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An Investigation of the ^{17}O NMR Chemical Shifts in Oxiranes Using Magnetically Corrected Basis Sets

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The results of theoretical and experimental investigation of ^{17}O NMR chemical shifts for a number of epoxidic compounds are reported. The calculations were performed for the MP2/6-311G(d) level reference geometries using the GIAO and CSGT methods within the coupled Hartree−Fock perturbation theory. Various basis sets were applied in calculations of the chemical shifts. The performance of recently developed magnetically consistent basis sets and their advantages over the standard ones are discussed. The obtained results allow one to assign NMR signals for epoxides for which experimental data were obtained for the mixtures of stereoisomers.

I. Introduction

Nuclear magnetic resonance (NMR) is one of the most commanding methods in structural chemistry.[1] An important part of the information contained in an NMR spectrum is represented by the chemical shift. Relations between chemical shifts and molecular structure have so far been mostly given by empirical rules. However, the augmentation of information from experimental NMR spectra by ab initio quantum mechanical predictions of chemical shifts is becoming vital.[1,2] This is of crucial importance for the oxygen nucleus, since the NMR active nucleus ^{17}O has only small natural abundance and a large quadrupole moment.

The ^{17}O chemical shifts of epoxidic compounds have been the subject of a number of experimental studies.[3−7] In particular, as has been shown earlier,[7] the values of the ^{17}O chemical shifts correlate well with the basicity of epoxides and can be used for the preliminary estimation of their reactivity in reactions that proceed with electrophilic activation of the oxygen atom. However, until now only the parent oxirane has been investigated using theoretical methods.[8] The choice of the comprehensive series of epoxides **1**−**12** permits us to study trends in chemical shifts by systematic variation of their structures. In addition to serving as a benchmark for calculations, such a study also addresses the problem of the signal assignments in the spectra of diepoxides.[11,12]

The goal of this project is an evaluation of ^{17}O NMR chemical shifts for series of epoxides. We compare different methods and various basis sets and demonstrate the advantages of magnetically corrected basis sets proposed here over the standard ones.

Experimental values of δ^{17}O for acyclic epoxides **1**−**6** are taken from refs 3−5 and for exo-epoxinorbornane **7** from refs 6 and 7. The^{17}O NMR shifts for mixtures of stereoisomeric bicyclic epoxides **9** and **10** have been reported in ref 9. The experimental ^{17}O NMR spectra of diepoxides **11** and **12** are reported here for the first time.

II. Magnetically Consistent Basis Sets

To properly describe the behavior of a molecule affected by an external uniform magnetic field, it is necessary to augment a standard basis set by diffuse and polarization functions obtained from the first-order correction functions (response functions) generated by the perturbation operator that represents a given molecular property. One possible way to obtain such physically justified additional functions is the approach based on the solution of the nonhomogeneous Schrödinger equation for the model problem “one-electron atom in an external uniform field” using the closed representation of the Green’s function that enables one to obtain the exact expression of these first-order correction functions $\chi^{(1)}(r)$.[10] From their functional form it follows that $\chi^{(1)}(\vec{r})$ can be represented as linear combinations of AOs of exactly defined type and number. It has been shown that unlike the London AOs for a magnetic field, the Green’s function method enables one to obtain the general solution of the inhomogeneous Schrödinger equation. Our methods of expanding the initial basis sets by adding the first-order correction functions are based generally on the idea of Epstein[11] that the initial, unperturbed function should span as much of the perturbed space as possible. In particular, for nuclear magnetic shielding it means that such functions become approximately gauge-origin independent without introduction of field-dependent orbitals. Following the above-mentioned idea an addition of functions with the same exponents but higher angular momentum may be used to extend any initial basis set. In contrast with the first-order functions of Sugimoto and Nukatsuji[12] our response functions have been obtained by Green’s function closed representation. This allows us not only to account for the contributions of both discrete and continuous spectra but also to improve the wave function in those regions of the perturbed space that provide the main contribution to the calculated property.

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TABLE 1: Comparison of Calculated Structural Data for Oxirane 1 with Experimental Data

bond/angle	HF/6-311G(d)	MP2/6-311G(d)	expt[a]
C−O	1.399	1.432	1.431
C−C	1.453	1.467	1.466
C−H	1.077	1.086	1.085
H−C−H	115.4	116.1	116.6

[a] Reference 13.

There are two ways to choose the exponents of AOs (for the atoms of first and second rows) that provide the so-called 6-31G$^{\#\#}$(I) and 6-31G$^{\#\#}$(II) basis sets.

1. The AOs whose exponents coincide with those of $\chi^{(1)}(r)$ from which the AOs are generated.

The initial 6-31G basis set consist of the following functions: $6s(\xi_1)3s(\xi_2)3p(\xi_2)1s(\xi_3)1p(\xi_3)$, where ξ_1 , ξ_2, and ξ_3 are generalized notations of group exponents for 6s, 3sp, and 1sp.

The scheme of generating the additional basis functions is

$$s^{(1)}(\xi) \rightarrow p^{(0)}(\xi)$$

$$p^{(1)}(\xi) \rightarrow s^{(0)}(\xi) + d^{(0)}(\xi)$$

Thus, to the initial basis 6-31G for heavy atoms the $6p(\xi_1)$, 3d (ξ_2), and 1d (ξ_3) functions have been added and the resulting basis can be written in the form 6-31++G (1p2d). In other words, we derive a new basis 6s3s1s6p3p1p3d1d, containing (10s10p4d) primitive Gaussians, contracted into [3s3p2d].

For hydrogen atom new functions $3p(\xi_1)1p(\xi_2)$ have been added to the initial basis $3s(\xi_1)1s(\xi_2)$, resulting in 3s1s3p1p basis containing (4s4p) primitives, contracted into [2s2p].

Thus the new basis 6-31$^{\#\#}$(I) can be written as 6-31++G(1p2d,2p).

2. The additional AOs derived from $\chi^{(1)}$ functions which should be the solution of the Schrödinger equation for a given value of effective charge $Z^* = \xi n$:

$$s^{(1)}(\xi) \rightarrow p^{(0)}(\xi/2)$$

$$p^{(1)}(\xi) \rightarrow s^{(0)}(2\xi) + d^{(0)}(2\xi/3)$$

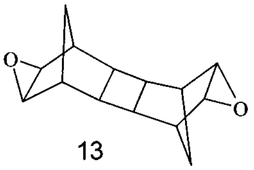
Thus, the $6p(\xi_1/2)$, $3s(2\xi_2)$, $3p(\xi_2/2)$, $1s(2\xi_3)$, $1p(\xi_3/2)$, $3d(2\xi_2/3)$, and $1d(2\xi_3/3)$ functions have been added to the initial 6-31G basis set for the heavy atoms. It leads to the 6s3s3s′1s1s′6p3p3p′1p1p′3d1d basis set containing (14s14p4d) primitive Gaussians that are contracted into [5s5p2d].

For hydrogen atom $3p(\xi_1/2)1p(\xi_2/2)$ functions have been added to the initial $3s(\xi_1)1s(\xi_2)$ basis set.

In summary, the new 6-31$^{\#\#}$(II) basis set can be formally written as 6-31++G(2s3p2d,2p).

III. Computational Details

A. Molecular Structures. The accuracy of the predicted shielding parameters depends on the method used, the quality of the basis sets, and the structural data. Since accurate experimental data are seldom available for the molecules of interest, theoretically optimized geometries are frequently used. Experimental structural data have been reported for oxirane **1**.[13] Table 1 displays the molecular parameters of **1** optimized at the HF[14] and MP2[15] levels of the theory using triple-ζ split valence basis sets augmented by polarization functions on carbon and oxygen atoms (6-311G(d)).[16] A comparison of the calculated geometrical parameters with experimental data demonstrates the importance of inclusion of the electron correlation effects. In particular, the HF approach gives significantly shorter values of C−O bond lengths of the epoxidic cycle; in contrast, the values obtained at the MP2 level are in good agreement with experimental data. To establish the reliability of MP2/6-311G(d) level geometry optimization for carcass epoxides we have compared X-ray[17] and MP2/6-311G(d) level geometries for 3,10-dioxaheptacyclo[9.1.1.^{8,12}0.^{2,4}0.^{6,14}0.^{7,13}0^{9,11}]hexadecane (**13**),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which consists of two exo-epoxinorbornane fragments. The comparison shows good agreement between the predicted geometry and experiment, within maximum deviation of 0.020 Å for bond lengths, 1.24° for bond angles, and 0.96° for dihedral angles (calculated and experimental geometrical parameters for compound **13** are given in Supporting Information). For this reason, molecular geometries of all other compounds were fully optimized (subject to molecular symmetry) at the MP2/6-311G(d) level. The calculations were performed using the Gaussian 98 code.[18]

B. Magnetic Shielding Calculations. The calculations of magnetic shielding were based on the CSGT (continuous set of gauge transformations),[19] IGAIM (individual gauges for atoms in molecules),[20] and GIAO (gauge including atomic orbitals)[21] formulations at the CHF level as implemented in the Gaussian 98 program.[18] Four Pople's basis sets of different size and quality (6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), and 6-311++G(3d,2p)[16]) as well as Dunning's correlation consistent (cc-pVTZ[22]) and Huzinaga III[23,24] basis sets have been employed in order to make constructive comparison of the reliability and efficiency of the 6-31G$^{\#\#}$(I) and 6-31G$^{\#\#}$(II) basis sets.

It is necessary to note that the CSGT method (a slight modification of the IGAIM method) developed by Keith and Bader[19,20] in the frame of CPHF theory gives sufficiently reliable results for nuclear magnetic shielding. The main idea of the above-mentioned method is consistent choice of the gauge-origin for the first-order electron current density that allows one to obtain correct perturbed molecular current density distribution close to nuclei. Such assumptions coincide with the underlying principles of our basis set construction method and one can expect that such concurrence will effect the accuracy of calculations.

The calculated ^{17}O isotropic magnetic shielding NMR data for H_2O, a direct reference compound, are displayed in Table 2. Chemical shifts were obtained by subtracting the calculated magnetic shielding for the ^{17}O nuclei of epoxide of interest from the reference compound (H_2O) shielding.

Because the CSGT and IGAIM methods give virtually the same values of magnetic shielding for all the studied epoxides, only the results of the CSGT method will be used in the following discussion.

IV. Experimental Details

Stereoisomeric diepoxides **11** and **12** were obtained by epoxidation of ethylidenenorbornene with peroxyphthalic acid as described in ref 25. The ^{17}O NMR spectra of compound **11** and **12** were obtained using the Brucker-CXP spectrometer at 27.131 MHz for solutions of equimolar mixtures of compounds in deuteriochloroform with use of the external standard (H_2O). The chemical shifts for **11** and **12** are collected in Table 4.

TABLE 2: Comparison of Calculated ^{17}O Magnetic Shieldings for the Reference Compound (H_2O) with Experimental Data (ppm)

method	6-31G(d,p)	6-311G(d,p)	6-311++G**	6-311++G(3d,2p)	cc-pVTZ	Huzinaga III	6-31G## (I)	6-31G## (II)	expt[a]
CSGT	290.5	283.0	306.4	326.3	313.08	323.34	324.4	325.4	334 ± 15
GIAO	339.0	342.8	325.7	327.0	335.03	328.03	325.4	327.8	

[a] Reference 19.

TABLE 3: Comparison of Calculated ^{17}O NMR Shifts for the Epoxides 1−10 with Experimental Data (ppm) and Parameters of the Linear Regression Equation $\delta_{expt} = a\delta_{calc} + b$

molecule	method	6-31G(d,p)	6-311G(d,p)	6-311++G(d,p)	6-311++G(3d.2p)	cc-pVTZ	Huzinaga III	6-31G##(I)	6-31G##(II)	expt
1	CSGT	−39.5	−46.7	−44.6	−49.1	−47.5	−46.2	−42.2	−47.2	−49[b,c]
	GIAO	−36.9	−32.2	−49.4	−47.3	−40.51	−49.1	−48.3	−51.9	
	N[a]	65	78	94	136	146	145	107	117	
2	CSGT	−27.0	−30.0	−19.0	−19.4	−24.7	−17.9	−15.1	−17.5	−16[c]
	GIAO	−14.2	−5.5	−28.7	−18.6	−12.3	−19.2	−22.1	−21.9	
	N[a]	90	108	130	188	204	200	148	160	
3	CSGT	−13.2	−12.6	3.8	5.1	−4.2	5.9	8.0	7.2	8[c]
	GIAO	5.7	17.6	5.4	5.9	11.0	5.6	0.2	3.0	
	N[a]	115	138	166	240	262	255	189	203	
4	CSGT	−15.8	−15.1	4.0	5.4	−4.8	6.4	7.8	7.1	14[c]
	GIAO	5.0	16.5	4.4	5.7	11.4	5.6	0.2	2.4	
	N[a]	115	138	166	240	262	255	189	203	
5	CSGT	−14.0	−12.0	7.2	9.4	−1.6	10.9	11.7	11.5	16[c]
	GIAO	8.3	20.8	9.5	9.7	15.3	9.9	3.5	6.9	
	N[a]	115	138	166	240	262	255	189	203	
6	CSGT	−30.2	−35.4	−23.8	−23.1	−28.9	−22.1	−17.5	−20.8	−18[c]
	GIAO	−16.5	−9.2	−23.1	−22.2	−16.1	−22.9	−24.7	−24.1	
	N[a]	115	138	166	240	262	255	189	203	
7	CSGT	−27.3	−33.1	−20.9	−13.8	−6.8	−13.8	−7.7	−11.0	−15[d]
	GIAO	−9.66	−1.28	−13.82	−13.63	−7.3	−13.6	−16.42	−15.87	
	N[a]	170	204	246	356	380	380	280	300	
8	CSGT	28.5	28.7	42.7	51.7	41.6	52.6	58.8	55.1	−
	GIAO	53.1	67.6	52.4	52.1	59.2	53.4	51.1	51.5	
	N[a]	170	204	246	356	380	380	280	300	
9	CSGT	0.2	−2.3	13.0	16.9	7.1	17.0	21.1	19.8	22.6[e]
	GIAO	19.2	29.7	16.1	17.6	22.9	17.6	14.3	15.5	
	N[a]	195	234	282	408	438	435	321	343	
10	CSGT	−22.9	3.9	−5.0	−2.3	−10.7	−2.1	5.7	0.5	0.7[e]
	GIAO	5.64	9.83	−3.18	−1.46	3.3	−1.7	−4.63	−3.9	
	N[a]	195	234	282	408	438	435	321	343	
CSGT	A	1.82	1.16	1.20	1.09	1.08	1.13	1.15	1.08	
	B	34.22	19.49	7.26	4.52	10.58	3.66	−0.49	2.00	
	R	0.9397	0.8585	0.9944	0.9941	0.8105	0.9955	0.9861	0.9925	
GIAO	A	1.30	1.07	1.04	1.11	1.14	1.08	1.18	1.08	
	B	0.75	−12.59	5.50	3.84	−2.52	4.07	8.77	6.75	
	R	0.9928	0.9928	0.9821	0.9941	0.9945	0.9938	0.9902	0.9930	

[a] The number of basis functions. [b] Calculated ^{17}O NMR shift for **1** is −37 (IGLO II[8]). [c] Reference 5. [d] Reference 6. [e] Reference 7.

TABLE 4: Comparison of Calculated ^{17}O NMR Shifts for the Epoxides 11, 12 with Experimental Data (ppm)

molecule	method	6-31G(d,p)	6-311G(d,p)	6-311++G(d,p)	6-311++G(3d,2p)	cc-pVTZ	Huzinaga III	6-31G##(I)	6-31G##(II)	expt
11 O_1	CSGT	−24.2	−28.8	−15.7	−7.6	−18.2	−8.0	−2.2	−4.7	−5.8
	GIAO	−4.2	5.4	−7.8	−7.4	−0.6	−7.2	−10.4	−8.8	
O_2	CSGT	4.9	7.3	28.9	33.3	19.7	33.6	36.1	36.1	39.8
	GIAO	30.7	45.1	32.6	33.7	38.8	34.7	28.6	32.5	
12 O_1	CSGT	−29.8	−35.4	−22.7	−15.4	−25.2	−15.7	−15.6	−12.6	−13.0
	GIAO	−10.0	−1.7	−15.9	−15.2	−8.1	−15.0	−18.0	−16.7	
O_2	CSGT	−7.3	−7.1	14.1	18.2	5.5	18.3	21.4	20.7	24.0
	GIAO	16.9	28.8	17.1	18.6	23.1	18.7	4.4	17.0	
	N[a]	225	270	326	472	498	505	338	426	

[a] The number of basis functions.

V. Results and Discussion

The calculated and experimental ^{17}O isotropic NMR chemical shifts (δ) for **1−10** are presented in Table 3. The parameters of the linear regression equation $\delta_{expt} = a\delta_{calcd} + b$ are given at the bottom of the columns.

One can see that the calculated values of the ^{17}O NMR chemical shifts are highly sensitive to the applied basis set and methods of calculation. In the case of the standard Pople basis sets, linear regression analyses show direct dependence of the quality of the ^{17}O NMR chemical shifts on the size of the basis set. This statement can be illustrated by values of intercept that decrease monotonically from 34.22 ppm for the 6-31G(d) basis set to 4.52 ppm in the case of the extended 6-311++G(3d,2p) basis set. The GIAO approach yields better agreement with experiment for small (6-31G(d,p) and 6-311G(d,p)) basis sets when compared to the CSGT results. Note that in the case of extended basis sets that include diffuse functions, CSGT and GIAO approaches give sufficiently close results. The same

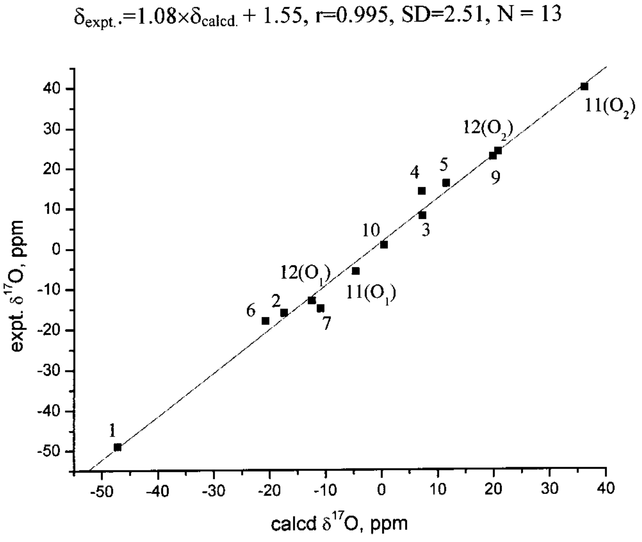

Figure 1. CSGT ^{17}O NMR shifts for epoxides **1**−**7** and **9**−**12** calculated at the HF/6-31G$^{\#\#}$(II) level plotted versus experimental data. The solid line corresponds to a linear regression equation for all of the plotted points.

conclusions are obtained in the case of the Huzinaga III basis set. In contrast, the results obtained with correlation-consistent basis set (cc-pVTZ) differ significantly for CSGT and GIAO calculations.

The data in Table 3 demonstrate the superiority of the proposed basis sets over the above-discussed basis sets. Thus, in case of CSGT calculations, linear regression equations for the 6-31$^{\#\#}$(I) and 6-31$^{\#\#}$(II) level results have a smaller value of intercept when compared to the standard 6-311G(3d,2p) and Huzinaga III basis sets, although the latter possess a larger number of basis functions.

We tested the performance of different theoretical approaches for calculations of the ^{17}O NMR chemical shifts of model epoxidic compounds. The proposed basis set was applied to address problems that cannot be solved on the basis of experimental data alone. The calculations predict much higher (60 ppm) magnetic shielding of ^{17}O nucleus in the case of exo-epoxinorbornane **7** compared to endo-isomer **8** (since known difficulties in the synthesis of the endo-epoxinorbornane **8**[26] experimental value of the ^{17}O chemical shift has not been obtained). Such a big difference in magnetic shielding underlines the large contribution of epoxinorbornanes' stereoisomeric particularities to their properties and reactivity.[6,7]

Since ^{17}O NMR spectra for epoxides **9** and **10** and diepoxides **11** and **12** have been measured for the mixtures of stereoisomers, a comparison of the calculated values of the ^{17}O chemical shift with experimental data is the only way to reliably assign NMR signals to the corresponding oxygen nucleus (see Tables 3 and 4). Using the 6-31G$^{\#\#}$(II) basis set, the calculated CSGT and GIAO isotropic ^{17}O NMR chemical shifts are plotted in Figure 1 versus the experimental data for all epoxides investigated here for which experimental data are available. One should also note that the epoxidic oxygens in the stereoisomeric epoximethylenenorbornanes **9** and **10** are characterized by noticeably different magnetic shielding (>23 ppm). Interestingly, in contrast to epoxinorbornanes **7** and **8**, in the case of spiroepoxides, exo-isomer **9** is characterized by a smaller magnetic shielding of the oxygen nucleus compared to endo-isomer **10**. A more complex problem has been accounted for by diepoxides **11** and **12** since it was necessary to assign four values of chemical shifts to the oxygen nucleus in different epoxidic fragments for exo- and endo-isomers. According to the results of the calculations, the signal of the most shielded nucleus ($\delta^{17}O_1 = -13.0$ ppm) corresponds to the epoxinorbornane oxygen in endo-isomer **12**. Note that this value is close to the corresponding value for unsubstituted exo-epoxinorbornane **7** (−15 ppm). On the contrary, the methyloxirane fragment in the exo-position leads to remarkable magnetic deshielding of the epoxinorbornane oxygen nucleus (δ^{17}O1 for **11** amounts to −5.8 ppm). The O_2 nuclei in diepoxides **11** and **12** are characterized by values of 39.8 and 24.0 ppm for δ^{17}O, respectively; thus, the oxygen nucleus in the endo-isomer is more shielded. This is in line with the above established trend for stereoisomeric epoximethylenenorbornenes **9** and **10**.

VI. Conclusions

This paper describes the method of construction of improved basis sets for nuclear magnetic shielding calculations. The calculated values of ^{17}O NMR chemical shifts for oxiranes clearly demonstrate the superiority of the developed basis set over standard basis sets. The results of our calculations allowed to solve a problem of the signal assignments in the mixtures of stereoisomeric epoxides **9** and **10** and **11** and **12**.

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Supporting Information Available: Calculated and experimental geometrical parameters for compound **13** and 6-31G$^{\#\#}$(I) and 6-31G$^{\#\#}$(II) basis sets for H, C, and O atoms in Gaussian format. This material is available free of charge via the Internet at http://pubs.acs.org.

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