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NOTE

INTERNAL MOTIONS OF *N*-ORGANOSILYL KETIMINES

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The present broad-line NMR study of some *N*-organosilyl ketimines, synthesized recently[1] in this laboratory, was done to seek relations between structure and internal mobility of the new compounds. The silicon compounds bis(benzophenone-imino)dimethylsilane (I), tris(benzophenone-imino)methylsilane (II), bis(benzophenone-imino)diphenylsilane (III) and tris(benzophenone-imino)phenylsilane (IV) were selected as well as the similar *N*-(triphenylmethyl)benzophenone imine (V) and the quite different compound *N,N,N'*-tris(trimethylsilyl)benzamidine (VI) from the large number of available ketimines. The line widths and second moments were determined at different temperatures.

EXPERIMENTAL

The compounds (I)–(VI) were first investigated with a broad-line spectrometer of the Mallinckrodt Laboratory, the details of which are described in earlier publications about studies of different compounds, most of them containing silicon[2,3]. Polycrystalline samples of the *N*-organosilyl ketimines* were sealed off in an atmosphere of argon in vials (diam. 11 mm) and measured at room temperature. The line shape could be varied and improved by suitable choice of the modulation amplitude, time constant and sweep time, but it remained unsatisfactory for a reliable quantitative evaluation. A specially-equipped commercial Varian instrument proved more satisfactory**. Sweep time, modulation amplitude, time constant, sweep field and RF power were changed over a wide range to give optimum results. The resulting spectra showed the first derivative of the absorption curve, and were recorded on 15 × 10-inch graph-paper ,which was calibrated in gauss. The line width was taken as the peak-to-peak distance, and by counting the spaces under the curves, a numerical integration produced the second moments quite accurately. During all investigations the time constant was limited to one tenth of the sweep time from peak to peak. The modulation amplitude always was set so that it did not exceed 50% of the line width.

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** This instrument became available through the mediation of Mr. Volpicelli (Harvard University) and the courtesy of Dr. T. Haas (Tufts University). Their assistance at the beginning of the work was very much appreciated.

Lower and higher temperatures were arranged by the gas-flow method, blowing dry nitrogen through a metal coil immersed in liquid nitrogen and heating the cooled gas to the desired temperature by a heating wire which was connected with a sensor unit. The samples were allowed to stay at least twenty minutes in the gas flow before the first spectrum was taken. The temperatures were controlled additionally by a copper–constantan thermocouple which was put beside the samples in the nitrogen stream. Because of the shape of the commercial Dewar vessel, vials with a diameter of 9 mm had to be used; for this reason the filling factor was 40% less, and the signal-to-noise ratio became correspondingly worse. Therefore, the compounds were melted to gain a denser filling of the ampoules.

Measurements at room temperature resulted in symmetrically-shaped signals with an excellent signal-to-noise ratio after proper choice of all parameters. The spectral line width for all the compounds was smaller than 200 milligauss, so the earlier difficulties with the Mallinckrodt instrument became explainable. At lower temperatures, the RF power was decreased considerably to avoid saturation. The other parameters were also adjusted to gain optimum conditions. The spectra of (I)–(VI) were taken as a function of the temperature (°C) between −170° and +20° to +75° at intervals of about 30°. At least three spectra were recorded at each temperature. The line-width was read easily from the spectra. The second moments, defined by Andrew[4], were determined by a numerical integration, using a simple FORTRAN program and an IBM 1620 computer. The second moments for each half of the spectrum were calculated separately, then an average value was determined and corrected for modulation broadening[5].

RESULTS

All the spectra showed a single absorption line. Table 1 contains the averaged

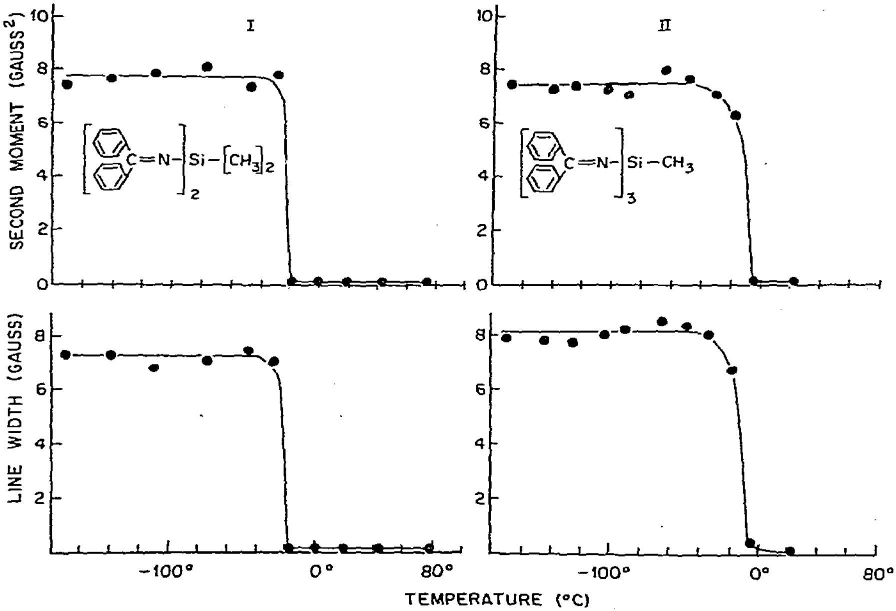

Fig. 1. Line width and second moment *vs.* temperature for compounds (I) and (II).

experimental values of the measured line widths and the corrected second moments at various temperatures, and Figs. 1–3 show graphs of the data.

Some theoretical calculations help to interpret the observed broad-line NMR results. A formula derived by van Vleck[6] is used to calculate the second moments of rigid configurations of complicated molecules. The formula can be modified for certain types of motion[7], considering the inter-proton resonance and the interaction of protons with the nuclear spins of other atoms. Table 2 shows the second moments which were calculated for isolated groups. Those parts of the second moments of compounds (I)–(VI) which are due to *internal* motion were then obtained by addition of the different contributions of protons in the methyl and phenyl groups. A complete reliable theoretical calculation including the *intermolecular* parts of the second moments was impossible, because the structures of compounds (I)–(VI) are unknown[8].

The plots of the line widths and second moments *vs.* temperature indicate that a transition in compounds (I) and (II) occurs at a lower temperature than the transition in (III) and (IV). Hence the assumption seems to be reasonable that the motion of the methyl groups bound to silicon needs less activation energy than the motion of the more bulky phenyl groups. Looking at the constitutions of compounds (III) and (IV), an explanation can be found for the fact that compound (III) shows a decrease of line width and second moment at slightly higher temperatures than (IV).

TABLE 1

LINE WIDTHS AND SECOND MOMENTS OF COMPOUNDS (I)–(VI)

Temp. (°C)	Averaged line width (gauss)	Averaged, corrected second moment (gauss^2)
Bis(benzophenone-imino)dimethylsilane (I)		
+75.5	0.067±0.007	$(2.0\pm0.2)\cdot10^{-3}$
+44.5	0.082±0.005	$(2.0\pm0.2)\cdot10^{-3}$
+20.0	0.077±0.001	$(2.1\pm0.2)\cdot10^{-3}$
+0.6	0.077±0.002	$(2.2\pm0.1)\cdot10^{-3}$
−19.0	0.097±0.003	$(3.5\pm0.3)\cdot10^{-3}$
−29.3	7.00 ±0.13	7.78±0.68
−46.0	7.44 ±0.31	7.34±0.26
−76.0	7.06 ±0.11	8.08±0.77
−110.6	6.72 ±0.05	7.80±0.29
−141.7	7.28 ±0.05	7.62±0.26
−170.0	7.30 ±0.20	7.38±0.26
Tris(benzophenone-imino)methylsilane (II)		
+21.7	0.112±0.004	$(6.3\pm0.1)\cdot10^{-3}$
−5.0	0.441±0.022	$(10.8\pm0.2)\cdot10^{-2}$
−18.0	6.67	6.21±0.27
−33.0	8.00 ±0.35	6.99±0.40
−49.0	8.45 ±0.13	7.56±0.28
−65.0	8.55 ±0.05	7.96±0.12
−90.0	8.28 ±0.15	6.99±0.17
−104.0	8.11 ±0.15	7.19±0.10
−127.0	7.72 ±0.05	7.34±0.24
−143.0	7.83 ±0.10	7.27±0.10
−170.0	7.89 ±0.15	7.50±0.23

(continued next page)

TABLE 1 (*continued*)

Temp. (°C)	Averaged line width (gauss)	Averaged, corrected second moment (gauss^2)
Bis(benzophenone-imino)diphenylsilane (III)		
+49.5	0.098±0.002	$(1.57\pm0.02)\cdot10^{-2}$
+31.5	1.36 ±0.07	2.43±0.05
+20.2	6.05 ±0.06	5.32±0.16
−3.6	6.60 ±0.15	6.26±0.15
−26.5	6.83 ±0.10	6.17±0.29
−47.0	7.50 ±0.10	6.60±0.27
−49.7	7.44 ±0.20	7.37±0.12
−76.2	7.69 ±0.12	7.01±0.10
−110.0	8.33 ±0.19	7.92±0.13
−142.5	8.48 ±0.10	8.15±0.08
−169.0	8.84 ±0.17	8.34±0.08
Tris(benzophenone-imino)phenylsilane (IV)		
+56.5	0.041±0.002	$(1.80\pm0.02)\cdot10^{-3}$
+27.6	0.278±0.005	$(2.06\pm0.02)\cdot10^{-3}$
+15.0	4.33 ±0.19	3.85±0.04
−3.5	7.17	6.26±0.28
−26.4	7.66 ±0.10	6.66±0.28
−58.8	8.22 ±0.12	8.17±0.42
−86.2	8.50 ±0.10	8.69±0.10
−114.0	9.30 ±0.03	8.71±0.26
−147.8	9.50 ±0.10	8.94±0.21
−165.8	9.55 ±0.05	9.31±0.20
N-(Triphenylmethyl)benzophenone imine (V)		
+12.2	0.078±0.005	$(2.5\pm0.1)\cdot10^{-3}$
−7.6	0.100±0.010	$(4.1\pm0.3)\cdot10^{-3}$
−31.0	0.104±0.015	$(3.7\pm0.5)\cdot10^{-3}$
−57.0	0.110±0.006	$(2.4\pm0.3)\cdot10^{-3}$
−82.0	8.89 ±0.11	9.09±0.11
−111.0	8.94 ±0.39	9.27±0.25
−140.5	9.39 ±0.11	9.34±0.20
−163.8	9.61 ±0.06	9.97±0.23
N,N,N′-Tris(trimethylsilyl)benzamidine (VI)		
+46.2	3.22±0.15	3.20±0.08
+17.0	3.08±0.11	4.10±0.33
−6.4	3.39±0.14	5.88±0.18
−31.0	3.61±0.20	5.80±0.14
−65.6	4.06±0.11	7.21±0.25
−95.7	5.55±0.22	9.23±0.55
−133.7	6.55±0.11	9.48±0.15
−162.4	6.44±0.11	10.25±0.05

The latter contains only one phenyl group on silicon, which can start rotating with less steric hindrance than the two rings in (III). This steric effect seems to be less important in (I) and (II) because the motion begins in the opposite order.

In contrast to the silicon compounds, compound (V) with its similar constitution (but carbon instead of silicon in the molecule) shows a very narrow line and a small second moment down to −60°. The line width of (VI) never dropped

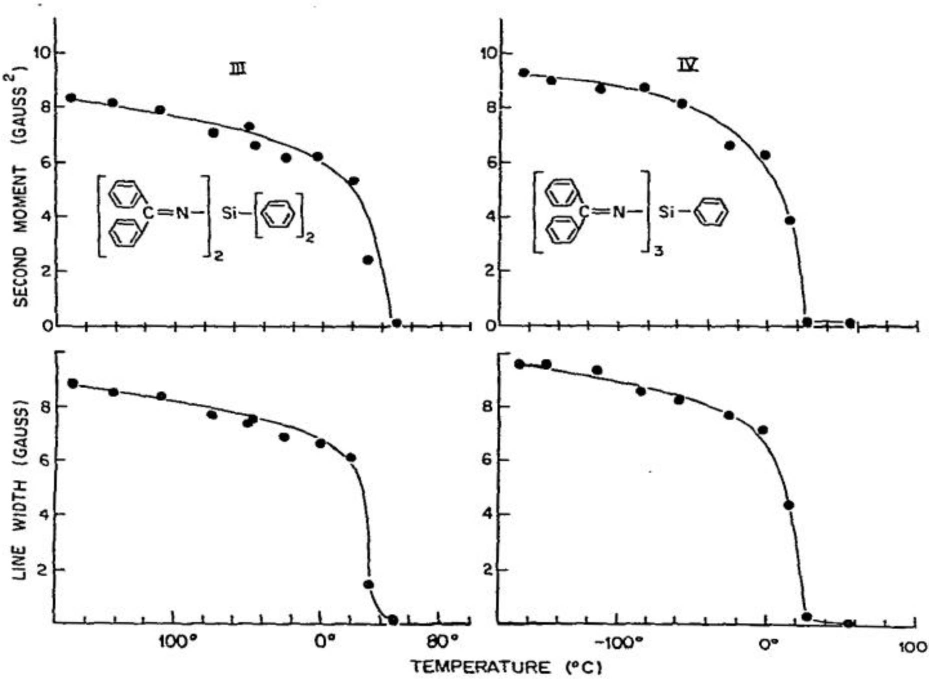

Fig. 2. Line width and second moment *vs.* temperature for compounds (III) and (IV).

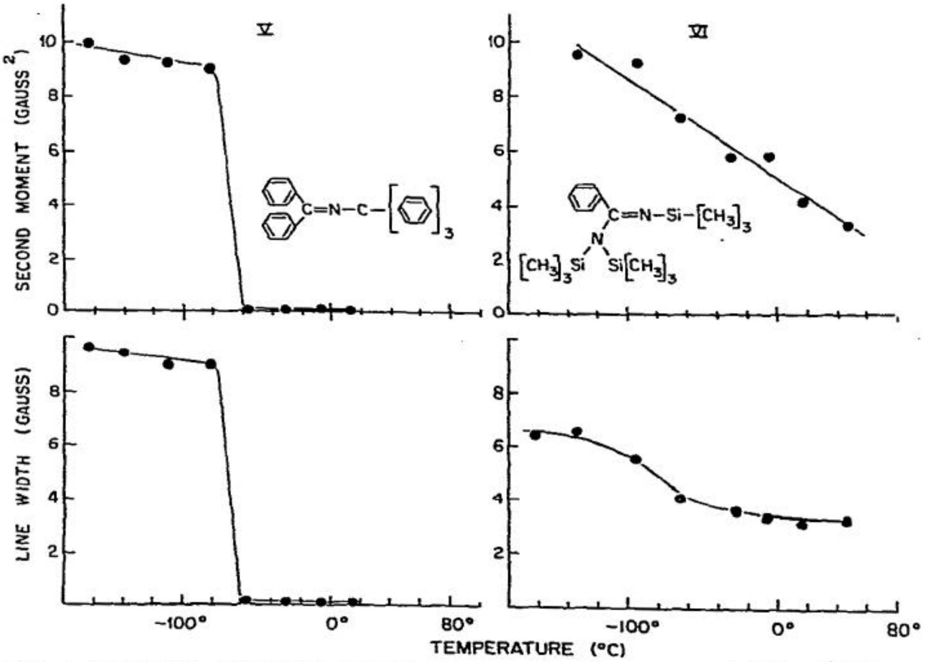

Fig. 3. Line width and second moment *vs.* temperature for compounds (V) and (VI). All values in gauss^2.

TABLE 2

INTERNAL CONTRIBUTIONS TO THE SECOND MOMENTS OF COMPOUNDS (I)–(VI)
All values in gauss^2.

Compound	Rigid configuration	Rotation around one axis	Rotation around two axis
(I)	7.0	1.13	2.11[a]
		3.23[a]	
(II)	4.2	1.22	2.29[a]
		2.72[a]	
(III)	2.56	1.28	
(IV)	2.56	1.28	
(V)	2.56	1.28	
(VI)	18.8	14.8[a]	3.63[a]
		5.0[a]	0.91[a]

[a] Methyl groups only.

below 3 gauss, and also the second moment stayed over 3 gauss^2. A transition is observed between −80° and −100° in this case. Although compounds (I)–(IV) show the sharp transitions which are characteristic of polymeric siloxanes and silazanes[3,9], compound (VI) shows a very gradual release of internal constraints.

The second moments obtained from the broad-line NMR spectra taken between −160° and −170° are not at all in agreement with the calculated values[8] for a rigid configuration. This is not surprising, because no intermolecular interaction was taken into account (because of the missing structures). The difference between experimental and calculated second moments increases from (I) and (II) to (III), (IV) and (V), and the absolute values do the same. The importance of the intermolecular part apparently grows and reaches a magnitude of 6–7 gauss, comparable to results found with benzene at low temperature[10]. On the other hand, the experimental values at higher temperatures are larger than all the calculated second moments for compounds (I)–(V). One has to assume that not only different types of rotation occur, but also diffusion processes. Possibly (I)–(V) resemble liquid crystals in some of their properties.

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