Role of Standard Diffuse Functions for Computing Hyperfine Splitting Constants in Radical Anions

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The effect of diffuse functions on geometry and isotropic hyperfine splitting (hfs) constants of radical anions ($FCN^{\bullet-}$, $HCN^{\bullet-}$, $HCCH^{\bullet-}$, $BF_3^{\bullet-}$, $BH_3^{\bullet-}$, and $HBO^{\bullet-}$) has been studied at the UQCISD/6-311G(d,p) level. The use of standard diffuse functions (6-311++G(d,p)) provides unreliable geometry and hfs constants for radical anions that are kinetically unstable in the gas phase ($HCN^{\bullet-}$, $HCCH^{\bullet-}$, $BH_3^{\bullet-}$, and $HBO^{\bullet-}$). Unreliable results for these radicals are obtained also enlarging the basis set (6-311++G(2df,p)). The reliability of the results can be assured constructing graphics as a function of the exponent of the diffuse functions and analyzing the population of the singly occupied molecular orbital (SOMO) to establish its nature (valence or diffuse MO). A procedure for computing reliable hfs constants in radical anions is proposed.

Introduction

Calculation of isotropic hyperfine splitting (hfs) constants for moderate-sized radicals has been a hard task for a long time. In past years computer technology and the development of efficient computational methods made the computation of reliable hfs constants feasible also for large-sized radicals. Carmichael[1] showed that experimental hfs constants of small-sized radicals can be closely reproduced by the unrestricted quadratic configuration interaction method with single and double substitutions (UQCISD) employing a moderately large triple-ζ basis set supplemented with polarization functions (TZP). Good hfs constants for moderate-sized radicals were computed with the Møller−Plesset second-order perturbation theory (UMP2) using the small full double-ζ (DZP)[2] and valence triple-ζ 6-311G(d,p) (VTZP)[3] basis sets, which requires much less computational resources. However, this approach provides unreliable hfs constants when the underlying unrestricted Hartree−Fock (UHF) reference wave function does not describe well the doublet state[4−6] and even the determination of the basic structure is problematic.[7] Hence, the evaluation of hfs constants with the UMP2 method must be checked case-by-case against the UQCISD method,[5,8] for example studying the simplest member of a class of radicals at both levels.[9] Hfs constants of large-sized radicals could be computed with reliability using the UB3LYP method,[10] which is based on the density functional theory (DFT).

Recently, Radom and co-workers[11] investigated the effects of different basis sets and computational methods including MP2, QCISD, and various DFT methods on the hfs constants of small-sized radicals. As expected, the UQCISD method provides the best performance. Agreement with experiment worsens slightly in increasing order employing the UB3LYP and UMP2 methods.

As far as the basis set effects are concerned, it was shown that experimental hfs constants are excellently reproduced employing the moderately large 6-311G(2df,p) basis set. As expected,[12] the more flexible valence correlated consistent basis sets (cc-pVXZ; X= D, T, Q) give poor agreement with experiment owing to unbalanced contraction of the s-shell. However, good results can be obtained including core and core-valence correlation effects (cc-pCVXZ; X = T, Q).[12,13] Addition of standard diffuse functions to heavy atoms (6-311+G(2df,p) improves significantly the agreement with experiment only in radical anions (namely, $HCN^{\bullet-}$, $FCN^{\bullet-}$, and $HCCH^{\bullet-}$).

In our opinion the study of the effect of diffuse functions on the hfs constants of radical anions is, however, incomplete for the following two reasons.

1. The use of diffuse functions on heavy atoms was found to be important in studying radical anions. Indeed, the 6-311+G(d,p) and 6-311+G(2df,p) basis sets give an adequate description of the s spin density at the nuclei. However, a large proton coupling constant was observed in $HCN^{\bullet-}$ and $HCCH^{\bullet-}$. Hence, the effect of addition of diffuse functions also to hydrogens should be investigated.

2. The electron transmission (ET) spectrum of HCN and HCCH shows a shape resonance at low energy which was ascribed to temporary capture of an incident electron in the lowest unoccupied molecular orbital (LUMO).[14] Hence, the use of diffuse functions might provide meaningless results for $HCN^{\bullet-}$ and $HCCH^{\bullet-}$ owing to their instability in the gas phase.

Indeed, it was shown by us that addition of standard diffuse functions provides unreliable values of the negative electron affinity (EA) determined by ET spectroscopy since such calculations tend to describe a system composed of the neutral molecule plus a free electron.[15] This explains why correlation between the EAs computed for a large number of different molecules and those determined experimentally by ETS was found to become unexpectedly very poor adding standard diffuse functions.[14] Unreliable results were also obtained in computing the relative stability of linear- and Y-conjugated dianions employing standard diffuse functions.[16] Nevertheless, the problem concerning the reliability of the results obtained with the use of diffuse functions for negatively charged species that could be unstable with respect to electron loss is systematically ignored. For example, the EA of DNA bases were computed using standard diffuse functions and, obviously, a poor correlation was found between theory and experiment.[17] Furthermore, in a recent review on gas-phase stability of small anions,[18] it was claimed that the use of diffuse functions is useful for describing the relative stability of linear- and Y-conjugated

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dianions when it was unequivocally demonstrated by us long before that the results referenced in the review have no physical meaning.[16]

We have thus studied the effect of diffuse functions on geometry and hfs constants of radical anions.

Computational Details

MO calculations have been performed on the radical anions $FCN^{\bullet-}$, $HCN^{\bullet-}$, $HCCH^{\bullet-}$, $BF_3^{\bullet-}$, $BH_3^{\bullet-}$, and $HBO^{\bullet-}$ and on their neutral parents with the GAUSSIAN 94 system of programs[19] running on either RISC-6000 IBM or DEC AlphaStation 500 computers. Geometry and hfs constants have been determined employing the 6-311G(d,p) basis set, i.e., a valence-triple-ζ (VTZ)[20] basis set supplemented with polarization functions (P), p-functions on hydrogens, and five-component d-functions on heavy atoms.[21] This basis set was, however, demonstrated to be of valence triple-ζ quality in the p-space but actually of full double-ζ quality in the s-space.[22]

Calculations have been also carried out augmenting the basis sets with diffuse functions, s-functions, and p-functions on heavy atoms and s-functions on hydrogens. To investigate their influence on both the structural parameters and magnetic properties, the exponents, $\alpha(\lambda)$, of the diffuse functions have been varied proportional to the difference between the exponents ($\alpha_{out-val}$) of the outermost valence functions and those (α_{diff}) of the standard diffuse functions.[23]

$$\alpha(\lambda) = \alpha_{out-val} + \lambda(\alpha_{diff} - \alpha_{out-val}) \qquad (1)$$

The effect of electron correlation has been estimated employing the QCISD method.[24] Core electrons have been held frozen since their inclusion is not expected to significantly influence optimum geometries and was found to give a small contribution to hfs constants using an unrestricted Hartree−Fock (UHF) reference determinant since spin-polarization effects are included explicitly.[6,25]

The results obtained with the small 6-311G(d,p) basis set have been checked against the more flexible 6-311G(2df,p) basis set carrying out calculations on $HCN^{\bullet-}$, $HCCH^{\bullet-}$, $BH_3^{\bullet-}$, and $HBO^{\bullet-}$.

Vibrational effects at a given temperature T have been estimated averaging the computed hfs constants a over the thermally populated vibrational states of the inversion mode about the central atoms[27]

$$\langle a(\mathrm{T})\rangle = \sum\nolimits_m \langle\psi_m|a(\delta)|\psi_m\rangle \exp(-E_m/KT)/\sum\nolimits_m \exp(-E_m/KT) \qquad (2)$$

The eigenfunctions ψ_m and eigenvalues E_m have been taken as solutions of the Hamiltonian H for the inversion mode that has been approximated with a one-dimensional double-minimum potential

$$H = -h^2\,\partial^2\psi_m/8\pi^2\mu\,\partial^2\delta + k\delta^2/2 + v\exp(-c\delta^2) \qquad (3)$$

where μ is the reduced mass kept fixed to the value calculated at the equilibrium geometry. For linear and planar radicals the last term of the potential, which determines the barrier height of double-well potentials, has been replaced by a quartic term that accounts for the anharmonicity:

$$H = -h^2\,\partial^2\psi_m/8\pi^2\mu\,\partial^2\delta + k\delta^2/2 + b\,\partial^4/2 \qquad (4)$$

TABLE 1: Vertical Ionization Potential (VIP)[a] of the Radical Anions Computed with the UQCISD Method along with Vertical Electron Affinity (VEA)[a] of the Parent Neutral Molecules

	6-311G(d,p)		6-311+G(d,p)		6-311++G(d,p)	
	VIP	VEA	VIP	VEA	VIP	VEA
$FCN^{\bullet-}$	1.84	−4.91	2.27	−4.23	−	−
$HCN^{\bullet-}$	−0.82	−4.04	−0.50	−2.25	−0.89	−0.89
$HCCH^{\bullet-}$	−0.63	−3.84	−0.32	−1.81	−1.19	−1.19
$BF_3^{\bullet-}$	0.66	4.14	1.03	1.80	−	−
$BH_3^{\bullet-}$	−0.46	−0.71	−0.30	−0.32	−0.30	−0.32
$HBO^{\bullet-}$	−0.54	−3.28	−0.33	−1.53	−0.33	−1.52

[a] Values in eV.

The potential-energy parameters are uniquely determined by the curvature at the minimum (k_m) in conjunction with the energy barrier to inversion (E_{inv}) for eq 3[28] and with the fourth derivative at $\delta = 0°$ for eq 4. Derivatives have been computed numerically. The hfs constant a has been expanded in an even-power series of δ:

$$a(\delta) = \sum\nolimits_n c_n\delta^2$$

The expansion coefficients have been determined by means of a least-squares fitting of the values computed as a function of δ at 2.5° intervals. The Hamiltonian H has been set up in the basis of the eigenfunctions of the harmonic oscillator.[29] An expansion up to the 40th term is sufficient to obtain complete convergence for the thermally populated states.

Results and Discussion

Effects of Diffuse Functions on the Properties of Radical Anions. We have first examined the effect of standard diffuse functions on the structural and magnetic properties of the radical anions previously studied in ref 11 using the QCISD method and the 6-311G(d,p) basis set. It should be remarked that the best performance in the calculation of hfs constants was obtained using the more flexible 6-311G(2df,p) basis set. However, agreement with experiment worsens only slightly using the small 6-311G(d,p) basis set, which was recommended for studying large-sized radicals.

The neutral molecules FCN, HCN, and HCCH are computed to have a linear structure at the UQCISD/6-311G(d,p) level of theory. Table 1 shows that the vertical electron affinity (VEA) of these molecules is negative. Interestingly, the absolute value decreases with successive addition of standard diffuse functions as expected for unstable anions. Hence, the parent radical anions might be kinetically unstable in the gas phase, so extreme caution should be exercised in estimating properties for these radical anions employing diffuse functions.[15]

Usually experimental geometry is not available for radical anions, so the structural parameters are determined theoretically by means of optimization techniques starting from the structure of the parent neutral molecule. The geometry of $FCN^{\bullet-}$, $HCN^{\bullet-}$, and $HCCH^{\bullet-}$ (trans D_{2h} conformation) has been optimized starting from a slightly bent structure to remove symmetry constraint; i.e., the bond angle θ about the carbon atom has been set equal to 175°. Table 2 shows that the configuration of these radical anions is strongly bent ($\theta \approx 125°$) employing the 6-311G(d,p) basis set. These radical anions are computed to be strongly bent also when standard diffuse functions are added to heavy atoms (6-311+G(d,p)). However, it should be remarked that optimization of $HCN^{\bullet-}$ and $HCCH^{\bullet-}$ leads to a nearly linear configuration using $\theta = 175°$ as a starting value. The bent structure can be obtained only employing in optimization a

TABLE 2: Effect of Standard Diffuse Functions on the Structural Parameters[a,b] of Radical Anions at the UQCISD/6-311(d,p) Level

radical	parameter	6-311G(d,p)	6-311+G(d,p)	6-311++G(d,p)
FCN$^{\bullet-}$	r(F−C)	1.638 (1.269)	1.603	–
	r(C−N)	1.195 (1.160)	1.199	–
	θ	128.9 (180.0)	128.1	–
HCN$^{\bullet-}$	r(H−C)	1.240 (1.069)	1.168	1.075
	r(C−N)	1.221 (1.159)	1.227	1.160
	θ	120.7 (180.0)	122.9	180.0
HCCH$^{\bullet-}$	r(H−C)	1.115 (1.066)	1.100	1.063
	r(C−C)	1.325 (1.210)	1.315	1.212
	θ	120.5 (180.0)	124.6	180.0
BF$_3$$^{\bullet-}$	r(B−F)	1.418 (1.314)	1.406	–
	γ	54.8 (0.0)	51.5	–
BH$_3$$^{\bullet-}$	r(B−H)	1.223 (1.194)	1.213	1.213
	γ	25.4 (0.0)	0.0	0.0
HBO$^{\bullet-}$	r(H−B)	1.291 (1.205)	1.234	1.234
	r(B−O)	1.269 (1.170)	1.259	1.258
	θ	126.8 (180.0)	133.5	134.3

[a] Bond lengths in angstroms and bond angles in degrees. [b] Values for the neutral parents are reported in parentheses for the 6-311G(d,p) basis set. They are not influenced by addition of diffuse functions.

starting value of θ less than 150° and 145° for HCN$^{\bullet-}$ and HCCH$^{\bullet-}$, respectively. The bent configuration is computed to be only slightly more stable than the linear one at this level of theory, the relative stability being 0.05 and 0.15 eV for HCN$^{\bullet-}$ and HCCH$^{\bullet-}$, respectively. When standard diffuse functions are added also to hydrogens (6-311+G(d,p) → 6-311++G(d,p)), these two radical anions adopt a nearly linear configuration. Interestingly, Table 2 shows that the optimized structural parameters do not differ significantly from those determined for the neutral parents. That is, the wave function describes a system composed by the neutral molecule interacting with a free electron. For HCCH$^{\bullet-}$ the optimum bent configuration, which can be obtained only using a starting value of θ less than 130°, lies 0.6 eV higher in energy. Importantly, no local minimum for the bent configuration has been found for HCN$^{\bullet-}$ even decreasing the starting value of θ down to 90°.

These findings suggest that FCN$^{\bullet-}$ could be kinetically stable owing to the presence of a strongly electronegative atom such as fluorine while HCN$^{\bullet-}$ and HCCH$^{\bullet-}$ could be unstable with respect to electron loss in the gas phase. Indeed, Table 1 shows that the vertical ionization potential (VIP) is computed to be positive for FCN$^{\bullet-}$ (kinetically stable anion) and negative for HCCH$^{\bullet-}$ and HCN$^{\bullet-}$ (kinetically unstable anion).

Table 3 shows that UQCISD/6-311G(d,p) calculations provide reasonable hfs constants. Agreement with experiment does not improve on adding standard diffuse functions to heavy atoms if the mean absolute deviation (MAD)

$$\mathrm{MAD} = (1/N)\sum |a_{\mathrm{exp}} - a_{\mathrm{calc}}| \qquad (5)$$

is taken into account as in ref 11.

In fact, the MAD worsens slightly increasing from 9.0 to 11.7 G. In particular, agreement with experiment worsens in FCN$^{\bullet-}$ (namely for ^{13}C and ^{19}F), improves sizably in HCCH$^{\bullet-}$ for ^{13}C, but does not change significantly in HCN$^{\bullet-}$ since the absolute deviation decreases sizably for ^{13}C but increases about the same amount for ^{1}H. The further addition of hydrogen diffuse functions leads to unreliable results. The hfs constants computed at the UQCISD/6-311++G(d,p) level for HCN$^{\bullet-}$ and HCCH$^{\bullet-}$ are completely different from the experimental ones (MAD = 49.0 G).

These findings might suggest that radical anions should be studied either excluding diffuse functions from the basis set or adding diffuse functions only to heavy atoms. On the other hand, population analysis at the UQCISD/6-311G(d,p) level shows that in HCN$^{\bullet-}$ the total spin density ρ at hydrogen ($\rho_{\mathrm{H}} = 0.38$) is much larger than at carbon ($\rho_{\mathrm{C}} = 0.15$). Addition of diffuse functions only to heavy atoms could force the extra electron to move artificially away from the hydrogen atom. It is evident that diffuse functions should be added also to hydrogen for obtaining a balanced description of the radical anion. This problem should not occur in HCCH$^{\bullet-}$ since ρ_{H} is small (0.06). Therefore, it is of interest to study the effect of the exponent of diffuse functions on the geometry and hfs constants of HCN$^{\bullet-}$. In fact, these radical anions are stable in solution because they are stabilized by medium or solvent effects. This influence can be modeled by artificially restricting the basis set (boxing procedure).[15,16,35−38]

Geometry and hfs constants have been computed varying the exponents of the diffuse functions as a function of the λ parameter (eq 1) at 0.1 intervals in the range 0.5−1.0. The geometry optimized without including diffuse functions (6-311G(d,p)) has been employed as starting geometry to be sure of obtaining the optimum bent structure.

Figure 1 shows that the value of the proton hfs constant decreases slightly and almost linearly with increasing value of λ but it decreases rapidly for $\lambda > 0.8$. For $\lambda = 1.0$ (6-311++G(d,p)) the configuration becomes nearly linear as mentioned above and the proton hfs constants drops to about zero. Therefore this point is not reported in Figure 1.

We have computed the mean percentage deviation (MPD)

$$\mathrm{MPD} = (1/N) \sum |(a_{\mathrm{exp}} - a_{\mathrm{calc}})/a_{\mathrm{exp}}| \times 100 \qquad (6)$$

to obtain a measure of the reliability of the calculated hfs constants. This statistical approach should provide a more objective measure for the accuracy of the theoretical results than that given by the MAD approach used in ref 11.

In Figure 2 the MPD values have been reported as a function of the λ parameter. Interestingly, the MPD value for HCN$^{\bullet-}$ decreases slightly with increasing λ value up to $\lambda = 0.7$ and then it increases rapidly for $\lambda > 0.8$. An analogous trend is observed for HCCH$^{\bullet-}$. The variation is, however, more pronounced and the minimum MPD value is reached at a slightly higher λ value ($\lambda = 0.8$).

It is then important to examine the nature of the SOMO for $\lambda = 0.7$. Table 4 shows that the electronic population of the diffuse functions for both anions is smaller than that of the outer-valence functions. Hence, the value of the hfs constants computed using moderate diffuse functions ($\lambda = 0.7$) can be considered reliable although these anions are kinetically unstable. It should be noted that unreliable values of the relative stability of linear- and Y-conjugated dianions was previously computed for $\lambda > 0.8$.[16]

We have then examined the radical anions BX$_3$$^{\bullet-}$ (X = H, F) and HBO$^{\bullet-}$. In these anions the extra electron should be localized to the electron-deficient boron atom. It is thus easier to study the effect of addition of diffuse functions to heavy atoms on geometry (linear vs bent in HBO$^{\bullet-}$ and planar vs pyramidal in BX$_3$$^{\bullet-}$) and hfs constants.

Table 2 shows that the neutral molecules BX$_3$ (X = H, F) are computed to have a planar structure, the out-of-plane angle γ being zero, while HBO is computed to be linear ($\theta = 180°$). Addition of standard diffuse functions does not change significantly the structural parameters.

At the UQCISD/6-311G(d,p) level BF$_3$$^{\bullet-}$ adopts a strongly pyramidal structure, which is not affected by addition of standard diffuse functions. Indeed, Table 1 shows that this radical anion

TABLE 3: Effect of Standard Diffuse Functions on hfs Constants (gauss) of the Radical Anions at the UQCISD/6−311(d,p) Level (MPD Values Reported in Italics[a])

radical	atom	6-311G(d,p)	6-311+G(d,p)	6-311++G(d,p)	exptl	T (K)	ref
$FCN^{\bullet-}$	^{19}F	488.8 (2.0)	532.7 (2.5)	−	486.0	4	30
	^{13}C	240.9 (−0.7)	222.7 (−1.0)	−	230.9		
	^{14}N	5.6 (−0.1)	6.7 (0.1)	−	6.4		
		5.8 (0.6)	*6.0 (0.9)*				
$HCN^{\bullet-}$	^{1}H	136.2 (1.8)	111.3 (0.2)	−2.1 (−1.0)	137.4	77	31
	^{13}C	116.8 (−2.9)	62.9 (−1.5)	27.1 (1.4)	74.5		
	^{14}N	5.2 (0.0)	7.9 (0.1)	−0.1 (−0.1)	6.7		
		26.8 (−1.4)	*17.5 (1.1)*	*88.9 (0.1)*			
$HCCH^{\bullet-}$	^{1}H	47.8 (0.1)	45.0 (−0.1)	1.2 (0.1)	48.0	77	32
	^{13}C	29.5 (0.4)	10.3 (0.1)	8.9 (0.1)	14.5		
		51.9 (1.3)	*17.6 (−0.2)*	*68.1 (−0.5)*			
$BF_3^{\bullet-}$	^{11}B	174.5 (0.5)	140.6 (1.1)	−	153	100	33
	^{19}F	160.7 (−1.2)	170.0 (−1.1)	−	178		
		11.9 (0.5)	*6.3 (−0.1)*				
$BH_3^{\bullet-}$	^{11}B	22.7 (−4.3)	2.1 (3.8)	2.4 (3.9)	25.0	20	34
	^{1}H	−17.5 (−1.2)	−16.6 (1.0)	−16.5 (1.1)	−16.5		
		7.6 (12.2)	*46.1 (−5.2)*	*45.2 (−4.5)*			
$HBO^{\bullet-}$	^{1}H	84.3 (1.5)	66.4 (−0.4)	62.4 (1.0)	94	20	34
	^{11}B	103.6 (−0.1)	40.7 (−0.1)	40.1 (0.6)	101		
		6.4 (−0.8)	*44.5 (0.3)*	*47.0 (−0.9)*			

[a] hfs constants have been computed at optimum geometries. Estimates of vibrational effects and the variations that they produce in the MPD values are given in parentheses. The reduced mass μ in au and the potential-energy parameters (curvatures at the minimum k_m in au rad^{-2}, inversion barriers E_{inv} in au, anharmonicity constants b in au rad^{-4}) are also reported. For the 6-311G(d,p) basis set: $\mu = 3.686$, $k_m = 0.120$, $E_{inv} = 0.02331$ for $FCN^{\bullet-}$; $\mu = 0.848$, $k_m = 0.119$, $E_{inv} = 0.074$ for $HCN^{\bullet-}$; $\mu = 0.666$, $k_m = 0.314$, $E_{inv} = 0.07377$ for $HCCH^{\bullet-}$; $\mu = 14.538$, $k_m = 1.693$, $E_{inv} = 0.07246$ for $BF_3^{\bullet-}$; $\mu = 2.371$, $k_m = 0.114$, $E_{inv} = 0.00034$ for $BH_3^{\bullet-}$; $\mu = 0.808$, $k_m = 0.161$, $E_{inv} = 0.05500$ for $HBO^{\bullet-}$. For the 6-311+G(d,p) basis set: $\mu = 3.742$, $k_m = 0.114$, $E_{inv} = 0.02247$ for $FCN^{\bullet-}$; $\mu = 0.796$, $k_m = 0.112$, $E_{inv} = 0.03418$ for $HCN^{\bullet-}$; $\mu = 0.647$, $k_m = 0.262$, $E_{inv} = 0.04808$ for $HCCH^{\bullet-}$; $\mu = 13.868$, $k_m = 1.331$, $E_{inv} = 0.05221$ for $BF_3^{\bullet-}$; $\mu = 2.357$, $k_m = 0.090$, $b = 0.792$ for $BH_3^{\bullet-}$; $\mu = 0.764$, $k_m = 0.103$, $E_{inv} = 0.01724$ for $HBO^{\bullet-}$. For the 6-311++G(d,p) basis set: $\mu = 0.688$, $k_m = 0.071$, $b = 0.006$ for $HCN^{\bullet-}$; $\mu = 0.554$, $k_m = 0.048$, $b = 1.015$ for $HCCH^{\bullet-}$; $\mu = 2.357$, $k_m = 0.086$, $b = 0.836$ for $BH_3^{\bullet-}$; $\mu = 0.762$, $k_m = 0.102$, $E_{inv} = 0.01798$ for $HBO^{\bullet-}$.

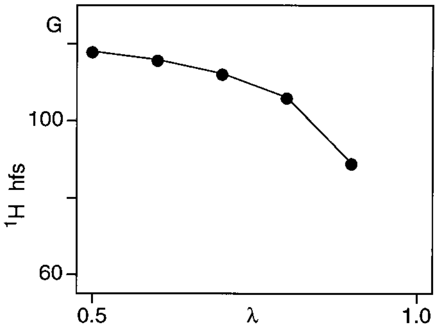

Figure 1. Proton hfs constant in $HCN^{\bullet-}$ computed at the UQCISD/6-311++G(d,p) level as a function of the λ parameter.

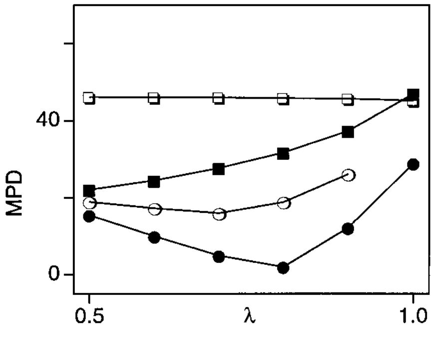

Figure 2. Mean percentage deviation (MPD) of the hfs constants computed at the UQCISD/6-311++G(d,p) level as a function of the λ parameter for $HCN^{\bullet-}$ (○), $HCCH^{\bullet-}$ (●), $HBO^{\bullet-}$ (■), and $BH_3^{\bullet-}$ (□).

TABLE 4: Electronic Population ρ in the SOMO and hfs Constants (gauss) along with MPD Values, in Italics, for Radical Anions Computed at the UQCISD/6-311++G(d,p) Level Using Moderate Diffuse Functions (λ = 0.7)[a−c]

radical	atom	ρ(outer-val)	ρ(diffuse)	hfs	hfs(exptl)
$FCN^{\bullet-}$	^{19}F	0.02	0.00	524.6 (2.8)	486.0
	^{13}C	0.19	0.09	225.1 (−0.3)	230.9
	^{14}N	0.11	0.01	6.6 (0.0)	6.4
				4.5 (0.3)	
$HCN^{\bullet-}$	^{1}H	0.10	0.04	112.3 (2.0)	137.4
	^{13}C	0.14	0.12	94.6 (−2.8)	74.5
	^{14}N	0.06	0.00	6.8 (−0.1)	6.7
				15.5 (−1.2)	
$HCCH^{\bullet-}$	^{1}H	0.00	0.00	48.1 (−0.1)	48.0
	^{13}C	0.13	0.10	15.9 (0.5)	14.5
				4.9 (1.6)	
$BF_3^{\bullet-}$	^{11}B	0.36	0.23	153.3 (1.1)	153
	^{19}F	0.00	0.00	173.8 (−1.2)	178
				1.3 (0.7)	
$BH_3^{\bullet-}$	^{11}B	0.18	0.50	4.4 (5.4)	25.0
	^{1}H	0.00	0.00	−18.1 (1.4)	−16.5
				46.0 (−15.0)	
$HBO^{\bullet-}$	^{1}H	0.03	0.00	74.1 (1.4)	94
	^{11}B	0.19	0.37	66.4 (0.5)	101
				27.7 (−1.0)	

[a] Exponents of diffuse functions: $\alpha_H = 0.05602$, $\alpha_B = 0.05171$, $\alpha_C = 0.07434$, $\alpha_N = 0.10499$, $\alpha_O = 0.13583$, $\alpha_F = 0.17189$. [b] In optimization the structure optimized without diffuse functions (6-311G(d,p)) has been used as starting geometry. [c] Estimates of vibrational effects and the variations that they produce in the MPD values are given in parentheses. The reduced mass μ in au and the potential-energy parameters (curvatures at the minimum k_m in au rad^{-2}, inversion barriers E_{inv} in au, anharmonicity constants b in au rad^{-4}) are also reported: $\mu = 3.767$, $k_m = 0.122$, $E_{inv} = 0.02605$ for $FCN^{\bullet-}$; $\mu = 0.817$, $k_m = 0.100$, $E_{inv} = 0.05588$ for $HCN^{\bullet-}$; $\mu = 0.652$, $k_m = 0.287$, $E_{inv} = 0.05991$ for $HCCH^{\bullet-}$; $\mu = 14.143$, $k_m = 1.496$, $E_{inv} = 0.06851$ for $BF_3^{\bullet-}$; $\mu = 2.357$, $k_m = 0.034$, $b = 1.066$ for $BH_3^{\bullet-}$; $\mu = 0.781$, $k_m = 0.132$, $E_{inv} = 0.03436$ for $HBO^{\bullet-}$.

is not only kinetically (VIP > 0) but also thermodynamically stable (VEA of the neutral parent > 0). Interestingly, Table 3 shows that the experimental hfs constants are reproduced fairly well and agreement with experiment increases with addition of standard diffuse functions.

On the other hand, the VEA of HBO and BH_3 as well as the VIP of their parent radical anions are computed to be negative at the UQCISD/6-311G(d,p) level, indicating that these radical anions are kinetically unstable. At this level of theory they are

TABLE 5: Effect of Standard Diffuse Functions on the hfs Constants (gauss) of the Radical Anions at the UQCISD/6−311(2df,p) Level (MPD Values Reported in Italics)

radical	atom	6-311G(2df,p)	6-311+G(2df,p)	6-311++G(2df,p) ($\lambda = 0.7$)	6-311++G(2df,p)	exptl
$HCN^{\bullet -}$	^{1}H	134.5	112.9	115.6	−6.2	137.4
	^{13}C	111.9	63.6	89.7	28.8	74.5
	^{14}N	5.5	7.5	6.7	−0.9	6.7
		24.3	*13.0*	*11.9*	*93.1*	
$HCCH^{\bullet -}$	^{1}H	49.9	46.1	48.1	1.3	48.0
	^{13}C	29.5	11.5	16.2	9.0	14.5
		53.7	*12.3*	*5.9*	*67.6*	
$BH_3^{\bullet -}$ [a]	^{11}B	16.6	5.7	9.1	6.1	25.0
	^{1}H	−17.5	−14.4	−15.6	−14.4	−16.5
		19.8	*44.2*	*34.5*	*45.0*	
$HBO^{\bullet -}$	^{1}H	85.3	69.4	75.3	65.2	94
	^{11}B	102.7	46.5	69.0	45.5	101
		5.4	*40.1*	*25.8*	*42.8*	

[a] Values computed taking into account vibrational effects. The reduced mass μ in au and the potential-energy parameters (curvatures at the minimum k_m in au rad^{-2}, inversion barriers E_{inv} in au, anharmonicity constants b in au rad^{-4}) are also reported: $\mu = 2.366$, $k_m = 0.068$, $E_{inv} = 0.00013$ for the 6-311G(2df,p) basis set; $\mu = 2.357$, $k_m = 0.107$, $b = 0.655$ for the 6-311+G(2df,p) basis set; $\mu = 2.357$, $k_m = 0.055$, $b = 0.918$ for the 6-311++G(2df,p) basis set and $\lambda = 0.7$; $\mu = 2.35714$, $k_m = 0.103$, $b = 0.718$ for the 6-311++G(2df,p) basis set.

computed to have a slightly pyramidal and a bent structure, respectively. The experimental hfs constants are reproduced fairly well. $HBO^{\bullet -}$ is computed to be bent also adding standard diffuse functions to all atoms. It should be remarked that a strongly bent structure ($\theta < 155°$) must be used as starting geometry in optimization as previously found for $HCN^{\bullet -}$ and $HCCH^{\bullet -}$. However, in this case addition of standard diffuse functions to heavy atoms worsens dramatically the agreement between experimental and theoretical hfs constants. Figure 2 shows that the MPD is large also using moderate diffuse functions ($\lambda = 0.7$) and increases with increasing λ value.

A more serious problem has been encountered in studying $BH_3^{\bullet -}$. At the UQCISD/6-311+G(d,p) level the radical anion is computed to be planar also starting from a tetrahedral arrangement of atoms ($\gamma = 54.7$) and the ^{11}B hfs constant is computed to be much lower than experiment. The further addition of hydrogen diffuse functions (6-311++G(d,p)) or the use of moderate diffuse functions ($\lambda = 0.5-0.7$) does not modify this situation. The MPD is very large and its value does not change significantly increasing the λ value.

Inspection of the electronic distribution in the SOMO for $\lambda = 0.7$ (see Table 4) shows that in $HBO^{\bullet -}$ and $BH_3^{\bullet -}$ the diffuse functions are much more populated than the outer-valence atomic orbitals. That is, addition of diffuse functions in these kinetically unstable radical anions leads to describe a neutral molecule interacting with a free electron. This explains why agreement with experiment worsens dramatically with addition of diffuse functions.

Comparison of the MPD values reported in Tables 3 and 4 shows that the use of moderate diffuse functions ($\lambda = 0.7$) leads to lower deviations not only when the radical anion is kinetically unstable and the SOMO has a valence character ($HCN^{\bullet -}$ and $HCCH^{\bullet -}$) but also when the radical anion is thermodynamically ($BF_3^{\bullet -}$) or kinetically stable ($FCN^{\bullet -}$) in the gas phase. Interestingly, the MPD values are comparable to those obtained by CCSD(T) calculations for organic radicals[39] (namely, 7.7% for ^{13}C and 11.9% for ^{1}H) employing the Chipman basis set which was tailored to compute hfs constants.[40] It thus appears that the use of moderate diffuse functions can be recommended for studying the magnetic properties of radical anions.

Vibrational Effects. Vibrational effects should be taken into account in comparing experimental and theoretical hfs constants when low-frequency vibrations such as rotational, out-of-plane, and inversion modes are possible. In the planar or slightly pyramidal $BH_3^{\bullet -}$ there is the possibility of large vibrational modulation of the computed hfs constants owing to the out-of-plane mode in the planar configuration or to the inversion mode in the pyramidal configuration. Thus, the vibrational corrections to hfs constants have been estimated using one-dimensional potential functions, namely single-well potentials for planar or linear radical anions and double-well potentials for pyramidal or bent radical anions. It is evident from Tables 3 and 4 that the vibrational corrections are small in percentage except for $BH_3^{\bullet -}$. In particular, $a(^{11}B)$ increases sizably for the planar 6-311+G(d,p) and 6-311++G(d,p) structures, reducing disagreement with experiment. On the other hand, $a(^{11}B)$ decreases slightly for the pyramidal 6-311G(d,p) structure, worsening agreement with experiment. However, only the hfs values obtained excluding diffuse functions from the basis set (MPD = 19.8) can be considered reasonably reliable, as previously found without taking into account the vibrational effects. Agreement with experiment remains very poor with inclusion of diffuse function on boron (MPD = 40.9) and also on hydrogens (MPD = 40.7). The use of moderate diffuse functions reduces only slightly the disagreement with experiment (MPD = 34.5).

Basis Set Effects. It was recommended to compute the hfs constants of small-sized radical anions at the UQCISD/6-311+G(2df,p) level for obtaining suitable accuracy.[11] Thus, we have reinvestigated at this higher level of theory the radical anions ($HCN^{\bullet -}$, $HCCH^{\bullet -}$, $BH_3^{\bullet -}$, and $HBO^{\bullet -}$) that have been found to be kinetically unstable at the UQCISD/6-311G(d,p) level. These radical anions remain kinetically unstable also at the higher level of theory, and the same problems discussed above have been encountered. In particular, a strongly bent structure should be used as starting geometry in optimization to obtain the bent configuration at the UQCISD/6-311+G(2df,p) level for $HCN^{\bullet -}$, $HCCH^{\bullet -}$, and $HBO^{\bullet -}$. At this level of theory the bent structure is more stable than the linear one; that is, the structures of $HCN^{\bullet -}$ and $HCCH^{\bullet -}$ obtained at the UQCISD/6-311+G(2df,p) level in ref 11 correctly produce the bent structures for these radical anions. The relative stability is, however, computed to be small, i.e., 0.09 and 0.21 eV for $HCN^{\bullet -}$ and $HCCH^{\bullet -}$, respectively. These two radical anions adopt a linear structure using the 6-311++G(2df,p) basis set. The bent configuration lies 0.4 eV higher in energy for $HCCH^{\bullet -}$, and no local minimum for the bent configuration has been found for $HCN^{\bullet -}$. Interestingly, the use of the more flexible valence only correlation consistent aug-cc-pVTZ basis set does not modify this finding. The UQCISD/aug-cc-pVTZ level erroneously predicts $HCN^{\bullet -}$ to have a linear structure that is the only stable configuration found in the potential surface. The $BH_3^{\bullet -}$ radical anion is computed to be planar using diffuse functions (6-311+G(2df), 6-311++G(2df), and 6-311++G(2df,p) with $\lambda = 0.7$), whereas it is computed to be slightly pyramidal without including diffuse functions in the basis set. However, the enlargement of the basis set reduces the degree of pyramidality, the out-of-plane angle γ decreasing from 24.5° to 20.4°.

The values of hfs constants computed employing the 6-311G-(2df,p) basis set and its derivatives are reported in Table 5. It has been shown above that the MPD values are little affected by the vibrational corrections except for $BH_3^{\bullet -}$ (see Tables 3 and 4). Hence we have reported the hfs constants averaged over the vibrational states only for this radical anion. Comparison of these values with those reported in Tables 3 and 4 for the 6-311G(2df,p) basis set shows that the variations are small and agreement with experiment improves slightly on enlarging the basis set in line with what found in ref 11.

Conclusions

In the present study we have investigated the effect of diffuse functions on the geometry and hfs constants of radical anions. It is found that inclusion of standard diffuse functions in the basis set might provide unreliable results in studying radical anions that are unstable in the gas phase. The following procedure should be adopted to be sure of obtaining reliable values of hfs constants in radical anions.

First of all, the VEA of the neutral molecule should be computed including standard diffuse functions in the basis set. If its value is positive, the geometry and hfs constants of the radical anion should be computed employing diffuse functions to obtain a better description of the radical anion. Otherwise (VEA < 0), the structure of the radical anion must be determined without employing diffuse functions. This ensures that the optimized geometry corresponds to that of the radical under study and not to that of the neutral molecule which interacts with a free electron. If the VIP of the anion is computed to be positive, the anion is kinetically stable so that the geometry and hfs constants can be recomputed adding diffuse functions to the basis set. On the other hand, geometry and hfs constants cannot be, in principle, determined by MO calculations when the radical anion is kinetically unstable (VIP < 0). In this case the reliability of the results can be assured, constructing graphics as a function of the exponent of the diffuse function and analyzing the population of the SOMO to establish its nature (valence or diffuse MO). The geometry determined without including diffuse functions in the basis set must be used as starting geometry in optimization. Calculations employing only a set of moderate diffuse functions ($\lambda = 0.7$; see Table 4 for basis set exponents) can be performed to save computer time. The results are reliable if the population of the valence outer atomic orbitals is greater than that of the diffuse functions. Otherwise, a less precise estimate of the structural and magnetic properties can be obtained only from the calculations performed without including diffuse functions in the basis set.

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