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Structure and Magnetic Properties of AH_3 and AMe_3 Inorganic Radicals and Radical Ions ($A = Al^-$, Si, and P^+) by *Ab Initio* Calculation*

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Abstract

Ab initio SCF–MO calculations are reported on the geometry and magnetic properties of some AH_3 and AMe_3 inorganic radicals and radical ions ($A = Al^-$, Si, P^+). A polarized split-valence procedure was used to determine the optimum geometry in each case and we find little change in the degree of pyramidality upon methylation. The spin density distribution was characterized by calculations employing a basis set of double-zeta quality with polarization functions on all non-hydrogenic atoms. In the hydrides, p-functions were included on the hydrogens. The reassignment of a spectrum originally attributed to $AlMe_3^-$ is supported. Instead we predict for the trimethylalane radical anion $A_{\parallel}(^{27}Al) \sim 20.5$ mT and $A_{\perp}(^{27}Al) \sim 13.5$ mT. In an isotropic spectrum $a(^{27}Al) = 17.0 \pm 0.5$ mT is expected. In addition some estimates are made of IR and Raman active vibrational frequencies for this unknown species.

Introduction

Recently Glidewell [1] has reported a series of semiempirical molecular orbital calculations on radicals and radical ions derived from third period hydrides and methyls which principally addressed issues of a structural nature. In addition, however, a comparison of the calculated spin populations between the radical anions of the aluminum containing species was used to imply that an ESR spectrum [2] produced by γ-radiolysis of trimethylaluminum had been inappropriately assigned. The original assignment has also been called into question on experimental grounds [3].

In the course of previous work [4], we have performed extensive *ab initio* self-consistent field (SCF) molecular orbital (MO) calculations within the unrestricted Hartree–Fock (UHF) approximation on some of the same species and have estimated the corresponding spin densities and coupling constants, both isotropic and anisotropic. Since the results obtained from these considerations alleviate the uncertainty in the MNDO scale factors (scaling between computed spin populations and observed hyperfine coupling constants) and are in substantial agreement with those obtained by Glidewell [1], at least concerning the problematic trimethylalane, $AlMe_3^-$ assignment, we felt it worthwhile to note them in these covers.

Calculations

All calculations were carried out with the Gaussian 82 series of programs [5], modified to run under VMS 4.2 operating system on a VAX 11/780 computer. Earlier work on the isoelectronic series AlH_3^-, SiH_3 and PH_3^+ was performed mainly as a prelude to the subsequent study of the trimethyls and has not been previously reported. Utilizing a small split-valence basis set augmented by polarization functions (d-functions) on the central atoms, denoted 3-21G* [6], a full geometry optimization was carried through for each hydride under the constraint of C_{3v} symmetry. The derived optimum geometry was then held fixed and a series of further calculations using basis sets of full double-zeta quality and beyond were done to arrive at satisfactory estimates of the spin densities. These employed the Dunning 6s, 4p contraction [7] of Huzinaga's 11s, 7p atom optimized Gaussian functions [8], denoted DZ below, and its augmentation with suitable polarization (d-) functions* first of the central atom only, denoted DZP and then on all atoms, with p-functions on hydrogen, denoted DZPP. A similar procedure was adopted in the calculations on the trimethyls, $AlMe_3^-$, $SiMe_3$ and PMe_3^+, the geometries being fully optimized again within the constraints of C_{3v} symmetry. No assumptions of 'frozen' geometry around the methyl centers were made and two different C–H

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*Exponents of $\zeta(Al) = 0.2500$ a.u., $\zeta(Si) = 0.3247$ a.u., and $\zeta(P) = 0.3700$ a.u. were used for the d-functions.

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bond lengths were found in each species. The Dunning 4s, 2p contraction [9] of Huzinaga's 9s, 5p atom optimized Gaussian functions [10] was used on all carbon atoms. However the addition of p-functions on hydrogen was not pursued here and calculations were thus truncated at the UHF/DZP// UHF/3-21G* level of theory. The double-slash delimiter separates the single point calculational method (UHF/DZP) from that used to obtain optimized geometries (UHF/3-21G*).

Results and Discussion

We have previously reported [4] the fully optimized geometries of the trimethyl species and list in Table I only the salient features for comparison with the semiempirical work and with estimates derived from experiment. We note a rather large bond length difference, 2.054 Å from the present work compared with 1.849 Å for Al–C from the MNDO study [1], the others are not reported, and discrepancies of the order of 3–5 degrees in the predicted angles. The structures determined from the semiempirical approach are generally flatter than those derived by *ab initio* calculation.

TABLE I. Structural Parameters in AMe_3 Species

Species	Method	r_{AC} (Å)	θ_{CAC} (deg)
$AlMe_3^-$	UHF/3-21G*	2.054	109.4
	UHF/MNDO	1.849	115.1[b]
	Experimental		107.9[c]
$SiMe_3$	UHF/3-21G*	1.894	110.2
	UHF/MNDO	–[a]	113.5[b]
	Experimental		113.3[d]
PMe_3^+	UHF/3-21G*	1.800	112.6
	UHF/MNDO	–[a]	118.1[b]
	Experimental		115.5[e]

[a] Not reported. [b] Ref. 1. [c] Ref. 2, but assignment questioned in ref. 3. [d] Ref. 2, inferred from ESR spectrum. [e] Ref. 2, but value for PEt_3^+.

The corresponding data for the hydrides are presented in Table II, from which it is immediately apparent that much closer accord exists between the results of the two calculation techniques for this series. Thus, the semiempirical prediction of flattening upon methylation is not seen in the present *ab initio* results.

The experimental bond angles reported in Tables I and II have all been inferred from observed ESR spectra by means of arguments [11] separating the s- and p-spin populations on the central atoms. Uncertainties in this procedure may be eliminated by computing the spin density distribution from an *ab initio* wavefunction of sufficiently high quality. The results of such calculations for the hydrides are displayed in Table III and establish confidence in the *ab initio* method. Given the notorious difficulties in the *ab initio* computation of satisfactory values for isotropic hyperfine coupling constants [12], even at much more sophisticated levels of theory than the SCF approach adopted here, the closeness of the accord attained with experiment for *a* (A) in each case is gratifying. Additionally, the above single point calculations yield a static value which may be slightly altered by vibrational motion. Indeed, for SiH_3, Ellinger *et al.* [13] have recently completed a study including such vibrational averaging which resulted in a lowering of 0.7 mT in the static value for *a* (^{29}Si) at 4 K, due mainly to pyramidal bending. It is unlikely that such a correction could be applied in a global fashion, even to the AH_3 series discussed here, since such vibrations are crucially dependent on the details of the potential (hyper)surface over which the nuclei move. A satisfactory description of this surface can only be obtained by further including the effects of electron correlation, in a manner such as has been implemented for the phosphinium radical [14]. This effort has not been made in the current work. It should also be noted that matrix effects on *a* (A) are expected, since many solvating environments will distort this potential.

TABLE II. Structural Parameters in AH_3 Species

Species	Method	r_{AH} (Å)	θ_{HAH} (deg)
AlH_3^-	UHF/3-21G*	1.644	110.9
	UHF/MNDO	–[a]	110.5[b]
	Experimental		110.3[c]
SiH_3	UHF/3-21G*	1.475	110.9
	UHF/MNDO	–[a]	110.0
	Experimental		112.8[c]
PH_3^+	UHF/3-21G*	1.381	112.6
	UHF/MNDO	–[a]	113.1[b]
	Experimental		113.9[c]

[a] Not reported. [b] Ref. 1. [c] Ref. 2, inferred from ESR spectra.

In the various trimethyl derivatives, the vibrational contribution to the central atom coupling is likely to be smaller than in the hydrides. The β-carbon atoms undergo excursions of smaller amplitude than the β-hydrogens in the corresponding hydrides. In addition an inspection of the calculated barriers to inversion for the third period trimethyls [4] suggests that no large amplitude motion in this direction is to be expected. In $AlMe_3^-$ this process is activated by about 130 kJ mol^{-1} [4]. Concerted methyl rotation is predicted [4] to take place over barriers of 11 kJ

TABLE III. Magnetic Properties of AH_3 Species

Species	Method	ρ (A) (a.u.)[a]	a (A) (mT)[b]	$2B$ (A) (mT)[c]	$\hat{S}^2$ (a.u.)
$^{27}AlH_3^-$	UHF/DZ	0.3896	16.2	3.5	0.7539
	UHF/DZP	0.3818	15.9	3.5	0.7533
	UHF/DZPP	0.3788	15.8	3.5	0.7533
	UHF/MNDO[d]	0.2673	–	–	
	Experimental	–	15.4 [19]	3.0 [20]	
$^{29}SiH_3$	UHF/DZ	0.6640	−21.1	−5.2	0.7549
	UHF/DZP	0.6461	−20.5	−5.3	0.7540
	UHF/DZPP	0.6428	−20.4	−5.3	0.7541
	UHF/MNDO[d]	0.2162	–	–	
	Experimental	–	(−)19.0 [21]	(−)4.8 [22]	
$^{31}PH_3^+$	UHF/DZ	0.8058	52.1	20.8	0.7570
	UHF/DZP	0.7950	51.4	20.4	0.7563
	UHF/DZPP	0.7894	51.0	20.3	0.7564
	UHF/MNDO[d]	0.1396			
	Experimental	–	51.7 [2]	18.9 [2]	

[a] Spin density at central atom in atomic units (1 a.u. = 0.148 e/Å^3). [b] Isotropic coupling constant in milliTesla (1 mT = 10 G). [c] Principal component of anisotropic coupling tensor in mT. [d] Spin population from ref. 1.

TABLE IV. Magnetic Properties of AMe_3 Species

Species	Method	ρ (A) (a.u.)[a]	a (A) (mT)[b]	$2B$ (A) (mT)[c]	$\hat{S}^2$ (a.u.)
$AlMe_3^-$	UHF/DZ	0.4208	17.5	3.4	0.7509
	UHF/DZP	0.4061	16.9	3.4	0.7512
	UHF/MNDO[d]	0.1757	–	–	
	Experimental	–	32.4[e]	4.2[e]	
$SiMe_3$	UHF/DZ	0.6590	−20.9	−5.1	0.7523
	UHF/DZP	0.6387	−20.2	−5.1	0.7526
	UHF/MNDO[d]	0.2050	–	–	
	Experimental	–	(−)19.1 [23]	(−)5.2 [24]	
PMe_3^+	UHF/DZ	0.7037	45.5	19.5	0.7554
	UHF/DZP	0.7087	45.8	19.2	0.7555
	UHF/MNDO[d]	0.0774	–	–	
	Experimental	–	38.5 [25]	19.9 [25]	

[a] Spin density at central atom in atomic units. [b] Isotropic coupling constant in mT. [c] Principal component of anisotropic coupling tensor. [d] Spin population from ref. 1. [e] Ref. 2, questionable, see ref. 3.

mol^{-1} in both $AlMe_3^-$ and PMe_3^+ and 14kJ mol^{-1} for $SiMe_3$. However, the value of the isotropic coupling constant at the central nucleus is relatively independent of this motion, at least in CMe_3 [4].

The static values of a (A) for the trimethyls are listed in Table IV together with the MNDO spin populations [1] and some of the available experimental observations. For $SiMe_3$ and PMe_3^+ the UHF/DZ values for the anisotropic tensor components are already in reasonable agreement with experiment. Based on the results for these two species it is apparent that the empirical values for $AlMe_3^-$ [2] are not appropriate. We would expect a (^{27}Al) = 17.0 ± 0.5 mT and $2B$ (^{27}Al) = 3.4 ± 0.1 mT. Thus an anisotropic spectrum is predicted with $A_{\parallel} \sim 20.5$ mT and $A_{\perp} \sim 13.5$ mT. The values of $\langle S^2 \rangle$, the expectation value of the square of the spin quantum number, S, in both Tables III and IV lend support to the above UHF predictions. For a pure doublet ($S = 1/2$) state $\langle S^2 \rangle = 0.75$. However the UHF approximation is spin unrestricted in the sense that different spatial orbitals are used for the different spin functions. The wavefunction may thus become contaminated with states of higher (spin-) multiplicity. This is reflected in the values obtained for $\langle S^2 \rangle$, and for values much greater than 0.75, predictions from UHF wavefunctions, including geometries, are suspect.

TABLE V. Vibrational Frequencies (cm^{-1}) in $AlMe_3^-$

Assignment	UHF/3-21G (symmetry)	Scaled wrt CMe_3 [a]	Scaled wrt $AlMe_3$ [b]
Antisymmetric C–H stretch	3170 (e) 3167 (a_2) 3160 (a_1) 3155 (e)	2869	2909
Symmetric C–H stretch	3107 (a_1) 3104 (e)	2797	2850
Antisymmetric internal Me deformation	1651 (a_1) 1646 (e) 1641 (e) 1641 (a_2)	1422	1442
Symmetric internal Me deformation	1357 (a_1) 1353 (e)	1182	1134
Methyl rocking	838 (a_1) 806 (e) 669 (e) 639 (a_2)	–	700
Antisymmetric C–C stretch	588 (e)	565	–
Symmetric C–C stretch	516 (a_1)	496	–

[a] Using experimental data in an argon matrix, ref. 13. [b] Using experimental data in an argon matrix, ref. 15.

A further aid to the identification of the trimethylalane radical anion is available from an estimation of the location of infrared and Raman absorption bands. We have calculated the complete harmonic force fields for each of the above trimethyls (with a split-valence basis set lacking polarization functions) as well as their closed-shell analogues, $AlMe_3$, $SiMe_3^+$ and PMe_3. The scaling of the computed harmonic frequencies to experiment may be accomplished in several ways. Firstly, similar calculations have been performed for CMe_3 [4] and an infrared spectrum attributed to this radical trapped in an argon matrix has been recorded and assigned [15]. Comparison here allows the determination of scale factors on a mode-by-mode basis [16]. Again in an argon matrix, the neutral species, $AlMe_3$, has been observed and characterized by infrared techniques [17]. Calculated values for this molecule can also be scaled as above. Alternatively, a global scale factor (0.89 for the current basis), which was inferred from a statistical analysis [18] of computed/observed frequencies for a wide range of simple molecules, may be applied. This global scaling is apparently unsuitable over the entire range of frequencies pertaining in the trimethyls considered here and the former, mode-specific scaling, procedure has been adopted. The predictions for $AlMe_3^-$, along with some other relevant data are included in Table V. Within the C_{3v} point group, that of the optimized geometry, modes of a_1 and e symmetry types are both IR and Raman allowed. a_2 species are symmetry forbidden in both spectra. It should be cautioned, however, that matrix effects might play a greater perturbative role in the case of an anion, the diffuse charge distribution of which undoubtedly interacts substantially with the surrounding medium.

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