

CNDO/2 STUDY OF ^{29}Si NMR CHEMICAL SHIFTS

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Summary

A CNDO-2 study of ^{29}Si NMR chemical shifts for compounds of the type $(\text{CH}_3)_n\text{SiX}_{4-n}$ ($\text{X} = \text{H}, \text{F}, \text{Cl}$) is reported. The paramagnetic screening constants σ_p are given. The general variation in σ_p with n agrees fairly well with the variation of the observed chemical shifts for $\text{X} = \text{H}$ and F , but the correlation is not so good for $\text{X} = \text{Cl}$.

Introduction

As part of a systematic physicochemical study of the bonding characteristics in compounds of the type $(\text{CH}_3)_{4-n}\text{M}_{\text{IVB}}\text{X}_n$ ($n = 0, 1, 2, 3, 4$), we describe here CNDO/2 calculations on ^{29}Si NMR shifts of the compounds with $\text{M}_{\text{IVB}} = \text{Si}$ and $\text{X} = \text{H}, \text{F}$ or Cl . For the F and Cl derivatives, these shifts move up-field with respect to TMS for high values of n , while for the lower n values they move down-field [1,2].

Recently Engelhardt et al. [3] performed some empirical calculations on the compounds studied here, and were able to reproduce most of the trends in the ^{29}Si NMR shifts of these compounds. Therefore they concluded that the differences in charge in the σ -orbitals of Si alone can to a large extent explain the observed chemical shifts.

Experimental

The calculations were performed by the CNDO/2 method of Pople and Segal [4]. The program used was a modified version of the original program given by Pople and Beveridge [5]. All calculations were performed on a

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TABLE 1

BOND DISTANCES IN $(\text{CH}_3)_{4-n}\text{SiX}_n$ (ALL VALUES IN Å)^a

	R(C-H)	R(Si-C)	R(Si-X)
$(\text{CH}_3)_4\text{Si}$	1.10	1.888	
$(\text{CH}_3)_3\text{SiH}$ ^b	1.093	1.88	1.48
$(\text{CH}_3)_2\text{SiH}_2$ ^b	1.093	1.88	1.48
CH_3SiH_3 ^c	1.09	1.8669	1.4798
$(\text{CH}_3)_3\text{SiF}$	1.09	1.89	1.57
$(\text{CH}_3)_2\text{SiF}_2$	1.093	1.89	1.56
CH_3SiF_3	1.093	1.876	1.555
SiF_4			1.55
$(\text{CH}_3)_3\text{SiCl}$	1.093	1.87	2.03
$(\text{CH}_3)_2\text{SiCl}_2$	1.093	1.88	1.99
CH_3SiCl_3	1.093	1.876	2.021
SiCl_4			2.03

^a Ref. 8, unless otherwise stated. ^b Estimated. ^c Ref. 9.

Siemens 4004/150 computer. The original parameters given in ref. 4 were used throughout. None of the atoms was allowed to have *d*-orbitals. The geometry chosen was in each case the most symmetric one, i.e. the conformation with the greatest possible number of staggered atoms. Relevant bond distances are given in Table 1; all angles were taken to be tetrahedral.

Results and discussion

According to Saika and Slichter [6] the NMR chemical shift of an atom in a molecule may be expressed as a sum of diamagnetic and paramagnetic contributions of the atom in question and of a contribution of the other atoms in the molecule. Following Jameson and Gutowski [7], the contribution of the diamagnetic term may be neglected for atoms other than hydrogen. Also the contribution of the neighbouring atoms in the molecule to the paramagnetic term will be of importance only for atoms with low atomic number.

Therefore we tried to calculate the ²⁹Si NMR chemical shift from the paramagnetic contribution given by eqn. 1 [7] but with omission of the term

$$\sigma_p = \frac{2e^2\hbar^2}{3m^2c^2} \frac{1}{\Delta E} \{ \langle r_{\text{Si}}^{-3} \rangle_{3p} P_u + \langle r_{\text{Si}}^{-3} \rangle_{3d} D_u \} \quad (1)$$

arising from the *d*-orbitals on the silicon atom [7]. ΔE is an average excitation energy and P_u is a term depending on the *p*-orbital population of the silicon atom. Its explicit form is given by Jameson and Gutowski [7]. The value of $\langle r^{-3} \rangle_{3p}$ was calculated from its theoretical value for Slater type orbitals, i.e.

$$\langle r^{-3} \rangle = \zeta^3 / n(n - \frac{1}{2})(n - 1) \quad (2)$$

where ζ is the orbital exponent of the Slater type orbital and n is the principal

quantum number. From eqn. 2 it is clear that it is the value of ζ_{Si} which most influences σ_p , and therefore it was varied until internal consistency was achieved with the charge on the silicon atom q_{Si} according to Slater's formula:

$$\zeta_{\text{Si}} = \frac{1}{3} Z_{\text{Si}}^{\text{eff}}$$

$$= \frac{1}{3} (Z_{\text{Si}}^{\text{Slater}} + 0.35 q_{\text{Si}}) \quad (3)$$

with $Z_{\text{Si}}^{\text{Slater}} = 4.15$. The criterion for consistency was taken to be a difference smaller than 10^{-3} in q_{Si} .

All values of the shielding constants σ_p were referred to that of TMS. The value of ΔE was arbitrarily taken to be 0.1 a.u. = 2.7 eV for all the compounds studied. A different value would not change the relative magnitudes of the paramagnetic contributions to the chemical shift.

The results of the calculations with and without variation of the orbital exponent of the Slater type orbitals on the Si atom are given in Tables 2 and 3.

As would be expected from the form of eqn. 3 the value of the charge on the silicon atom is reduced by requiring q and ζ to be consistent with each other. A comparison with the corresponding q values given by Engelhardt et al., however, shows that whereas for X = Cl, F these quantities vary in the same direction with increasing n , this is not so for X = H. This holds also for the corresponding P_u and $\langle r^{-3} \rangle$ values.

As to the absolute values of the calculated paramagnetic contributions to the chemical shift, they are generally calculated to be much too low in comparison with the observed values. A different choice of ΔE would remedy this, although its value would then be very much lower than that commonly assumed, e.g. the ionisation potential or the first excitation energy. In the case of the chlorides,

TABLE 2

ATOMIC CHARGES q ON THE SILICON ATOM AND SLATER TYPE ORBITAL EXPONENTS ζ FOR THE SILICON ATOM

	$\zeta = 1.383$ q	With variation of orbital exponent ζ			
		P_u	q	ζ	$\langle r^{-3} \rangle$
(CH ₃) ₄ Si	0.564	1.462	0.498	1.4414	0.1996
(CH ₃) ₃ SiH	0.576	1.457	0.516	1.4437	0.2006
(CH ₃) ₂ SiH ₂	0.576	1.451	0.526	1.4448	0.2011
CH ₃ SiH ₃	0.569	1.445	0.533	1.4456	0.2014
SiH ₄	0.548	1.438	0.530	1.4451	0.2012
(CH ₃) ₃ SiF	0.924	1.414	0.788	1.4752	0.2140
(CH ₃) ₂ SiF ₂	1.260	1.343	1.061	1.5072	0.2283
CH ₃ SiF ₃	1.599	1.254	1.333	1.5389	0.2429
SiF ₄	1.933	1.167	1.602	1.5703	0.2581
(CH ₃) ₃ SiCl	0.714	1.442	0.626	1.4564	0.2059
(CH ₃) ₂ SiCl ₂	0.850	1.416	0.744	1.4701	0.2118
CH ₃ SiCl ₃	0.958	1.386	0.839	1.4812	0.2166
SiCl ₄	1.060	1.360	0.928	1.4916	0.2212

TABLE 3

PARAMAGNETIC CONTRIBUTION TO CHEMICAL SHIFT REFERRED TO TMS; EXPERIMENTAL VALUES OF THE CHEMICAL SHIFTS, AND RELATIVE VALUES OF PARAMAGNETIC SHIELDING CONSTANTS ACCORDING TO ENGELHARDT ET AL. [3]

	$\Delta\sigma_p$ ($\zeta = 1.383$) (ppm)	$\Delta\sigma_p$ (ζ varied) (ppm)	$\Delta\sigma$ (exp.) (ppm)	σ^* (ref. 3)	σ^* ($f = 1$)
$(\text{CH}_3)_4\text{Si}$				1.0114	1.0892
$(\text{CH}_3)_3\text{SiH}$	-0.30	0.13	-18	1.0112	1.0784
$(\text{CH}_3)_2\text{SiH}_2$	-0.59	-0.04	-41	1.0104	1.0673
CH_3SiH_3	-0.88	-0.33		1.0093	1.0558
SiH_4	-1.91	-0.88		1.0077	1.0439
$(\text{CH}_3)_3\text{SiF}$	4.25	3.79	35.4	1.0119	1.1076
$(\text{CH}_3)_2\text{SiF}_2$	10.20	5.22	8.8	1.0111	1.1243
CH_3SiF_3	-17.62	4.55	-51.8	1.0090	1.1407
SiF_4	-24.60	3.35	-109.0	1.0056	1.1551
$(\text{CH}_3)_3\text{SiCl}$	1.60	1.83	29.5	1.0117	1.1000
$(\text{CH}_3)_2\text{SiCl}_2$	3.67	2.81	32.0	1.0116	1.1105
CH_3SiCl_3	5.77	2.98	12.1	1.0110	1.1205
SiCl_4	7.60	3.20	-18.5	1.0099	1.3000

even the experimental trend is not reproduced; however, for the fluorides, the calculated trend is quite close to the experimental one, except for $(\text{CH}_3)_2\text{SiF}_2$ which has too low a value for the shift. A lack of experimental values for CH_3SiH_3 and SiH_4 prevents definite conclusions for this series.

The values we obtained closely parallel those of Engelhardt et al. [3] if the arbitrary parameter f they use in determining $\langle r^{-3} \rangle$ is given its original value of 1. Clearly here also the trend is determined by the relative values of P_u and $\langle r^{-3} \rangle$ (eqn. 1), which vary in opposite directions.

It is not evident that it is possible in all cases to obtain good agreement between calculated and experimental trends, without introduction of an arbitrary fitting parameter. This suggests that the theoretical approach used here contains too many simplifications (average excitation energy, variation of ζ only on the silicon atom, omission of d -orbitals, neglect of diamagnetic and neighbour atom contributions to the chemical shift) to reproduce the observed chemical shift from the calculated paramagnetic contribution. Alternatively, we could argue that other effects may play an important role in determining the ^{29}Si chemical shift in these compounds as has already been suggested in ref. 1. It is however, quite remarkable that use of a single fitting parameter as in ref. 3, seems to cover all the factors that were neglected. In ref. 3 chemically very different systems were studied, and it is rather difficult to believe that all the factors should vary to the same extent in all the systems and so be covered by a single fitting parameter.

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