} for doublet ground state, 2 μ_{B} for triplet ground state, etc.) and Fermi contact analysis representing the computed hfcc's results in units of mT. We converted the mT units into Gauss units to enable the comparison with experimental hfcc's data that usually given in Gauss (1 G=0.1 mT=2.8025 MHz).

TABLE I Experimental coupling constants of EPR of 2,6-dimethylanthracene and 1,4,5,8-tetramethylanthrancene cations and UB3LYP calculations.

Compound	Position	a/G	UB3LYP/ 6-31G(d,p)	UB3LYP/ 6-31+G(d,p)
R1[a] shown in Fig.1	H-1	3.28	−3.52	−3.36
	2-CH_3	2.76	2.71	2.72
	H-3	0.50	−0.45	−0.52
	H-4	3.16	−3.32	−3.13
	H-9	6.33	−6.37	−6.00
R2[a] shown in Fig.1	1-CH_3	3.60	3.76	3.79
	H-2	1.55	−1.49	−1.50
	H-9	5.40	−5.55	−5.18

[a] R1 and R2 were optimized by the unrestricted B3LYP/6-31G(d) with the C_2 symmetry imposed. Because of the symmetry, the same value of the hfcc appears twice.

III. RESULTS AND DISCUSSION

A. Identification of structure by EPR spectrum

1. m-xylene and 1,1,2,2-tetrachloroethane system

The reaction of 1,1,2,2-tetrachloroethane and m-xylene in the presence of excess $AlCl_3$ was carried out. The reaction took place rapidly when the mixture was gently heated and a well-resolved hyperfine coupling structure was observed. The EPR hyperfine coupling constants in gauss obtained from the analysis of spectrum are given in Table I.

This EPR spectrum is very similar to that observed for 2,6-dimethylanthracene in concentrated H_2SO_4, shown in Fig.2(a) [22]. Therefore, we could consider the radical cation as 2,6-dimethylanthracene radical cation. Its simulated spectrum (Fig.2(b)) using the coupling constants shown in Table I is in good agreement with the experimental spectrum. The formation process

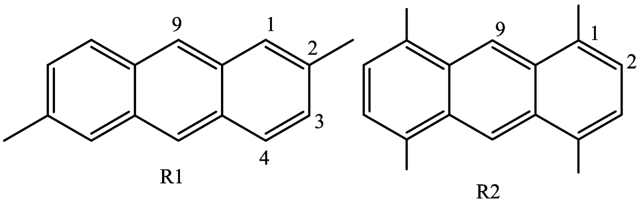

FIG. 1 The structure of 2,6-dimethylanthracene radical cation (R1) and 1,4,5,8-tetramethylanthracene radical cation (R2).

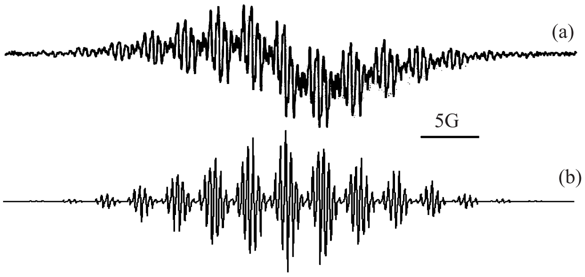

FIG. 2 (a) EPR spectrum of 2,6-dimethylanthracene radical cation. (b) Simulated spectrum.

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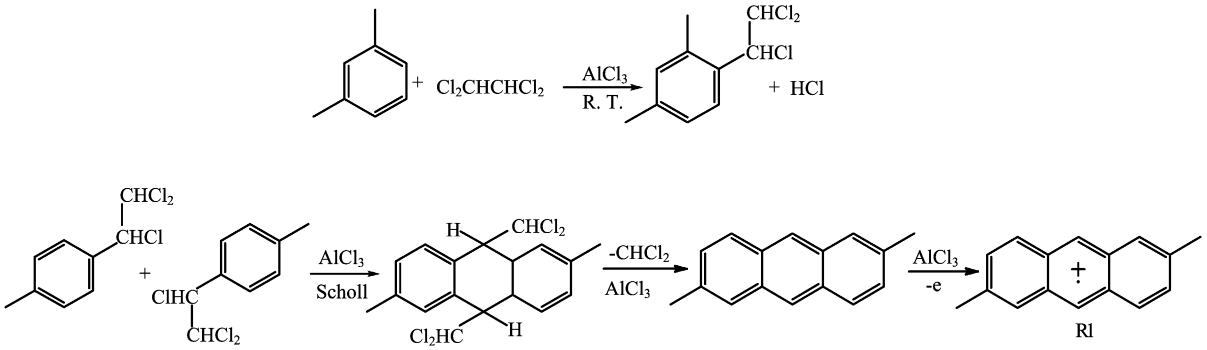

FIG. 3 The possible mechanism for the formation of the 2,6-dimethyltrancene radical cation.

of substituted anthracene radical cations is shown in Fig.3. 2,6-dimethylanthracene was formed through an intermolecular Scholl condensation reaction with benzyl chloride. 2,6-dimethylanthracene is converted into the corresponding radical cation (R1, the structure is shown in Fig.1), in the presence of $AlCl_3$. This indicated that two methyl groups had broken away from the compound 1 in the presence of HCl during the reaction. Based on these observations, the formation of the 2,6-dimethylanthracene radical cation can be interpreted by Fig.3. Another investigation supported this result, and the same radical cation was seen in the reaction of toluene and CH_2Cl_2 in the presence of $AlCl_3$ [5].

2. *p*-xylene and $CHCl_3$ (or CH_2Cl_2) system

The same EPR spectrum (Fig.4(a)) was observed for the system of *p*-xylene and excess $AlCl_3$ either in $CHCl_3$ or in CH_2Cl_2. The ENDOR spectrum of the reaction of *p*-xylene and excess $AlCl_3$ in $CHCl_3$ is shown in Fig.5. There are three ENDOR lines above the free proton frequency of 14.52 MHz: 16743.164, 19614.258, 22143.555 kHz, indicating three possible nonequivalent coupling constants. This radical may be assigned to 1,4,5,8-tetramethylanthracene radical cation (R2). Then a reasonable chemical assignment of coupling constant to particular protons could be made (see Table I). Based on these coupling constants of each set of equivalent protons, the simulated spectrum (Fig.4(b)) was obtained, which is identical with its experimental one. Its formation may be explained by Fig.6.

Comparing the reaction of benzene and $CHCl_3$ with the reaction of toluene and $CHCl_3$, in both cases 9,10-substituted anthracene radical cations are obtained. In the reaction of benzene and excess $AlCl_3$ in $CHCl_3$, the detected radical cation is 2,6-dimethyl-9,10 di(*p*-methylbenzyl) anthracene. However, no 9,10-substituted anthracene radical cation has been observed in the reaction of *p*-xylene and excess $AlCl_3$ in $CHCl_3$ or CH_2Cl_2. This is probably because of the steric hindrance resulting from four methyl-groups located at C1, C4, C5, and C8 positions. Therefore, only 1,4,5,8-tetramethyl anthracene radical cation was observed.

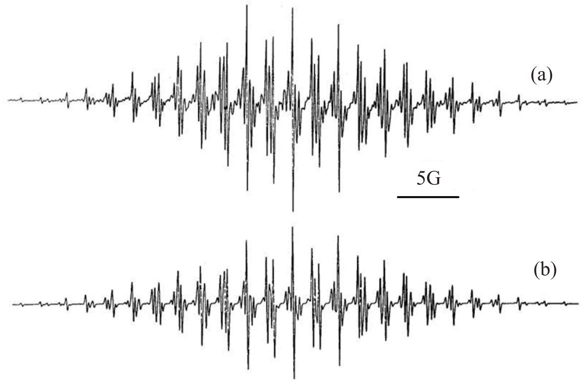

FIG. 4 (a) EPR spectrum of 1,4,5,8-tetramethylanthracene radical cation. (b) simulated spectrum.

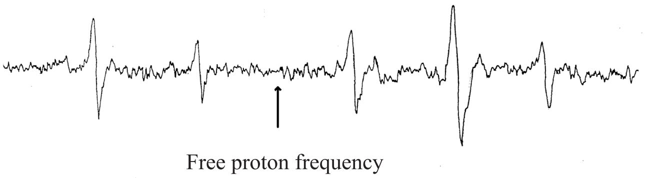

FIG. 5 ENDOR spectrum of 1,4,5,8-tetramethylanthracene radical cation.

B. DFT calculations: spin distribution and hyperfine coupling constants

The radical model was selected, starting from the assumption that benzyl halides produced in the Friedel-Crafts alkylation reaction undergo Scholl condensation to give polycyclic aromatic hydrocarbon, which is converted into the corresponding aromatic radical cations R1 and R2 in the presence of $AlCl_3$ (see Fig.2 and Fig.6). Because these two radicals were potentially consistent with the experimental results of EPR obtained

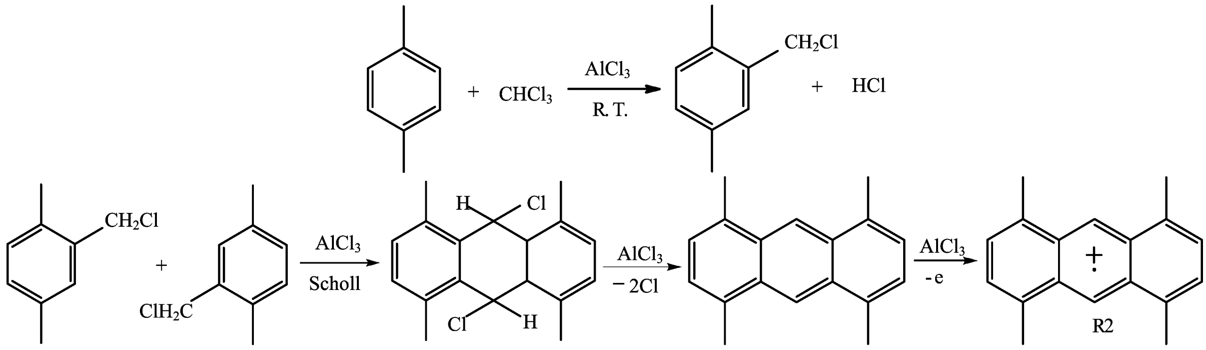

FIG. 6 The possible mechanism for the formation of the 1,4,5,8-tetramethylanthracene radical cation.

in the present work, it was retained as a possible candidate for the experimentally observed radical.

The geometrical optimization was carried out by using the B3LYP/6-31G(d). Several studies [18] have already indicated that this functional gives a reliable description of the geometry of a radical. From the DFT calculation, it is evident that 2,6-dimethylanthracene (R1) and 1,4,5,8-tetramethylanthracene radical cations (R2) geometry retain a planar conformation upon optimization, with a dihedral angle of 180.0° about two adjacent aromatic rings in anthracene rings.

DFT has been proven to be an accurate predictive tool, not only for the calculation of the molecular geometries, but also for the computation hyperfine coupling of organic radicals. In the both optimized aromatic radical cations, the spin density is completely delocalized. The spin density distribution in the radical R1 is very similar to that of R2. It is well-known that hfcc can be decomposed into two contributions: a delocalization term, which is always positive (or null), and a spin polarization, or indirect contribution, which is positive at the radical center and generally negative for hydrogen atoms. The standard computational approach in the work was to optimize the geometries using the B3LYP functional and the 6-31G(d) basis set. The hfcc values were calculated subsequently using the 6-31G(d,p) and 6-31+G(d,p) basis sets. The corresponding hfccs values evaluated at the B3LYP/6-31G(d,p) and the B3LYP/6-31+G(d,p) level are shown in Table I for comparison. Because these two radicals are present in solution and the experiments are performed at room temperature, the experimental equivalence of methyl protons implies their rapid rotation. The averages of the calculated methyl proton hyperfine coupling of each methyl group match the experimental coupling perfectly. From Table I, we can see that the calculated hfcc at the B3LYP level with 6-31G(d,p) basis set are in good agreement with experimental values. The results are quite similar to those obtained with B3LYP/6-31+G(d,p). Both radicals are conjugated radical cations that show a very great delocalization of the unpaired electron, and thus, the hfcc values are logically very small. All calculated values, presented in Table I, differ less than 5% from the experimental couplings. Hence, the experimental assignment is supported by the calculations. As is well known, the sign of a_{iso} is not determined when an experimental EPR spectrum is analyzed. The corresponding sign is assigned on the basis of the theoretical results. Thus, the absolute values for the experimental data are given.

IV. CONCLUSION

In the Friedel-Crafts alkylation system, polycyclic aromatic radical cations formed their parent hydrocarbons. The alky aromatics produced in Friedel-Crafts reactions undergo intermolecular Scholl condensation to give polycyclic aromatic hydrocarbons, which are converted into the corresponding polycyclic aromatic radical cations in the presence of $AlCl_3$.

DFT calculations of isotropic hyperfine coupling constants of anthracene-derived radicals, produced from Friedel-Crafts alkylation reactions, show that the theoretical coupling constants support the experimental assignment of the observed radicals. Combination of the B3LYP functional with Pople-6-31G(d,p) and 6-31+G(d,p) basis sets results in proton hfcc with a maximal deviation of about 5% from the experimental values.

The presented results explain the nature and structure of radical species in Friedel-Crafts alkylation systems. They form another example of the feasibility of DFT calculations of EPR spectroscopic properties of molecular species which are of real interest to experimental scientists.

V. ACKNOWLEDGMENT

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[1] G. A. Olah, *Friedel-Crafts and Related Reactions*, 2nd Ed. New York: Interscience, 1253 (1964).
[2] H. Q. Wang, L. D. Kispert, and H. Sang, J. Chem. Soc. Perkin Trans. II, 1463 (1989).
[3] A. T. Balaban and C. D. Nenitzescu, *Friedel-Crafts and Related Reactions*, 2nd Ed., New York: Interscience, 979 (1964).
[4] D. A. Nightingale, Chem. Rev. **25**, 329 (1939).
[5] H. Sang, H. Q. Wang, K. P. Such, and F. Jent, Magn. Reson. Chem. **30**, 150 (1992).
[6] B. C. Gilbert, M. J. Davies, and D. M. Murphy, *Electron Paramagnetic Resonance*, Cambridge: Royal Society of Chemistry, 18 (2002).
[7] W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Weinheim: Wiley-VCH (2002).
[8] C. J. Cramer, J. Am. Chem. Soc. **113**, 2439 (1991).
[9] M. Kaupp, M. Buhl, and V. G. Malkin, *Calculation of NMR and EPR Parameters. Theory and Applications*, Weinheim: Wiley-VCH (2004).
[10] L. Hermosilla, P. Calle, J. M. Garcia de la Vega, and C. J. Sieiro, J. Phys. Chem. A **109**, 7626 (2005).
[11] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
[12] R. Batra, B. Giese, M. Spichty, G. Geschedt, and K. N. Houk, J. Phys. Chem. **100**, 18371 (1996).
[13] A. Lund, L. D. Macomber, M. Danilczuk, J. E. Stevens, and S. Schlick, J. Phys. Chem. B **111**, 94849 (2007).
[14] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[15] M. Leopoldini, T. Marino, N. Russo, and M. Toscano, Theor. Chem. Acc. **111**, 210 (2004).
[16] A. R. Rakitin, D. Yff, and C. Trapp, J. Phys. Chem. A **107**, 6281 (2003).
[17] B. J. Lynch, P. L. Fast, M. Harrs, and D. G. Truhlar, J. Phys. Chem. A **104**, 4811 (2000).
[18] L. Hermosilla, P. Calle, J. M. Garcia de la Vega, and C. J. Sieiro, J. Phys. Chem. A **109**, 1114 (2005).
[19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C, Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M, W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *Gaussian 03*, Pittsburgh: Gaussian Inc., (2003).
[20] X. Li, Z. Cai, and M. D. Sevilla, J. Phys. Chem. A **106**, 1596 (2002).
[21] J. B. Foresman and A. Frisch, *Exploring Chemistry with Electronic Structure Method*, 2nd. Ed., Pittsburgh, PA: Gaussian, Inc. (1996).
[22] J. A. Valenzunela and A. J. Bard, J. Phys. Chem. **73**, 779 (1969).

DOI:10.1088/1674-0068/22/01/51-56