Nuclear Magnetic Resonance Spectra of Organosilicon Compounds

Part 1.—2-Cyanoethylsilanes

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^{1}H high resolution nuclear magnetic resonance spectra of three 2-cyanoethylsilanes at 60·00 and 25·00 MHz are described. Analyses of the spectra are presented. Extra-analytical information is utilized in the prediction of spectral parameters not revealed by the analyses.

The high resolution ^{1}H nuclear magnetic resonance spectra of 1,2-substituted ethanes, XCH_2CH_2Y at ambient temperatures are effectively time averages of separate spectra due to gauche and trans forms of the molecules.[1, 2] In favourable circumstances, analysis of the spectra on the basis of an AA'BB' (or AA'XX') spin system [3] yields, in addition to the two time-averaged chemical shifts, all four time-averaged coupling constants between the hydrogens of the dimethylene group, i.e., two geminal couplings and two distinct vicinal couplings. The relationship of " average " vicinal coupling constants to the sum of electronegativities of the atoms in X and Y directly attached to the dimethylene carbons approximates [2] to a linear one. The present work is a study of a further three 1,2-substituted ethanes in the form of 2-cyanoethylsilanes. In these compounds, a cyanide group and a silicon atom were in each case directly bonded to the dimethylene group. The variation arose in the silicon substituents. Since these substituents produced observable variations in ^{1}H chemical shifts and coupling constants, the work is an extension of previous investigations on the effects of atoms *directly* attached to the dimethylene group.

EXPERIMENTAL

All three compounds were prepared by Dr. V. B. McCann [4] in this Department. 2-Cyanoethyltrichlorosilane $NCCH_2CH_2SiCl_3$, and 2-cyanoethylmethyldichlorosilane $NCCH_2CH_2SiMeCl_2$, were prepared by the catalyzed addition of trichlorosilane and methyldichlorosilane respectively to acrylonitrile. 2-Cyanoethyltrimethylsilane $NCCH_2CH_2SiMe_3$ was prepared by the treatment of trichloro-2-cyanoethylsilane with methyl iodide.

Nuclear magnetic resonance spectra were obtained at 60·00 and 25·00 MHz and at ambient temperature using an Associated Electrical Industries Ltd. R.S.2. Spectrometer. In each case, the sample was examined as the neat liquid, tetramethylsilane was employed as internal reference and calibration was achieved by use of audio side-bands. For comparison purposes, AA'BB' spectra were calculated from given spectral parameters using the Manchester Atlas Computer.

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RESULTS

SPECTRAL ANALYSIS

The dimethylene portion of the 60·00 and 25·00 MHz spectra are shown in fig. 1. Chemical shifts associated with the remaining absorption are: $NCCH_2CH_2SiC\underline{H}_3Cl_2$, 9·13 τ; $NCCH_2CH_2Si(C\underline{H}_3)_3$, 9·95 τ. In no case was coupling observed between the dimethylene group and other silicon substituents, so that the dimethylene absorption could be analyzed on the basis of an AA′BB′ spin system.

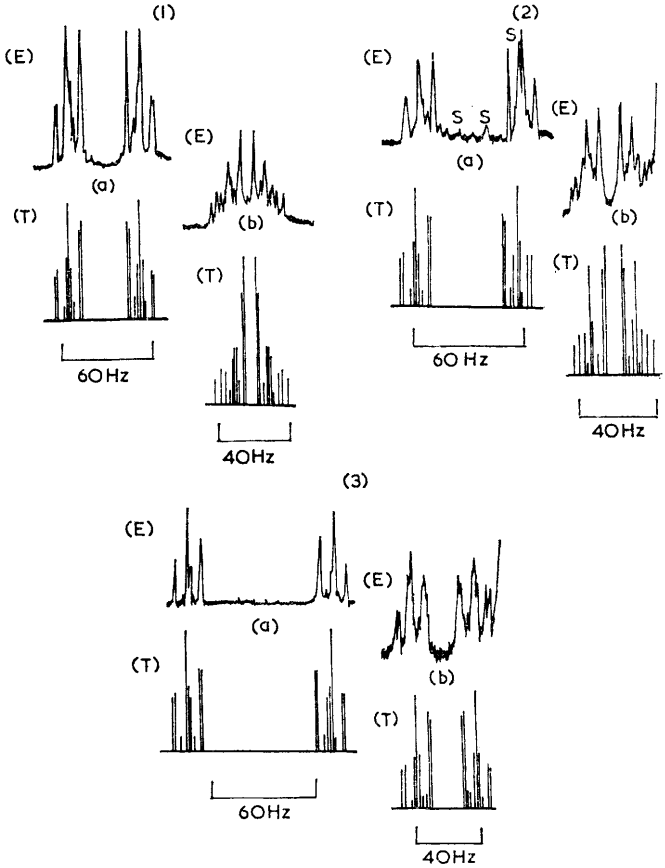

FIG. 1.—Expt. (E) and theor. (T), 60·00 (*a*) and 25·00 (*b*) MHz, dimethylene spectra of (1) $NCCH_2CH_2SiCl_3$, (2) $NCCH_2CH_2SiMeCl_2$, and (3) $NCCH_2CH_2SiMe_3$. (S = spinning side bands).

The analysis of AA′BB′ spectra has normally [3] been considered in terms of the AB internal chemical shift, $\delta\nu$ $(= \nu_A - \nu_B)$, and four coupling constant combinations $K = J_{AA'} + J_{BB'}$, $L = J_{AB} - J_{AB'}$, $M = J_{AA'} - J_{BB'}$, $N = J_{AB} + J_{AB'}$. The observed spectra are dependent upon the moduli of these combinations and upon the relative signs of K and N.[5] The construction of basic wavefunctions as combinations of products of one-spin functions symmetrical or antisymmetrical to the reflection operation of the C_s (or C_{2v}) group, the deduction of the Hamiltonian matrix, its diagonalization, and the calculation of transition frequencies and intensities has been described.[3] The combinations used were of one or four terms; two term combinations, although acceptable on symmetry grounds, were not employed. Transitions between antisymmetrical wave functions are dependent upon ν_A, ν_B, $|M|$ and $|L|$. For the symmetric functions, only four transitions from twenty can be given in analytical form. The restriction arises from the fourth order nature of that Hamiltonian sub-matrix corresponding to zero spin component (in the magnetic field direction). Of the four diagonal elements in this sub-matrix, only that corresponding to the basic spin function $\frac{1}{2}(\alpha\beta\alpha\beta+\beta\alpha\beta\alpha-\beta\alpha\alpha\beta-\alpha\beta\beta\alpha)$—the order of nuclei being AA′BB′—has a different term in the quantity K; none of the off-diagonal elements involve K. In circumstances where there is little mixing of the above basic function, the spectrum becomes [2] virtually independent of K; the probabilities of transitions to and from the state with this approximate function are negligible—in the limit of no mixing they are zero.

Typical values of geminal and vicinal coupling constants have been summarized by Banwell and Sheppard.[6] Furthermore, the average vicinal coupling,[2] $J = \frac{1}{2}N+\frac{1}{6}L$,

TABLE 1.—SPECTRAL PARAMETERS FOR 2-CYANOMETHYLSILANES ($NCCH_2CH_2SiXYZ$)

X	Y	Z	radio-freq. (MHz)	$\delta\nu$	$\lvert L\rvert$ (in Hz)	$\lvert M\rvert$ (in Hz)	$\lvert N\rvert$ (in Hz)	internal shift (p.p.m.)	$\frac{1}{2}(\tau_A+\tau_B)$
Cl	Cl	Cl	60·00	47·8	3·0	1·8	16·2	0·80	7·75
			25·00	19·4	3·0	1·7	16·2	0·78	7·75
			a	—	3·0	1·7	16·2	0·79	7·75
Me	Cl	Cl	60·00	62·8	3·3	2·2	16·5	1·05	7·97
			25·00	24·9	3·3	2·2	16·5	1·00	7·97
			a	—	3·3	2·2	16·5	1·03	7·97
Me	Me	Me	60·00	88·4	3·5	2·6	16·5	1·47	8·40
			25·00	36·4	3·5	2·6	16·5	1·46	8·39
			a	—	3·5	2·6	16·5	1·47	8·40

a, average value.

is approximately related to the sum of Huggins electronegativities E of atoms directly attached to the dimethylene group by [2] $J = (9{\cdot}41-0{\cdot}80\,E)$ Hz. On this basis, J should approximate to 6 Hz. With this background information, AA′BB′ spectra were calculated for a variety of input parameters (not including band shape) and compared in general form with experimental spectra, the sole purpose here being the assignment of transitions, particularly the more intense ones. This then allowed the direct deduction from band spacings [3] of $|N|$, $\pm N+[(\delta\nu)^2+N^2]^{\frac{1}{2}}$, $(M^2+L^2)^{\frac{1}{2}}$ and $[(\delta\nu\pm M)^2+L^2]^{\frac{1}{2}}$. Where two signs are presented, both quantities were determinable but distinction was not possible. Spacings not involving $\delta\nu$ were independent of radio-frequency, a factor which acted as a further aid to analysis. From the spacings, $|L|$, $|M|$, $|N|$ and $\delta\nu$ (a positive quantity by convention) were calculated for each of the three compounds. Table 1 presents values of these parameters, as derived from the 60 and the 25 MHz spectra, the internal chemical shift (in p.p.m.) and the mean chemical shift, $\frac{1}{2}(\tau_A+\tau_B)$. It also presents average values appropriate to the two radio-frequencies; theoretical spectra calculated from these are included in fig. 1.

Absent from the table are values for K or its modulus. Transitions to and from the state approximated by the function $\frac{1}{2}(\alpha\beta\alpha\beta+\beta\alpha\beta\alpha-\beta\alpha\alpha\beta-\alpha\beta\beta\alpha)$ were in no case observed. On the basis of second-order perturbation theory and the known elements of the Hamiltonian matrix,[3] the conditions under which this function is virtually unmixed with other functions of the same symmetry and spin component are that $|K|$ and (both) $|K \pm \delta\nu - \frac{1}{2}N|$ should be substantially greater than $|\frac{1}{2}L|$.[7] Table 1 indicates the smallness of $|\frac{1}{2}L|$ for all three compounds, i.e., less than 2 Hz. $|K|$ on the other hand would normally[6] exceed 16 Hz. With regard to the second comparison, values of K which make $K \pm \delta\nu - \frac{1}{2}N$ zero are:

60 MHz: $NCCH_2CH_2SiCl_3$, +56 or −39; $NCCH_2CH_2SiMeCl_2$, +70 or −54; $NCCH_2CH_2SiMe_3$, +96 or −80 Hz.

25 MHz: $NCCH_2CH_2SiCl_3$, +28 or −12; $NCCH_2CH_2SiMeCl_2$, +34 or −17; $NCCH_2CH_2SiMe_3$, +45 or −28 Hz.

The signs are relative to N. Vicinal and geminal H—H couplings (averaged over the internal rotation) are generally of opposite sign[8-12] so that a negative K (relative to N) is appropriate. Furthermore, a magnitude of K in the range 20-25 Hz would seem reasonable.[2,6] On this basis and noting that $|\frac{1}{2}L|$ is *ca.* 1·5 Hz for each compound, one might expect a slight observable dependence upon K in the 60 MHz spectrum for the trichloro-compound. Indeed, although the calculated spectrum is not sensitive to a value of K near to −25 Hz, correlation with the observed spectrum is better with the negative than with a positive sign. Overlap of transition and a less favourable signal-to-noise ratio at 25 MHz makes the distinction more difficult at this radio-frequency, despite the fact that both the methyldichloro- and the trimethyl-compounds should, in principle, be favourable cases for determination of the relative sign of K, at least.

From the average values of $|L|$ and $|N|$ in table 1, the following values of $|J_{AB}|$, $|J_{AB'}|$, undistinguished as one might expect from the arbitrariness of the A,A′ and B,B′ designation, were calculated: $NCCH_2CH_2SiCl_3$, 6·6, 9·6; $NCCH_2CH_2SiMeCl_2$, 6·6, 9·9; $NCCH_2CH_2SiMe_3$, 6·5, 10·0 Hz. In each case, the coupling constants were of like sign.

DISCUSSION

The assignment of A and B nuclei to the 1- and 2-methylene hydrogens has been made on the basis of (*a*) previous data (and electronegativity considerations), and (*b*) the expectation of a smaller variation for the hydrogens of the 2-methylene group. From the internal and the mean chemical shifts for each compound, the chemical shifts (as τ-values) have been calculated as follows:

1-CH_2(BB′): $NCCH_2CH_2SiCl_3$, 8·15; $NCCH_2CH_2SiMeCl_2$, 8·47; $NCCH_2CH_2SiMe_3$, 9·14.
2-CH_2(AA′): $NCCH_2CH_2SiCl_3$, 7·35; $NCCH_2CH_2SiMeCl_2$ 7·45; $NCCH_2CH_2SiMe_3$, 7·68.

The internal chemical shift for the first three compounds fits well the formula $\delta = 4{\cdot}55\text{-}1{\cdot}35\,\chi$, where χ is the electronegativity of the silicon group as calculated by Huheey,[13] viz., 2·78 for $SiCl_3$, 2·28 for $SiMe_3$ and (by linear interpolation) 2·61 for $SiMeCl_2$. The calculated shifts are, for the compounds in the order given 0·79, 1·03, and 1·47 p.p.m. Caution must be applied to a relationship based upon so few experimental points.

The geminal F—F coupling constant in substituted ethanes is related to the electronegativity of the remaining atom bonded to the same carbon, increased electronegativity reducing the coupling constant modulus.[14, 15] Assuming that this may be extended to H—H coupling and utilizing the fact that the electronegativity of carbon is greater than that of silicon, $|J_{1\text{-}CH_2}|$ (= $|J_{BB'}|$, BB′ being the higher field or lower frequency group) should exceed $|J_{2\text{-CH}_2}|$ ($= |J_{AA'}|$). If the atoms directly attached to the dimethylene group were the only factors affecting the geminal couplings, no variation in these couplings would occur for the three compounds considered here. Nevertheless, a small variation has been observed in the values of $|M| = |J_{AA'} - J_{BB'}|$, indicating some dependence of couplings upon the more remote atoms. One might expect a greater dependence for the 1-methylene than for the 2-methylene coupling, much in the same way as for the chemical shifts. Because of the absence of precise values of $|K|$, determination of individual $|J_{AA'}|$ and $|J_{BB'}|$ was not possible. Three approaches were considered for estimating values of these moduli *relative to one particular value*, e.g., $|J_{AA'}|$ for $NCCH_2CH_2SiCl_3 = C$ Hz. In each case, it is assumed that the two geminal couplings are of like sign. The results of these extra-analytical predictions (all compatible with the experimental $|M|$) are shown in table 2. There is no gross distinction between the predictions of (*a*), (*b*) and (*c*). Furthermore, $|J_{BB'}|$ shows the expected[14, 15] decrease with increasing group electronegativity.[13] The value of C unfortunately remains indeterminate but is expected to be *ca.* 10 Hz.

TABLE 2.—ESTIMATED GEMINAL COUPLING CONSTANT MODULI (Hz) FOR (I) $NCCH_2CH_2SiMe_3$, (II) $NCCH_2CH_2SiMeCl_2$, AND (III) $NCCH_2CH_2SiCl_3$.

assumption :	$\lvert J_{AA'}\rvert$ invariant		$\lvert J_{BB'}\rvert$ (I)$-$ $\lvert J_{BB'}\rvert$ (III) $=$ 3[$\lvert J_{AA'}\rvert$ (I)$-$ $\lvert J_{AA'}\rvert$ (III)] (by analogy with the expt. obs.: τ_B (I)$-\tau_B$ (III) $=$ 3[τ_A (I)$-\tau_A$ (III)])		(i) $\lvert J_{AA'}\rvert$ (I)$-$ $\lvert J_{AA'}\rvert$ (III) $= D[\tau_A$(I)$-\tau_A$ (III)] (ii) $\lvert J_{BB'}\rvert$ (I)$-$ $\lvert J_{BB'}\rvert$ (III) $= D[\tau_B$ (I)$-\tau_B$ (III)] with D = common constant	
compound	$\lvert J_{AA'}\rvert$	$\lvert J_{BB'}\rvert$	$\lvert J_{AA'}\rvert$	$\lvert J_{BB'}\rvert$	$\lvert J_{AA'}\rvert$	$\lvert J_{BB'}\rvert$
I	C	$C+2{\cdot}6$	$C+0{\cdot}5$	$C+3{\cdot}1$	$C+0{\cdot}6$	$C+3{\cdot}4$
II	C	$C+2{\cdot}2$	$C+0{\cdot}3$	$C+2{\cdot}5$	$C+0{\cdot}2$	$C+2{\cdot}2$
III	C	$C+1{\cdot}7$	C	$C+1{\cdot}7$	C	$C+1{\cdot}6$
	method (*a*)		method (*b*)		method (*c*)	

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