Quantum-chemical estimates of geometric parameters of free radicals

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Experimental geometries of the $HCO^{\cdot}$ and $H_2CO^{\cdot+}$ σ-electron radicals were compared with those obtained from calculations with the total energy optimization carried out in the framework of widely used *ab initio* and semiempirical computational procedures. For each structural form of the radicals, the magnetic resonance parameters calculated in the MNDO approximation were correlated with experimental values determined by ESR spectroscopy. Comparative analysis of the results obtained indicates the possibility of systematic correction of the optimized geometric parameters of free radicals using the results of ESR measurements. A simple computational procedure for automatic geometry correction in the MNDO approximation is developed and evaluated.

Key words: free radicals, geometric parameters, magnetic resonance parameters, quantum-chemical calculations, geometry correction procedure.

Considerable advances in reliable establishment of the spatial structures of various organic molecules with closed electron shells have been made using quantum-chemical methods. The results of calculations performed in the framework of both modern semiempirical approximations and versions of the *ab initio* approach are, as a rule, close to the experimental results.[1,2] Much worse is agreement between the experimental results and those of quantum-chemical calculations (especially, semiempirical ones) of the geometry of open-shell systems, in particular, free radicals (see Refs. 1—5). Moreover, the absence of experimental data on the structure of complex free-radical systems is a rule rather than exception. In these circumstances it is of prime importance to perform quantum-chemical calculations of the geometry of a particular polyatomic radical using all available information on its properties obtained by physicochemical methods rather than rely only on semiempirical computational procedure for the total energy minimization.[6—8]

In the case of free radicals, their experimental ESR spectra undoubtedly pretend to play the role of the main source of additional information. If a free-radical species contains the atoms with magnetic nuclei, structural informativity of its ESR spectra can be appreciably enhanced. This allows the specially developed computational procedures[3,9—11] to be used for systematic correction of the geometric parameters obtained from semiempirical calculations with optimization of the total energy. In this work, we compared the experimental geometric and magnetic resonance parameters with the results of quantum-chemical calculations of three simple, related, and most reliably (both experimentally and theoretically) studied systems H_2CO, $HCO^{\cdot}$, and $H_2CO^{\cdot+}$. In addition, we analyzed the differences between the results of calculations and radiospectroscopic experiments in some cases where the optimized radical geometry differs from experimental geometry. The σ-electron radical $HCO^{\cdot}$ was systematically used previously[3,4,12—15] as a test system in evaluation of semiempirical procedures successively developed for free-radical systems.

Results and Discussion

Molecule H_2CO. The C—H and C=O bond lengths and the φ(H—C—O) bond angle in the H_2CO molecule calculated assuming a C_{2h} symmetry are listed in Table 1. Calculations were carried out using three semiempirical approximations (MNDO, AM1, and PM3), the Hartree—Fock (HF) *ab initio* method with the 3-21G, 3-21G*,★ 6-31G, and 6-31G** basis sets,[16] and the density functional theory (DFT) with the B3LYP density functional and the 6-31G(d,p), 6-311G(d,p), and 6-311+G(3df,2p) extended basis sets.[17] For comparison, Table 1 also lists the corresponding experimental values determined[18] by microwave spectroscopy and gas-phase electron diffraction.

Comparison of the data listed in Table 1 shows that the C—H bond lengths calculated by the semiempirical methods are (i) somewhat larger than those obtained using the *ab initio* approach and (ii) closer to both the

★ The 3-21G* basis set is the 3-21G basis set augmented with polarization p-functions for H atoms.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 183—188, February, 2001.

1066-5285/00/5002-188 $25.00

Table 1. Bond lengths (r/Å) and bond angle (φ/deg) in H_2CO molecule

Parameter	Semiempirical			*Ab initio* HF				DFT B3LYP			Experiment, Ref. 18
	MNDO	AM1	PM3	3-21G	3-21G**	6-31G	6-31G**	6-31G (d,p)	6-311G (d,p)	6-311+ G(3df,2p)	
r(CH)	1.106	1.111	1.091	1.083	1.090	1.082	1.087	1.110	1.110	1.106	1.116
r(CO)	1.216	1.227	1.202	1.207	1.205	1.210	1.207	1.207	1.200	1.199	1.208
φ(H—C—O)	123.5	122.2	121.8	122.5	123.0	121.7	121.9	122.4	122.3	122.0	116.5

result of DFT calculations (r(CH) ≈ 1.11 Å) and the experimental value, r(CH) = 1.116 Å. The C=O bond length obtained from the MNDO and AM1 calculations is appreciably larger than the results of optimization by the PM3 method, by the four versions of the *ab initio* HF calculations, and by the DFT B3LYP/6-31G(d,p) method. Many of the r(CO) values calculated by the PM3 and nonempirical methods are close to the experimental value. In all cases, the calculated magnitude of the φ(H—C—O) angle was found to be close to 120°, which agrees with the experiment.

All versions of calculations using the *ab initio* HF approach gave very similar geometric parameters of the H_2CO molecule. Augmentation of the basis set with polarization functions leads only to a slight increase in the C—H bond length and H—C—O bond angle and to a small shortening of the C=O bond. Mention may be made that the semiempirical methods employed reproduce both the experimental geometry of formaldehyde molecule and that obtained from the B3LYP/6-31G(d,p) calculations as well as the *ab initio* method. In other words, the semiempirical approximation was found to be quite competitive with the *ab initio* approach in the case of the closed-shell system.

Radicals $HCO^{\bullet}$ and $H_2CO^{\bullet+}$. The geometry of a free radical, optimized using semiempirical computational schemes developed in order to describe molecular systems, can be appreciably different from the experimental geometry.[3—8] This is every so often the main reason for large discrepancies between the theoretical values of the magnetic resonance parameters and corresponding experimental values found from ESR spectra, since the former are calculated for a certain "given" radical geometry. These discrepancies can be substantially reduced by performing calculations with experimental radical geometries. Therefore, particular emphasis should be placed on correct determination of structural characteristics of a free-radical system when estimating its magnetic resonance parameters by semiempirical methods. Moreover, it is possible to approximate the actual spatial structure of a system under study by using the same specially developed computational procedures[3,9—11] and striving to obtain the smallest deviations between the calculated and experimental values of magnetic resonance parameters.[3,4,8,9]

Previously,[9—11] we developed a scheme which allows calculations of all magnetic resonance parameters in the framework of semiempirical MNDO approximation. This scheme was evaluated taking a number of well-studied free radicals as examples. To obtain the estimates of the constants of isotropic hyperfine coupling (IHFC) with protons, a_{iso}^{H}, we also proposed[19] a formalism of calculations of the coefficient of proportionality between the spin population of the s-AO of H and the a_{iso}^{H} value. This procedure takes into account (i) the validity of the NDO approximation in the basis set of AOs symmetrically orthogonalized according to Löwdin and (ii) the symmetry of a radical under study (*i.e.*, the σ- or π-type of the radical) and allows the contradictions between recommendations of different authors[4,20—23] about the choice of this coefficient to be smoothed over. It was also shown[10,11] that simplified procedures for calculations of the anisotropic hyperfine coupling (AHFC) tensor and *g*-tensor in the MNDO approximation appear to be as least as efficient as those systematically used in the *ab initio* and DFT calculations.

Let us consider the totality of the results obtained by applying specially developed and evaluated[9—11] computational procedures to the well-studied (both experimentally and theoretically) σ-electron radical $HCO^{\bullet}$. Two appreciably different sets of experimental geometric parameters are known for this radical.[24,25] In principle, quantum-chemical analysis makes it possible to decide between the two radical geometries from the standpoint of the ESR spectral parameters. We obtained the geometric parameters of $HCO^{\bullet}$ radical using the same methods as in the case of H_2CO molecule. The calculated bond lengths, H—C—O bond angle, and the magnetic resonance parameters are listed in Table 2.

The C—H bond lengths calculated by the semiempirical and *ab initio* HF approaches are much smaller than the values found experimentally or from DFT B3LYP calculations (see Table 2). Unlike the H_2CO molecule, in this case the results of semiempirical calculations differ appreciably from experimental data. It should also be noted that, in contrast to the experiment and results of B3LYP calculations, all semiempirical methods led to a shortening of the C—H bond on going from H_2CO to $HCO^{\bullet}$ and that all four versions of the *ab initio* HF scheme qualitatively reproduced the actual lengthening of this bond. All computational methods employed reproduced the experimental C=O bond length in the $HCO^{\bullet}$ radical as satisfactorily (see Table 2) as in the case of H_2CO molecule (see Table 1). Noteworthy is

Table 2. Geometric and magnetic resonance parameters of HCO• radical

Parameter	Semiempirical			*Ab initio* HF				DFT B3LYP			Experiment		
	MNDO	AM1	PM3	3-21G	3-21G**	6-31G	6-31G**	6-31G (d,p)	6-311G (d,p)	6-311+ G(3df,2p)	Ref. 24	Ref. 25	Ref. 26
r(CH)	1.074	1.083	1.088	1.095	1.099	1.091	1.096	1.129	1.127	1.123	1.125	1.148	
r(CO)	1.185	1.192	1.166	1.180	1.180	1.184	1.183	1.183	1.174	1.171	1.175	1.177	
φ(H—C—O)	143.1	141.0	136.5	129.0	129.7	128.5	128.8	123.9	124.1	124.5	125.0	123.3	
	SEI	SEII	SEIII	NEI	NEII	NEIII	NEIV	DFI	DFII	DFIII	EI	EII	
$a_{iso}{}^{H}$	80.7	87.0	102.6	117.4	116.9	116.8	117.6	134.9	135.7	134.5	138.3	142.6	135.4
$a_{iso}{}^{C}$	99.3	105.0	111.3	118.3	117.7	118.6	118.4	118.0	118.3	118.3	117.9	118.0	133.9
$a_{iso}{}^{O}$	−12.5	−12.0	−12.2	−10.8	−10.8	−10.7	−10.7	−9.9	−10.2	−10.4	−10.3	−9.9	−15.1
$T_{11}{}^{H}$	−9.3	−8.9	−8.2	−7.4	−7.4	−7.5	−7.4	−6.3	−6.3	−6.4	−6.3	−5.8	−6.1
$T_{22}{}^{H}$	−4.5	−4.4	−4.0	−3.6	−3.6	−3.6	−3.6	−3.0	−3.0	−3.1	−3.0	−2.8	−2.9
$T_{33}{}^{H}$	13.8	13.3	12.2	11.0	11.0	11.1	11.0	9.3	9.3	9.5	9.3	8.6	9.0
$T_{11}{}^{C}$	−14.5	−13.9	−13.1	−11.7	−11.8	−11.7	−11.6	−10.5	−10.5	−10.7	−10.7	−10.1	−8.6
$T_{22}{}^{C}$	−17.7	−17.6	−16.6	−16.1	−16.1	−16.1	−16.1	−15.6	−15.5	−15.5	−15.2	−15.4	−17.3
$T_{33}{}^{C}$	32.2	31.5	29.7	27.8	27.9	27.8	27.7	26.1	26.0	26.2	25.9	25.5	25.9
$T_{11}{}^{O}$	11.9	11.8	12.2	12.3	12.3	12.3	12.3	12.6	12.6	12.6	12.6	12.6	—
$T_{22}{}^{O}$	18.4	18.4	18.0	18.2	18.1	18.3	18.2	17.9	17.8	17.8	17.4	17.6	—
$T_{33}{}^{O}$	−30.3	−30.2	−30.2	−30.5	−30.4	−30.6	−30.5	−30.5	−30.4	−30.4	−30.0	−30.2	—
g_{iso}	2.0012	2.0013	2.0012	2.0015	2.0015	2.0015	2.0015	2.0017	2.0017	2.0017	2.0017	2.0018	2.0003
g_{11}	2.0037	2.0037	2.0043	2.0038	2.0038	2.0038	2.0038	2.0039	2.0038	2.0038	2.0038	2.0038	2.0037
g_{22}	2.0024	2.0024	2.0025	2.0024	2.0024	2.0024	2.0024	2.0025	2.0025	2.0025	2.0024	2.0025	2.0023
g_{33}	1.9975	1.9977	1.9967	1.9984	1.9983	1.9984	1.9984	1.9988	1.9988	1.9988	1.9988	1.9990	1.9948

Note. The bond lengths r(CH) and r(CO) are given in Å, the angle φ(H—C—O) is given in degrees, and the constants of isotropic (a_{iso}) and anisotropic (T_{qq}) hyperfine coupling are given in Oe.

that the r(CO) value calculated in the PM3 approximation again appeared to be somewhat smaller than that obtained by other methods (see Table 2).

Unlike the H_2CO molecule, the differences between the estimates of the bond angle in the HCO• radical obtained using the semiempirical and *ab initio* approaches are large. However, the values obtained from *ab initio* calculations are much closer to the experimental results and those found using DFT B3LYP approach (see Table 2). Again (as for H_2CO), the results of all *ab initio* calculations are close to one another and differ from the experimental values and results of DFT calculations by about 5° to 7°. For semiempirical calculations, the differences are much larger and reach ~20° (the MNDO approximation). This indicates that the semiempirical methods based on the NDO approximation can roughly reproduce the actual geometry of H_2CO molecule, but not HCO• radical (*cf.* also the data listed in Table 1).

The reason for such a "failure" of all three versions of semiempirical NDDO approach is first of all that their parametrization was based on the experimental data for typical stable molecules and cannot therefore adequately take into account specific inter-electron interactions in open-shell systems. Often, similar "failures" of calculations for other molecular systems were smoothed over by corresponding modification of the semiempirical parametrization (development of numerous CNDO, INDO, and NDDO versions). However, in the case of free radical systems such a modification can hardly be done because of the lack of experimental data.

The magnetic resonance parameters listed in Table 2 were obtained for twelve variants of the geometry of σ-electron radical HCO• (three "semiempirical" structures, SEI—SEIII; four "*ab initio*" structures, NEI—NEIV; three "functional" structures, DFI—DFIII; and two experimental structures, EI and EII) using computational procedures[9—11] developed specially in the framework of the MNDO approximation. In addition to the theoretical values, Table 2 also presents the experimental values[3,26] of the constants of isotropic hyperfine coupling with the ^{1}H, ^{13}C, and ^{17}O nuclei, as well as corresponding principal values of the AHFC tensors, T_{qq}; isotropic g-factors, g_{iso}; and principal values of g-tensors. Let us consider them in detail.

As can be seen in Table 2, the $a_{iso}{}^{H}$ and $a_{iso}{}^{C}$ constants are particularly susceptible to the choice of the radical geometry. As was emphasized above, the struc-

Table 3. Isotropic hyperfine coupling constants (a_{iso}/Oe) in σ-electron radicals HCO• and $H_2CO^{\bullet+}$ obtained from DFT calculations with the B3LYP density functional

Constant	HCO•			$H_2CO^{\bullet+}$		
	6-31G (d,p)	6-311G (d,p)	6-311+ G(3df,2p)	6-31G (d,p)	6-311G (d,p)	6-311+ G(3df,2p)
$a_{iso}{}^{H}$	129.2	124.4	126.0	119.6	119.6	121.2
$a_{iso}{}^{C}$	151.2	138.0	134.0	−29.7	−34.1	−32.9
$a_{iso}{}^{O}$	−11.7	−9.5	−10.4	−11.4	−10.4	−9.7

ture SEI optimized in the MNDO approximation differs from the experimental structures (EI and EII) and "functional" structures (DFI—DFIII) to the greatest extent. In this case, the differences between the calculated and experimental constants a_{iso}^{H} and a_{iso}^{C} are also the greatest. For nearly identical structures NEI—NEIV, these differences are much smaller, though the theoretical a_{iso}^{H} and a_{iso}^{C} values are appreciably underestimated as compared to both the experimental values (see Table 2) and the results of DFT calculations for $HCO^{\bullet}$ radical (Table 3).

On the other hand, the IHFC constants a_{iso}^{H} estimated in the MNDO approximation for the experimental structures EI (138.3 Oe) and EII (143.8 Oe) are in good agreement with the experimental value (135.4 Oe), the structure EI being more preferable. The a_{iso}^{C} constants for the structures EI and EII obtained from calculations with the Hartree—Fock coefficient of proportionality, $K(C) = 1130$ Oe,[3,27] are nearly equal. This appeared to be somewhat unexpected. It is noteworthy that for all the twelve sets of geometric parameters of $HCO^{\bullet}$ radical the calculated a_{iso}^{O} constants are comparable in magnitude with the experimental value and have correct signs (see Table 2). Usually, quantum-chemical estimates of the constants of isotropic hyperfine coupling with heavy nuclei (in particular, ^{17}O and ^{13}C) are much more ambiguous and quantitative agreement is much worse than for the a_{iso}^{H} constants, especially in the framework of semiempirical approach.[3,4,22,23] The a_{iso}^{O} values obtained from DFT calculations are −11.7, −9.5, and −10.4 Oe for the structures DFI, DFII, and DFIII, respectively (see Table 3).

Unlike the IHFC constants, the components of the AHFC tensors of σ-electron radical $HCO^{\bullet}$ exhibit rather low sensitivity to variations of its geometric parameters (see Table 2). As in the case of the IHFC constants a_{iso}^{H} and a_{iso}^{C}, the calculated principal values of the T_{qq}^{H} and T_{qq}^{C} tensors for the structures NEI—NEIV and DFI—DFIII are closer to the experimental values than the corresponding values for the structures SEI—SEIII. The differences between the estimated (in the MNDO approximation) and experimental T_{qq}^{H} and T_{qq}^{C} values for the experimental structures EI and EII are nearly the same as those for the structures DFI—DFIII. Here, the structure EI seems to be more preferable. Unfortunately, no ESR data on the constant of anisotropic hyperfine coupling with the ^{17}O nucleus in the isotopomer of formyl radical are available. On the other hand, the results of calculations (see Table 2) suggest that the T_{qq}^{O} values are inappropriate to be used as a criterion for the choice of preferable geometry of $HCO^{\bullet}$.

The differences between the corresponding principal values of *g*-tensor calculated for the twelve variants of the structure of $HCO^{\bullet}$ radical (see Table 2) are small, which means that this tensor is also low "structurally sensitive". In all cases, the theoretical g_{11} and g_{22} components are in good agreement with experimental values. However, the calculated g_{33} components and, hence, the isotropic values, g_{iso}, appeared to be much larger than those found experimentally. On the other hand, the data listed in Table 2 show that their deviations from the *g*-factor of free electron ($g_e = 2.0023$) were reproduced correctly. From the standpoint of coincidence of the principal values of calculated and experimental *g*-tensors, structure EI again seems to be more preferable than structure EII.

Let us consider the σ-electron radical cation $H_2CO^{\bullet+}$ as yet another example. This radical is formed upon abstraction of an electron from formaldehyde molecule. The geometry of $H_2CO^{\bullet+}$ radical was optimized using the above-mentioned methods and different variants of its structure were denoted analogously, namely, SEI^{+}—$SEIII^{+}$, NEI^{+}—$NEIV^{+}$, and DFI^{+}—$DFIII^{+}$. Since the experimental geometry for the radical cation $H_2CO^{\bullet+}$ is unknown, we chose the structure determined[28] by multiconfigurational SCF calculations with the [5s, 3p, 2d, 1f/4s, 2p, 1d] basis set as a reference. By analogy, it was named RI^{+}. For all the eleven structural forms of this radical cation, Table 4 first lists the bond lengths *r*(CH) and *r*(CO), the bond angles H—C—O and then (similarly to $HCO^{\bullet}$, see Table 2) the constants of isotropic hyperfine coupling with the ^{1}H, ^{13}C, and ^{17}O nuclei, the principal values of the AHFC tensors, isotropic *g*-factors, and the principal values of *g*-tensors calculated in the MNDO approximation. The experimental values[24,29] of magnetic resonance parameters are also presented in Table 4.

Analysis of the data listed in Table 4 shows that, unlike neutral σ-radical $HCO^{\bullet}$, semiempirical NDO methods describe the C—H bond length in the radical cation $H_2CO^{\bullet+}$ more correctly than *ab initio* methods. Generally, a slight lengthening of the C—H bond must be observed on going from H_2CO to $H_2CO^{\bullet+}$. Semiempirical methods MNDO, PM3 and, especially, AM1 substantially overestimate this lengthening. On the contrary, all versions of the *ab initio* HF calculations gave an appreciable shortening of this bond instead of its lengthening (see Tables 1 and 4). Unlike DFT calculations with the B3LYP density functional, the semiempirical MNDO approximation and all versions of the *ab initio* HF calculations were found to be incapable of reproducing (even qualitatively!) a decrease in the C=O bond length in $H_2CO^{\bullet+}$ compared to H_2CO. On the other hand, the values of the H—C—O bond angle in $H_2CO^{\bullet+}$ obtained from semiempirical calculations (122.4—122.8°) are in good agreement with the corresponding value in the reference structure (123.0°).

Let us consider the magnetic resonance parameters of radical cation $H_2CO^{\bullet+}$ obtained using the same computational procedure as in the case of neutral σ-radical $HCO^{\bullet}$ (see Table 4). As can be seen, the differences between the experimental and theoretical values of the IHFC constants a_{iso}^{H} in $H_2CO^{\bullet+}$ for the structures NEI^{+}—$NEIV^{+}$ are much larger than for the structures SEI^{+}—$SEIII^{+}$ and RI^{+}. This is most likely due to the fact that semiempirical methods reproduce

Table 4. Geometric and magnetic resonance parameters of $H_2CO^{\bullet+}$ radical

Parameter	Semiempirical			*Ab initio* HF				DFT B3LYP			Reference[28]	Experiment, Ref. 24, 29
	MNDO	AM1	PM3	3-21G	3-21G**	6-31G	6-31G**	6-31G (d,p)	6-311G (d,p)	6-311+ G(3df,2p)		
r(CH)	1.122	1.142	1.117	1.084	1.087	1.084	1.085	1.120	1.121	1.120	1.117	
r(CO)	1.228	1.218	1.183	1.239	1.240	1.236	1.236	1.199	1.188	1.185	1.198	
φ(H—C—O)	122.4	122.8	122.5	118.4	118.7	118.4	118.2	119.9	120.2	120.2	123.0	
	SEI^+	$SEII^+$	$SEIII^+$	NEI^+	$NEII^+$	$NEIII^+$	$NEIV^+$	DFI^+	$DFII^+$	$DFIII^+$	RI^+	
a_{iso}^H	101.5	107.9	120.0	89.0	89.1	89.9	89.6	108.5	113.6	114.7	114.7	132.7
a_{iso}^C	−16.9	−18.4	−18.3	−14.4	−14.6	−14.5	−14.5	−17.1	−17.6	−17.7	−17.4	−38.8
a_{iso}^O	−22.0	−22.2	−23.3	−21.9	−21.9	−22.0	−22.0	−23.0	−23.3	−23.4	−22.9	
T_{11}^H	−4.3	−4.2	−4.4	−4.7	−4.6	−4.7	−4.7	−4.5	−4.5	−4.5	−4.4	
T_{22}^H	0.0	0.2	0.1	−0.8	−0.8	−0.8	−0.8	−0.3	−0.2	−0.2	0.2	
T_{33}^H	4.3	4.0	4.3	5.5	5.4	5.5	5.5	4.8	4.7	4.7	4.2	
T_{11}^C	−4.1	−3.7	−3.2	−4.6	−4.6	−4.6	−4.6	−3.7	−3.5	−3.4	−3.5	
T_{22}^C	−1.9	−2.1	−2.1	−1.4	−1.4	−1.4	−1.4	−1.8	−1.9	−1.9	−2.1	
T_{33}^C	6.0	5.8	5.3	6.0	6.0	6.0	6.0	5.5	5.4	5.3	5.6	
T_{11}^O	44.7	43.6	41.8	46.3	46.2	46.1	46.1	43.3	42.5	42.3	42.7	
T_{22}^O	33.1	32.2	31.1	34.9	34.9	34.8	34.8	32.4	31.8	31.7	31.7	
T_{33}^O	−77.8	−75.8	72.9	−81.2	−81.1	−80.9	−80.9	−75.7	−74.3	−74.0	−76.1	
g_{iso}	2.0037	2.0036	2.0036	2.0038	2.0038	2.0038	2.0038	2.0037	2.0036	2.0037	2.0036	2.0036
g_{11}	2.0060	2.0059	2.0059	2.0062	2.0062	2.0062	2.0062	2.0060	2.0060	2.0061	2.0059	2.0069
g_{22}	2.0037	2.0036	2.0035	2.0037	2.0037	2.0037	2.0037	2.0035	2.0035	2.0035	2.0036	2.0025
g_{33}	2.0013	2.0014	2.0014	2.0014	2.0014	2.0014	2.0014	2.0015	2.0014	2.0015	2.0014	2.0015

Note. The bond lengths r(CH) and r(CO) are given in Å, the angle φ(H—C—O) is given in degrees, and the constants of isotropic (a_{iso}) and anisotropic (T_{qq}) hyperfine coupling are given in Oe.

the C—H bond length in this radical cation better than the *ab initio* methods (see above). For each out of the eleven sets of geometric parameters of σ-radical $H_2CO^{\bullet+}$, the absolute value of the calculated IHFC constant a_{iso}^C was found to be nearly halved as compared with the experimental value and to have a correct sign. It should be noted that all methods reproduced the decrease in absolute values of the IHFC constants a_{iso}^H and a_{iso}^C on going from $HCO^{\bullet}$ to $H_2CO^{\bullet+}$. Noteworthy is also that the calculated principal components of g-tensor of the radical cation $H_2CO^{\bullet+}$ are low "structurally sensitive" and that in all cases their values are in reasonable agreement with the corresponding experimental value.

It should be noted that the difference between the calculated and experimental constants Δa_{iso}^H for the reference structure RI^+ ($|\Delta a_{iso}^H| \approx 25$ Oe, see Table 4) is much larger than for the experimental structure EI of $HCO^{\bullet}$ radical (~3 Oe, see Table 2). Previously, similar difficulties emerged in high-level *ab initio* calculations[24] of $H_2CO^{\bullet+}$; however, the above-mentioned difference was further reduced[28] from ~44 to ~17 Oe. It is also worthwhile to analyze the IHFC constants in the σ-electron radicals $HCO^{\bullet}$ and $H_2CO^{\bullet+}$ obtained from DFT B3LYP calculations (see Table 3). As can be seen, the a_{iso}^H values listed in Table 3 differ from the experimental values by ~6—11 Oe for $HCO^{\bullet}$ (see Table 2) and by ~12—13 Oe for $H_2CO^{\bullet+}$ (see Table 4).

Thus, analysis of all geometric and magnetic resonance parameters (see Tables 2 and 4) suggests the possibility of determining a realistic geometry of a free radical by comparing the results of seemingly inadequate semiempirical MNDO calculations with the experimental data obtained by radiospectroscopic methods. This can be done at relatively low computational cost. If the radical system has markedly different structural forms, the results of quantum-chemical calculations of their magnetic resonance parameters can also be used as additional argument in favor of a particular experimental structure. Usually, the a_{iso}^H constants appear to be particularly sensitive criterion for the choice of the radical geometry.

We developed an external (with respect to the GAMESS program package[16]) automated computational procedure for correction of the geometry obtained from calculations with optimization of the total energy. This procedure is applicable to paramagnetic systems and uses their magnetic resonance parameters. It minimizes the function, which characterizes the deviation of the calculated magnetic resonance parameters of a particular free-radical species from the corresponding experimental values:

$$G(\Delta E,\{\mathbf{R}\}) = \sum_A c_a(A)\left[a_{iso}^{calc}(A,\{\mathbf{R}\}) - a_{iso}^{exp}(A)\right]^2 + \sum_A c_t(A) \sum_{q=1,2}\left[T_{qq}^{calc}(A,\{\mathbf{R}\}) - T_{qq}^{exp}(A)\right]^2 + c_g \sum_{q=1,3}\left[g_{qq}^{calc}(\{\mathbf{R}\}) - g_{qq}^{exp}\right]^2 + \delta(\Delta E), \quad (1)$$

where $\{\mathbf{R}\}$ is the set of structural parameters to be corrected and summation is performed over the atoms A with the known hyperfine coupling constants and over

the independent principal components of tensors. The coefficients c_a, c_t, and c_g in expression (1) depend on the admissible statistical significance of the errors of calculations of the corresponding magnetic resonance parameters. The set of geometric parameters, {**R**}, is corrected if the deviation of the total energy of the system from the optimized value does not exceed a preliminarily specified ΔE value. This correction procedure can to some extent be considered as a way of both modification of semiempirical parametrization (see above) and taking into account possible effect of medium on the structure of a free-radical species.

This procedure was evaluated taking the σ-radical $HCO^{\bullet}$ as an example. For this radical, the differences between the experimental geometric parameters and the geometry optimized in the MNDO approximation are large (see Table 2). For the function (1), the increment ΔE to the minimum total energy was considered admissible if $\Delta E < 10$ kcal mol^{-1}. Statistically significant errors were assumed those exceeding 1 Oe for the constants of IHFC and AHFC with protons (A = H), 4 and 2 Oe for the constants of IHFC and AHFC with heavy nuclei (A ≠ H), respectively, and $4 \cdot 10^{-4}$ for the components of g-tensor. This holds for the following coefficients used in the expression (1): $c_a(\mathrm{H}) = c_t(\mathrm{H}) = 4 \cdot 10^{-2}$, $c_a(\mathrm{A} \neq \mathrm{H}) = 2.5 \cdot 10^{-3}$, $c_t(\mathrm{A} \neq \mathrm{H}) = 10^{-2}$, and $c_g = 2.5 \cdot 10^5$.

This computational procedure was applied to two experimental sets of geometric parameters of $HCO^{\bullet}$ radical (see Table 2). The values of the function G obtained after single-step (in each case) implementation were 4.88 for structure EI and 7.19 for alternative structure EII. This is in agreement with the previously drawn conclusion that structure EI is more preferable.

Minimization of the function (1) was performed using the geometric parameters of $HCO^{\bullet}$ radical obtained from calculations with optimization of the total energy in the MNDO approximation (see Table 2) as initial approximation. This corresponds to G(SEI) = 125.30. After minimization, we found that the value of the function (1) equals 2.62 and the ΔE value equals only 5.4 kcal mol^{-1}. The calculated geometric parameters of σ-radical $HCO^{\bullet}$ are as follows: the bond lengths r(CH) = 1.123 Å and r(CO) = 1.160 Å and the bond angle φ(H—C—O) = 125.4°. Thus, the geometry of formyl radical corrected using the function (1) is in much better agreement with the experimental geometry (EI) or the structures obtained from DFT B3LYP calculations than with any structure calculated using either three semiempirical NDO approximations with optimization of the total energy or four versions of the *ab initio* HF approach (see Table 2). The magnetic resonance parameters obtained in this case are close to those listed in Table 2 for the structures DFI—DFIII and EI. In particular, a_{iso}^{H} = 135.1 Oe, a_{iso}^{C} = 118.1 Oe, and $a_{iso}^{O} = -10.8$ Oe.

Similar results were obtained after minimization of the function (1) for the $H_2CO^{\bullet +}$ radical cation. Single-step (in each case) implementation of the computational procedure showed that the structures $SEIII^+$ and RI^+ are the most preferable. After minimization of the function (1) we found that the ΔE equals 2.6 kcal mol^{-1} and the geometric and magnetic resonance parameters are as follows: r(CH) = 1.129 Å, r(CO) = 1.183 Å, the bond angle φ(H—C—O) = 127.7°, a_{iso}^{H} = 132.8 Oe, $a_{iso}^{C} = -19.3$ Oe, g_{iso} = 2.0035, g_{11} = 2.0057, g_{22} = 2.0036, and g_{33} = 2.0012. Currently, testing of this correction procedure for applicability to more complex paramagnetic systems is in progress.

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Received December 2, 1999;
in revised form April 26, 2000