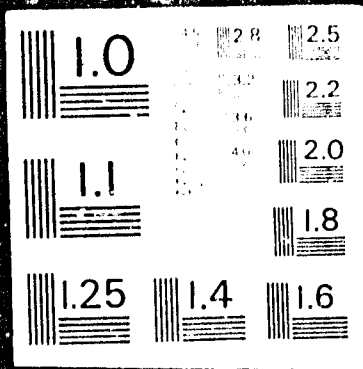


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I. SYNTHESSES OF IRON AND COBALT COMPLEXES WITH
LIGANDS CONTAINING SILICON-NITROGEN BONDS
II. INTERNAL MOTIONS OF N-ORGANOSILYL KETIMINES

by

Friedrich Wilhelm Kuepper

Technical Report No. ARPA 35

Contract ARPA SD-88

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August 1968

Submitted to:

Advanced Research Projects Agency

The Department of Defense

Division of Engineering and Applied Physics

Harvard University

Cambridge, Massachusetts

I. SYNTHESSES OF IRON AND COBALT COMPLEXES WITH
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ABSTRACT

This report presents results on two research programs, one on inorganic synthesis and one on structural study by means of broad-line NMR, which were pursued simultaneously during the year ending August 31, 1968. The first had to do with the synthesis of compounds of the transition metals containing organosilicon groups. Organosilyl amines were used as electron-donor ligands to form six new stable coordination compounds of iron and cobalt. All previous attempts (extending over the past 7 years) to do this had failed; the present success stems from a thorough study of the equilibrium considerations and the choice of a polar solvent for the reactions. The chemical behavior of the six new compounds is now being examined by Chang Kim, a graduate student in the Program.

The second project concerned the structures and behavior of five new compounds prepared last year, all with C-N-Si linkages (plus one additional compound with C=N-C linkage, for comparison). Earlier examination of the UV absorption spectra of these compounds had shown that there is little $d\pi - p\pi$ interaction between the nitrogen and silicon, because the

C=N-Si sequence is not linear but bent at an angle of 120° . It was expected that such an inflection also would hinder intramolecular motion, and that some distinctions between the several compounds would appear in their proton magnetic resonances as solids. The spectra were obtained, and calculation of line widths and second moments showed that intramolecular motion in all five organosilicon compounds was indeed hindered more than in the organic compound, and that one of the five (the only one which had an Si-N-C=N-Si structure) had a much more persistent restriction of motion with rise of temperature than the others.

I. SYNTHESSES OF IRON AND COBALT COMPLEXES WITH
LIGANDS CONTAINING SILICON-NITROGEN BONDS

Several attempts have been made to synthesize polymeric¹ and monomeric^{2,3} coordination compounds of metal halides with amines, substituted by a different number of trialkylsilyl groups. The report of Weiss² discusses reasons for the little interest in earlier days, expected difficulties during the synthesis, as well as some expectations about properties of the silicon-nitrogen bond coordinated to transition metal halides.

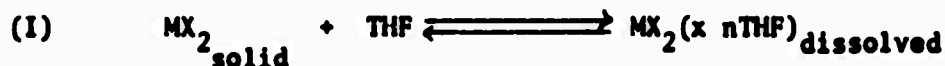
Weiss made attempts with anhydrous CuCl_2 , CoCl_2 , NiCl_2 , CrCl_3 , AlCl_3 , and ThCl_4 in benzene, light petroleum, tetrahydrofuran, dioxane and acetonitrile, of which he reported benzene and light petroleum as the most suitable solvents. C. Kim³ has used mainly benzene, and his favorite metal halide was anhydrous CuCl_2 , which he reacted with different ligands, partly synthesized for the first time. Analyses proved that the compounds contained unreacted CuCl_2 , which was probably covered by the coordination compound. The presence of the latter was inferred from the change of color, the analytical determinations, and from IR-spectra.

Confronted with these problems, a method for the isolation of pure compounds was sought. It was proposed to complete the reaction between the transition metal halides and the different ligands by: (1) the use of a more reactive metal halide, obtained for example, by powdering the anhydrous salts with an Ultrathorax in an inert solvent, (2) the use of a more polar solvent to achieve more homogeneous conditions. The number of possible solvents is limited by: a) the sensitivity of the silicon-nitrogen bond to the attack by protons; b) the possible formation of coordination compounds between solvent and metal halides. The first reason excludes, for example,

alcohols, which were successfully used during the synthesis of transition-metal complexes of tetra-alkyl-substituted ethylenediamines⁴. The second prohibits attempts with nitriles or dioxane, of which transition-metal coordination compounds are well known.

Therefore, an ether such as tetrahydrofuran seemed to me to be the best choice. Tetrahydrofuran forms solvates with different transition-metal halides also, but it is known as a relatively weak ligand, which can be replaced by stronger ligands. This was achieved during the synthesis of a coordination compound between iron(II) chloride and an aryl-alkyl-substituted ethylenediamine.⁵

The syntheses, described below, were based on the following assumptions: In the first reaction step the transition metal halide is partly dissolved in tetrahydrofuran and an equilibrium between solid and dissolved metal halide (solvated or unsolvated) is established:



In the second step the dissolved metal halide reacts with the added ligand, provided that this is a stronger ligand than tetrahydrofuran:

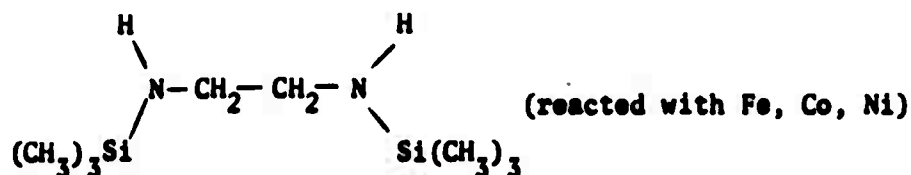


The formed coordination compound should be more soluble than the pure metal halide or the metal halide tetrahydrofuranate, because the organic portion of the molecule is larger. The coordination compound itself exists probably in equilibrium with the metal halide and ligand (lower arrow of eq. II); while the equilibrium constant is unknown, the solubility of pure MX_2 will be depressed, when all of the ligand is consumed. Provided that these

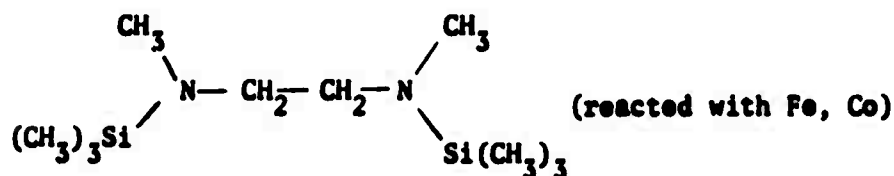
assumptions are correct, reaction of an excess of metal halide (Method A) with bidentate ligands should give a solution of probably the 1:1 coordination compounds, from which the excess of insoluble metal halide is separated by filtration. The coordination compounds can be isolated by evaporation of the solvent and drying of the residue with an oil-pump, to remove the last traces of adherent solvent. An amount of solvent, insufficient for dissolving all of the metal halide in the beginning of the reaction, must be used. In case of less soluble coordination compounds, for example complex polymers, an excess of ligand (Method B) should be used, the tetrahydrofuran filtrate discarded and the filter residue analyzed.

The anhydrous chlorides of iron, cobalt and nickel were treated in the way just proposed with the following ligands, which were synthesized and kindly placed at my disposal by C. Kim:

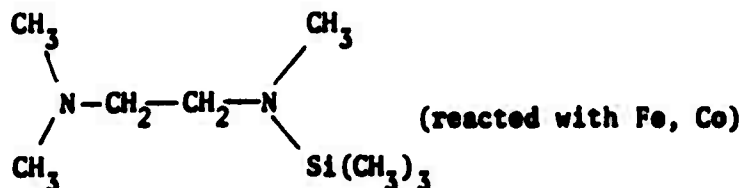
(L1) Bis-N,N'-trimethylsilyl-ethylenediamine



(L2) Bis-N,N'-trimethylsilyl-bis-N,N'-methyl-ethylenediamine



(L3) N,N,N'-trimethyl-N'-trimethylsilyl-ethylenediamine



General procedure:

Anhydrous cobalt and nickel chloride were obtained by treatment of the hydrates of these salts with thionyl chloride. Iron-dichloride was a commercial product (Alfa-Inorganic). Tetrahydrofuran was purified by refluxing with potassium hydroxide pellets, then over sodium wire, and distillation; the distilled solvent was stored over sodium wire.

About 0.01 mole of the anhydrous metal halide was suspended in about 100 ml of carefully dried tetrahydrofuran in an atmosphere of argon in a three-necked flask, equipped with gas-inlet tube, a dropping funnel and a magnetic stirring bar. About 0.009 mole of the ligand was dissolved in about 50 ml of tetrahydrofuran and added. The mixture was stirred for at least 48 hours at room temperature, filtered and the solvent evaporated. The residue was dried for several hours at reduced pressure (oil-pump), powdered with a magnetic stirring bar and analyzed.

Results:

Nickel(II)chloride was treated with ligand I in a preliminary attempt. A red solution was formed, from which a small amount of inhomogeneous material (partly oily) was isolated after filtration and evaporation of the solvent. The residue of "nickel(II)chloride" on the filterplate had changed its color from yellow to red-brown. It might be worthwhile to try method B (as mentioned above) to prepare this apparently less soluble complex in a pure state. We had to discard the residue, because an excess of metal halide was used.

Six compounds were isolated from the dark brown or dark blue reaction mixtures, respectively, of iron(II)chloride and cobalt(II)chloride with the ligands L1-L3. The analyses show that in all six cases these are 1:1 coordination compounds. The purity of three compounds is in good agreement

with the calculated analytical values ($\text{FeCl}_2 \times \text{L1}$; $\text{FeCl}_2 \times \text{L2}$; $\text{CoCl}_2 \times \text{L2}$). The preparation of the other ones should be repeated with freshly distilled ligands and tetrahydrofuran. All iron compounds are brown, all cobalt complexes blue or violet ($\text{CoCl}_2 \times \text{L3}$) powders.

$\text{FeCl}_2 \times \text{C}_8\text{H}_{24}\text{N}_2\text{Si}_2$ (L1)

calcd.	Fe 16,86	Cl 21,41	C 29,00	H 7,30	Si 16,96	N 8,46
found	17,06	21,11				

$\text{FeCl}_2 \times \text{C}_{10}\text{H}_{28}\text{N}_2\text{Si}_2$ (L2)

calcd.	Fe 15,55	Cl 19,74	C 33,43	H 7,86	Si 15,64	N 7,80
found	15,27	19,83				

$\text{FeCl}_2 \times \text{C}_8\text{H}_{22}\text{N}_2\text{Si}$ (L3)

calcd.	Fe 18,55	Cl 23,55	C 31,91	H 7,36	Si 9,33	N 9,30
found	19,38	22,31				

$\text{CoCl}_2 \times \text{C}_8\text{H}_{24}\text{N}_2\text{Si}$ (L1)

calcd.	Co 17,63	Cl 21,21	C 28,74	H 7,24	Si 16,80	N 8,28
found	16,41**	22,64				

$\text{CoCl}_2 \times \text{C}_{10}\text{H}_{28}\text{N}_2\text{Si}_2$ (L2)

calcd.	Co 16,26	Cl 19,57	C 33,14	H 7,79	Si 15,50	N 7,73
found	16,13**	19,89				

$\text{CoCl}_2 \times \text{C}_8\text{H}_{22}\text{N}_2\text{Si}$ (L3)

calcd.	Co 19,37	Cl 23,31	C 31,59	H 7,29	Si 9,23	N 9,21
found		21,46				

*Isolation of this compound was earlier reported by Weiss², but no analytical data were reported.

**Analysis of cobalt performed by C. Kim.

The work should be continued by varying metals and ligands. Further the physical and chemical properties of the compounds will be investigated. It will be interesting also to compare the results with those of similar coordination compounds, in which silicon has been replaced by carbon.

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1. Minné and Rechow, J. Am. Chem. Soc. 82 (1960), 5625, 5628.
 2. R. Weiss, Technical Report, Office of Naval Research 1961.
 3. C. Kim, unpublished work (thesis in preparation).
 4. L. Sacconi, I. Bertini, F. Mani, Inorg. Chem. 6 (1967) 262; I. Bertini, F. Mani, Inorg. Chem. 6 (1967) 2032.
 5. F.W. Küpper, J. Organometal. Chem. 13 (1968) 219.

II. INTERNAL MOTIONS OF N-ORGANOSILYL KETIMINES

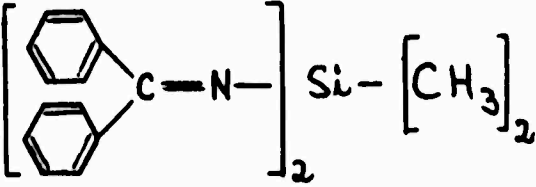
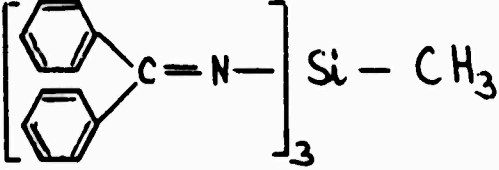
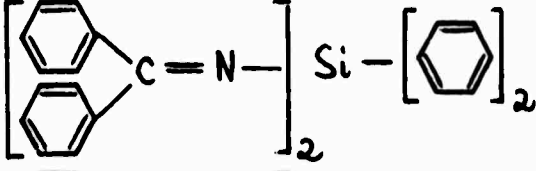
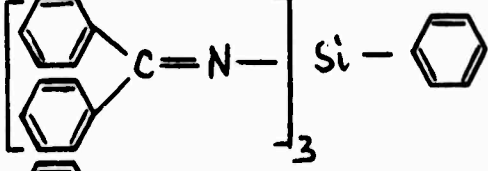
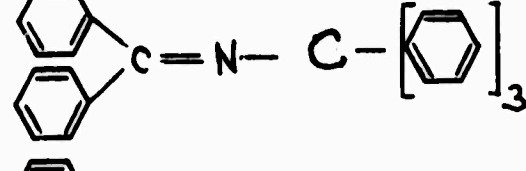
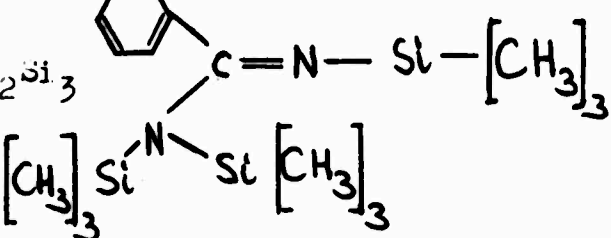
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A short time ago the syntheses of a large number of N-organosilyl ketimines were reported¹. These ketimines contained various substituents in the N-organosilyl and ketone parts of the molecules, respectively. The influence of these groups on the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ absorptions in the UV spectra of the compounds was studied, and then discussed with view to a possible $\underline{d}\pi - \underline{p}\pi$ interaction of the C=N-Si system. It was concluded from the interpretation of absorption shifts and intensities that the most probable arrangement for the compounds includes a C=N-Si framework with an angle of less than 180° at the nitrogen atom, presumably 120° . In this case, the $\underline{d}\pi - \underline{p}\pi$ interaction should be a minimum.

The present work was done to study the internal motions of some of these new compounds by broad-line-NMR-spectroscopy, and to seek relations between structure and internal mobility. The method has been used for a long time in this laboratory for studies of different compounds, most of them containing silicon. Details of the spectrometer and the method are described in earlier publications.²

Dibenzophenone-imino dimethylsilane (I), tribenzophenone-imino methylsilane (II), dibenzophenone-imino diphenylsilane (III) and tribenzophenone-imino phenylsilane (IV) were selected as suitable silicon compounds. For purposes of comparison the similar N-triphenylmethyl-benzophenone-imine (V) and also the quite different compound N-trimethylsilyl-N',N'-bis-trimethylsilyl-benzamidine (VI) were investigated. Table I shows the formulas and constitution of these compounds. (I am grateful to Lui-Heung Chan, who made all the substances during her graduate work at Harvard.)

Table I

Compound	Formula	Constitution	Melting Point
I	$C_{28}H_{26}N_2Si$		
II	$C_{40}H_{33}N_3Si$		114 - 117°
III	$C_{38}H_{40}N_2Si$		108 - 109°
IV	$C_{45}H_{35}N_3Si$		142 - 143°
V	$C_{32}H_{25}N_3Si$		161 - 162°
VI	$C_{16}H_{32}N_2Si_3$		

Experimental

Polycrystalline samples of I-VI were sealed off in an atmosphere of argon in vials with a diameter of 11 mm. These were measured with the above-mentioned broad-line NMR-spectrometer of the Mallinckrodt Laboratories at room temperature. Surprisingly, mostly distorted lines were observed.

The line shapes could be improved to some extent by a suitable choice of the modulation, time-constants and sweep time, but they remained unsatisfactory for a reliable quantitative evaluation. A commercial Varian broad-line NMR-instrument became available through the mediation of Mr. R. Volpicelli (Harvard University) and Dr. T. Haas (Tufts University). (I want especially to thank them for their help and assistance at the beginning of my work.) The Varian instrument proved more satisfactory; it worked with a fixed frequency and a variable strength of the magnetic field. It offered the possibility of moving and adjusting the sample probe horizontally and vertically, perpendicular to the magnetic field. Besides this, the sweep times, modulation amplitudes, time constants, sweep field and rf-power could be changed in a wide range, too. The spectra showed the first derivative of the absorption curve, and were recorded on a 15 x 10-inch graph-paper, which was calibrated in Gauss. The determination of the line width became quite easy, 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 at most 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. Before and after all measurements a spectrum of the probe without a sample was taken as a precaution against errors caused by contamination of the probe by other users of the instrument. To arrange for lower or higher temperatures, dry nitrogen was blown through a metal coil immersed in liquid nitrogen, and then was heated 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, chosen with the sensor unit, were controlled additionally by a copper-constantan thermocouple which was put beside the samples in the nitrogen stream.

Results

First measurements were carried out at room temperature, using the above-mentioned ampoules with a diameter of 11 mm and containing the polycrystalline materials. Table II shows the results for the different compounds. Symmetrically shaped signals with an excellent signal-to-noise ratio were recorded after careful adjustment of the probe in the magnetic field, and after proper choice of the other parameters. The spectral line-width for all the compounds was smaller than 200 mG, so the earlier difficulties with the Mallinckrodt instrument therefore became explainable. Attempted measurements at lower temperatures required vials with a diameter of 9 mm, because of the shape of the commercial Dewar vessel. Using the same sort of polycrystalline material as before, the filling factor therefore became reduced by about 40%. The signal-to-noise ratio became correspondingly worse. Lowering the temperature to about -30°C resulted in saturation effects and inexplicable disappearance of the signals, although the rf-power was decreased considerably. Therefore, the compounds were melted to gain a denser filling in the ampoules. The glasses formed by cooling the melted samples of I-IV, and the crystalline solids of V-VI, respectively, were investigated as described above but with two changes of the conditions:

- (1) The rf-power was further decreased, but tuning of the probe was still possible.
- (2) A very high modulation was used to detect the occurrence of the signal, and then the modulation was successively reduced until the decreasing line

Table II

Line widths and second moments at room temperature (in 11mm-vials)

Compound	Average line width (Gauss)	Average second moment (Gauss ²)
I	0.113 ± 0.002	(3.6 ± 0.2).10 ⁻³
II	0.083 ± 0.001	(4.4 ± 0.3).10 ⁻³
III	0.081 ± 0.003	(3.5 ± 0.1).10 ⁻³
IV	0.082 ± 0.001	(4.4 ± 0.2).10 ⁻³
VI	3.60 ± 0.01	4.75 ± 0.03

width remained constant.

In this way, a sudden and quite unexpected transition of the line width to several Gauss was discovered. Furthermore, it was found that the molten and resolidified substances showed line widths and second moments at room temperature which differed from those measured before.

The broad-line NMR-spectra of I-VI were taken as a function of the temperature at intervals of about 30°C between -170°C and +20°C to +75°C. At least three spectra were recorded at each temperature. The line width, the peak-to-peak distance of the first derivative curve, is read easily from the spectra taken on graph-paper with a Gauss calibration. To determine the second moments, defined by Andrew³ for the first derivative of an absorption curve as

$$\langle H_2 \rangle^2 = \frac{1/3 \int g'(H) (H-H_0)^3 dH}{\int g'(H) (H-H_0) dH}$$

($g'(H)$ = derivative of the line shape function $g(H)$,

$H-H_0$ = distance from the line center in Gauss)

the space under each half of a spectrum was tabulated, the data were then punched on cards and, using a simple FORTRAN-program, the calculations were done with an IBM 1620 computer. The second moments for each half of a spectrum were calculated separately, before an average value for the total spectrum was determined. For correction of modulation broadening, a term of $1/4 H_{\text{mod}}^2$ must be subtracted⁴. The tables III - VIII contain the measured line widths and second moments, with averaged values and errors for the different compounds at various temperatures. Only the average values of the second moments were corrected for modulation broadening. (Table IX-XI) Figures I-VI show graphs of the measured data.

Table III

Line widths and second moments of dibenzophenone-imino dimethylsilane
(Compound 1)

Temperature (°C)	Line width (Gauss)	Average l.w. (Gauss)	Second moment (Gauss ²)	Average sec.mom. (Gauss ²)
+75.5	0.053	0.067±0.007	2.04.10 ⁻³	(2.4±0.2).10 ⁻³
	0.077		3.09	
	0.070		2.02	
+44.5	0.087	0.082±0.005	2.77.10 ⁻³	(2.4 ± 0.2).10 ⁻³
	0.087		2.36	
	0.073		1.90	
+20.0	0.075	0.077±0.001	2.79.10 ⁻³	(2.5 ± 0.2).10 ⁻³
	0.080		2.17	
	0.077		2.61	
+0.6	0.073	0.077±0.002	2.62.10 ⁻³	(2.6 ± 0.1).10 ⁻³
	0.076		2.51.	
	0.080		2.73	
-19.0	0.100	0.097±0.003	3.34.10 ⁻³	(3.9 ± 0.3).10 ⁻³
	0.087		4.17	
	0.097		4.37	
	0.103		3.75	
-29.3	7.00	7.00±0.13	7.85	8.71 ± 0.68
	7.33		8.62	
	7.00		10.07	
	6.67		8.29	
-46.0	6.83	7.44±0.31	10.26	9.74 ± 0.26
	7.83		9.40	
	7.67		9.57	
-76.0	6.83	7.06±0.11	9.13	10.48 ± 0.77
	7.17		10.51	
	7.17		11.82	
-110.6	6.83	6.72±0.05	10.16	10.20 ± 0.29
	6.67		9.72	
	6.67		10.73	
-141.7	7.17	7.28±0.05	9.53	10.02 ± 0.26
	7.33		10.10	
	7.33		10.42	
-170.0	7.00	7.30±0.20	9.63	9.78 ± 0.25
	7.23		10.27	
	7.67		9.45	

Table IV

Line widths and second moments of tribenzophenone-imino methylsilane
(Compound II)

Temperature (°C)	Line width (Gauss)	Average l.w. (Gauss)	Second moment (Gauss ²)	Average sec.mom. (Gauss ²)
+21,7	0,110 0,106 0,120	0,112±0,004	6,92.10 ⁻³ 6,53 6,54	(6,66±0,13).10 ⁻³
-5,0	0,407 0,433 0,483	0,441±0,022	11,28.10 ⁻² 11,18 10,15	(10,87±0,15).10 ⁻²
-18,0	6,67 6,67 6,67	6,67	8,36 8,33 9,14	8,61 ± 0,27
-33,0	7,33 8,17 8,50	8,00±0,35	10,18 8,72 9,27	9,39 ± 0,40
-49,0	8,33 8,66 8,16 8,66	8,45±0,13	9,42 10,32 9,92 10,19	9,96 ± 0,28
-65,0	8,66 8,50 8,50	8,55±0,05	10,60 10,29 10,19	10,36 ± 0,12
-90,0	8,00 8,33 8,50	8,28±0,15	9,22 9,73 9,21	9,39 ± 0,17
-104,0	8,33 7,83 8,17	8,11±0,15	9,40 9,64 9,74	9,59 ± 0,10
-127,0	7,83 7,67 7,67	7,72±0,05	9,92 10,04 9,26	9,74 ± 0,24
-143,0	8,00 7,67 7,83	7,83± 0,10	9,61 9,54 9,87	9,67 ± 0,10
-170,0	8,17 7,83 7,67	7,89±0,15	10,25 9,89 9,57	9,90 ± 0,23

Table V

line widths and second moments of dibenzophenone-imino diphenylsilane
(Compound III)

Temperature (°C)	Line width (Gauss)	Average l.w. (Gauss)	Second moment (Gauss ²)	Average sec.mom. (Gauss ²)
+49.5	0.095	0.098±0.002	1.59.10 ⁻²	(1.61±0.02).10 ⁻²
	0.100		1.61.10 ⁻²	
	0.100		1.64.10 ⁻²	
+31.5	1.33	1.36±0.07	2.43	2.47 ± 0.05
	1.50		2.42	
	1.25		2.57	
+20.2	6.00	6.06±0.05	6.31	6.25 ± 0.16
	6.17		6.48	
	6.00		5.95	
-3.6	6.33	6.60±0.15	7.13	7.19 ± 0.15
	6.83		6.95	
	6.67		7.48	
-26.5	6.67	6.83±0.10	7.57	7.10 ± 0.29
	7.00		7.17	
	6.83		6.57	
-47.0	7.67	7.50±0.10	8.04	7.53 ± 0.27
	7.33		7.15	
	7.50		7.39	
-49.7	7.17	7.44±0.20	8.49	8.30 ± 0.12
	7.83		8.14	
	7.33		8.26	
-76.2	7.90	7.69±0.12	7.82	7.94 ± 0.10
	7.67		8.14	
	7.50		7.86	
-110.0	8.33	8.53±0.19	9.12	8.85 ± 0.13
	8.67		8.71	
	8.00		8.73	
-142.5	8.67	8.48±0.10	9.02	9.08 ± 0.08
	8.33		9.24	
	8.43		8.98	
-169.0	8.67	8.84±0.17	9.36	9.27 ± 0.17
	8.67		9.51	
	9.17		8.95	

Table VI

Line widths and second moments of tribenzophenone-imino phenylsilane
(Compound IV)

Temperature (°C)	Line width (Gauss)	Average l.w. (Gauss)	Second moment (Gauss ²)	Average sec.mom. (Gauss ²)
+56.5	0,040	0,041±0,002	1,87.10 ⁻³	(1,89±0,02).10 ⁻³
	0,040		1,87	
	0,040		1,90	
	0,046		1,94	
+27,6	0,267	0,278±0,005	2,09.10 ⁻¹	(2,08±0,02).10 ⁻¹
	0,283		2,11	
	0,283		2,05	
+15,0	4,66	4,33±0,19	4,02	4,09 ± 0,04
	4,33		4,10	
	4,00		4,14	
-3,5	7,17	7,17	6,11	6,50 ± 0,28
	7,17		7,04	
	7,17		6,35	
-26,4	7,66	7,66±0,10	6,46	6,90 ± 0,23
	7,50		7,24	
	7,83		6,98	
-58,8	8,00	8,22±0,12	9,26	9,10 ± 0,42
	8,50		9,74	
	8,17		8,29	
-86,2	8,50	8,50±0,10	9,66	9,62 ± 0,10
	8,33		9,44	
	8,66		9,77	
-114,0	9,33	9,30±0,03	9,46	9,74 ± 0,26
	9,17		10,27	
	9,33		9,72	
	9,33		9,54	
	9,33		9,72	
-147,8	9,50	9,50±0,10	10,12	9,87 ± 0,21
	9,66		10,04	
	9,33		9,45	
-165,8	9,66	9,55±0,05	10,55	10,24 ± 0,20
	9,50		10,32	
	9,50		9,86	

Table VII

Line widths and second moments of N-triphenylmethyl-benzophenone-imine
(Compound V)

Temperature (°C)	Line width (Gauss)	Average l.w. (Gauss)	Second moment (Gauss ²)	Average sec.mom. (Gauss ²)
+12.2	0.073	0.078±0.005	2.71.10 ⁻³	(2.76±0.10).10 ⁻³
	0.087		2.96	
	0.073		2.61	
-7.6	0.087	0.100±0.010	4.61.10 ⁻³	(4.37±0.31).10 ⁻³
	0.093		3.76	
	0.120		4.74	
-31.0	0.130	0.104±0.015	3.33.10 ⁻³	(4.12±0.50).10 ⁻³
	0.100		5.05	
	0.083		3.99	
-57.0	0.105	0.110±0.006	3.62.10 ⁻³	(3.43±0.33).10 ⁻³
	0.103		3.90	
	0.123		2.78	
-82.0	9.00	8.89±0.11	10.69	10.46 ± 0.11
	8.67		10.35	
	9.00		10.34	
-111.0	9.67	8.94±0.39	11.12	10.64 ± 0.25
	8.83		10.53	
	8.33		10.27	
-140.5	9.50	9.39±0.11	10.75	10.71 ± 0.20
	9.17		11.03	
	9.50		10.34	
-163.8	9.67	9.61±0.06	10.89	11.34 ± 0.23
	9.50		11.33	
	9.67		11.79	

Table VIII

Line widths and second moments of N-trimethylsilyl-N',N'-bis-trimethylsilyl-benzamidine (Compound VI)

Temperature (°C)	Line width (Gauss)	Average l.w. (Gauss)	Second moment (Gauss ²)	Average sec.mom. (Gauss ²)
+46.2	3.00	3.22±0.15	3.10	3.24 ± 0.08
	3.17		3.36	
	3.50		3.25	
+17.0	3.33	3.08±0.11	3.67	4.14 ± 0.33
	2.83		5.02	
	3.17		4.30	
	3.00		3.58	
-6.4	3.17	3.39±0.14	6.32	5.92 ± 0.18
	3.66		5.74	
	3.33		5.80	
-31.0	3.33	3.61±0.20	5.76	5.84 ± 0.14
	4.00		6.11	
	3.50		5.64	
-65.6	4.17	4.06±0.11	7.01	7.37 ± 0.25
	4.17		7.84	
	3.83		7.25	
-95.7	6.00	5.55±0.22	8.40	9.39 ± 0.55
	5.33		9.48	
	5.33		10.30	
-133.7	6.33	6.55±0.11	9.38	9.64 ± 0.15
	6.66		9.66	
	6.66		9.89	
-162.4	6.33	6.44±0.11	10.35	10.41 ± 0.05
	6.33		10.52	
	6.66		10.36	
-31.0	0.083	0.075	2.18.10 ⁻³	2.28.10 ⁻⁵
	0.067		2.38.10 ⁻³	

(superposed narrow signal)

Table IX

Second moments, before and after correction for modulation broadening

Compound	Temperature (°C)	Average value of the second moment		
		uncorrected (Gauss ²)	corrected (Gauss ²)	
I	+75,5	$(2,4 \pm 0,2) \cdot 10^{-3}$	$(2,0 \pm 0,2) \cdot 10^{-3}$	
	+44,5	$(2,4 \pm 0,2) \cdot 10^{-3}$	$(2,0 \pm 0,2) \cdot 10^{-3}$	
	+20,0	$(2,5 \pm 0,2) \cdot 10^{-3}$	$(2,1 \pm 0,2) \cdot 10^{-3}$	
	+0,6	$(2,6 \pm 0,1) \cdot 10^{-3}$	$(2,2 \pm 0,1) \cdot 10^{-3}$	
	-19,0	$(3,9 \pm 0,3) \cdot 10^{-3}$	$(3,5 \pm 0,3) \cdot 10^{-3}$	
	-29,3	$8,71 \pm 0,68$	$7,78 \pm 0,68$	
	-46,0	$9,74 \pm 0,26$	$7,34 \pm 0,26$	
	-76,0	$10,48 \pm 0,77$	$8,08 \pm 0,77$	
	-110,6	$10,20 \pm 0,29$	$7,80 \pm 0,29$	
	-141,7	$10,02 \pm 0,26$	$7,62 \pm 0,26$	
	-170,0	$9,78 \pm 0,25$	$7,38 \pm 0,26$	
	II	+21,7	$(6,7 \pm 0,1) \cdot 10^{-3}$	$(6,3 \pm 0,1) \cdot 10^{-3}$
		-5,0	$(10,9 \pm 0,2) \cdot 10^{-2}$	$(10,8 \pm 0,2) \cdot 10^{-2}$
-18,0		$8,61 \pm 0,27$	$6,21 \pm 0,27$	
-33,0		$9,39 \pm 0,40$	$6,99 \pm 0,40$	
-49,0		$9,96 \pm 0,28$	$7,56 \pm 0,28$	
-65,0		$10,36 \pm 0,12$	$7,96 \pm 0,12$	
-90,0		$9,39 \pm 0,17$	$6,99 \pm 0,17$	
-104,0		$9,59 \pm 0,10$	$7,19 \pm 0,10$	
-127,0		$9,74 \pm 0,24$	$7,34 \pm 0,24$	
-143,0		$9,67 \pm 0,10$	$7,27 \pm 0,10$	
-170,0		$9,90 \pm 0,23$	$7,50 \pm 0,23$	

Table X

Second moments, before and after correction for
modulation broadening

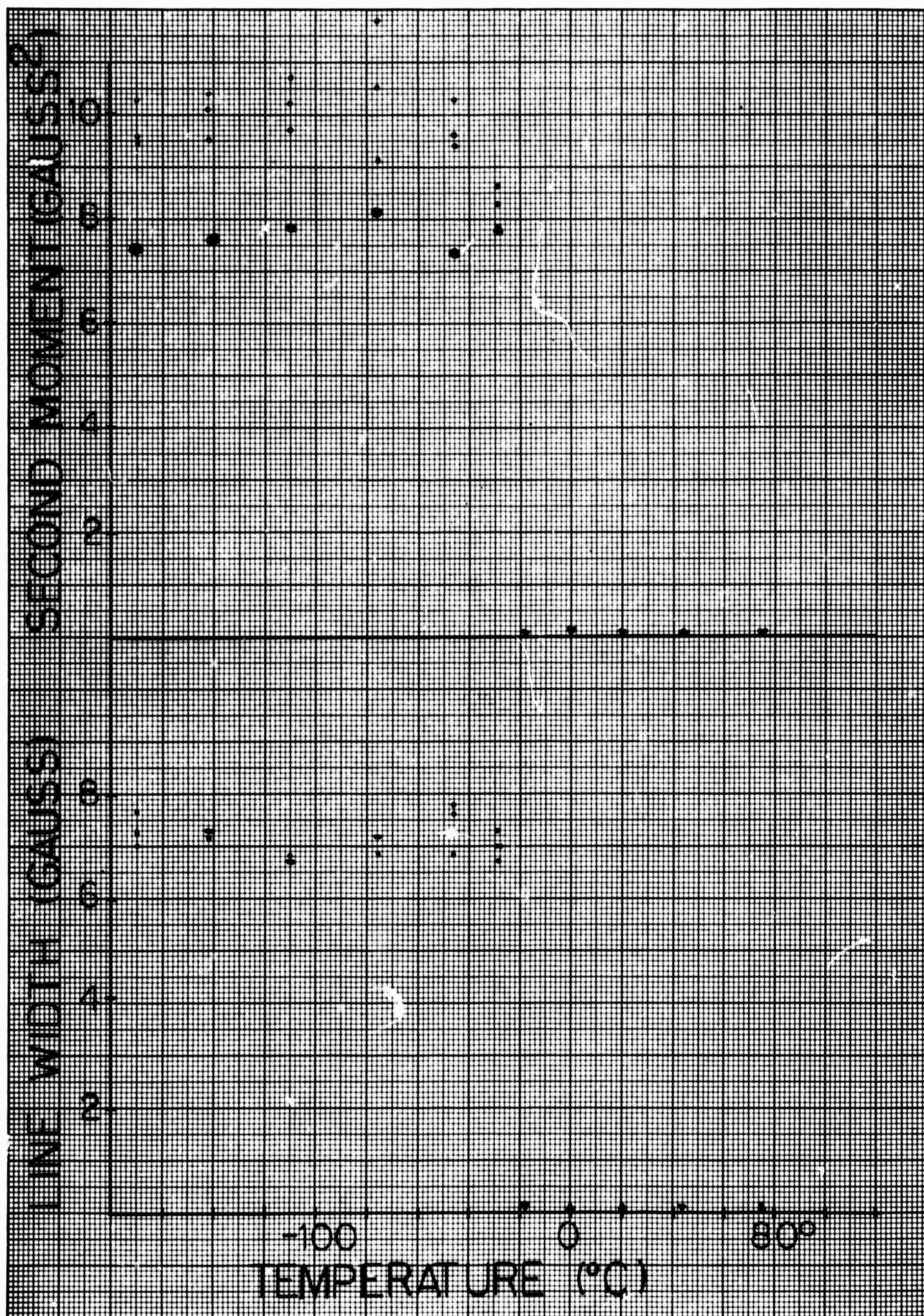
Compound	Temperature (°C)	Average value of the second moment	
		uncorrected (Gauss ²)	corrected (Gauss ²)
III	+49,5	$(1,61 \pm 0,02) \cdot 10^{-2}$	$(1,57 \pm 0,02) \cdot 10^{-2}$
	+31,5	$2,47 \pm 0,05$	$2,43 \pm 0,05$
	+20,2	$6,25 \pm 0,16$	$5,32 \pm 0,16$
	-3,6	$7,19 \pm 0,15$	$6,26 \pm 0,15$
	-26,5	$7,10 \pm 0,29$	$6,17 \pm 0,29$
	-47,0	$7,53 \pm 0,27$	$6,60 \pm 0,27$
	-49,7	$8,30 \pm 0,12$	$7,37 \pm 0,12$
	-76,2	$7,94 \pm 0,10$	$7,01 \pm 0,10$
	-110,0	$8,85 \pm 0,13$	$7,92 \pm 0,13$
	-142,5	$9,08 \pm 0,08$	$8,15 \pm 0,08$
	-169,0	$9,27 \pm 0,17$	$8,34 \pm 0,08$
	IV	+56,5	$(1,89 \pm 0,02) \cdot 10^{-3}$
+27,6		$(2,08 \pm 0,02) \cdot 10^{-3}$	$(2,06 \pm 0,02) \cdot 10^{-3}$
+15,0		$4,09 \pm 0,04$	$3,85 \pm 0,04$
-3,5		$6,50 \pm 0,28$	$6,26 \pm 0,28$
-26,4		$6,90 \pm 0,23$	$6,66 \pm 0,28$
-58,8		$9,10 \pm 0,42$	$8,17 \pm 0,42$
-86,2		$9,62 \pm 0,10$	$8,69 \pm 0,10$
-114,0		$9,74 \pm 0,26$	$8,71 \pm 0,26$
-147,8		$9,87 \pm 0,21$	$8,94 \pm 0,21$
-165,8		$10,24 \pm 0,20$	$9,31 \pm 0,20$

Table XI

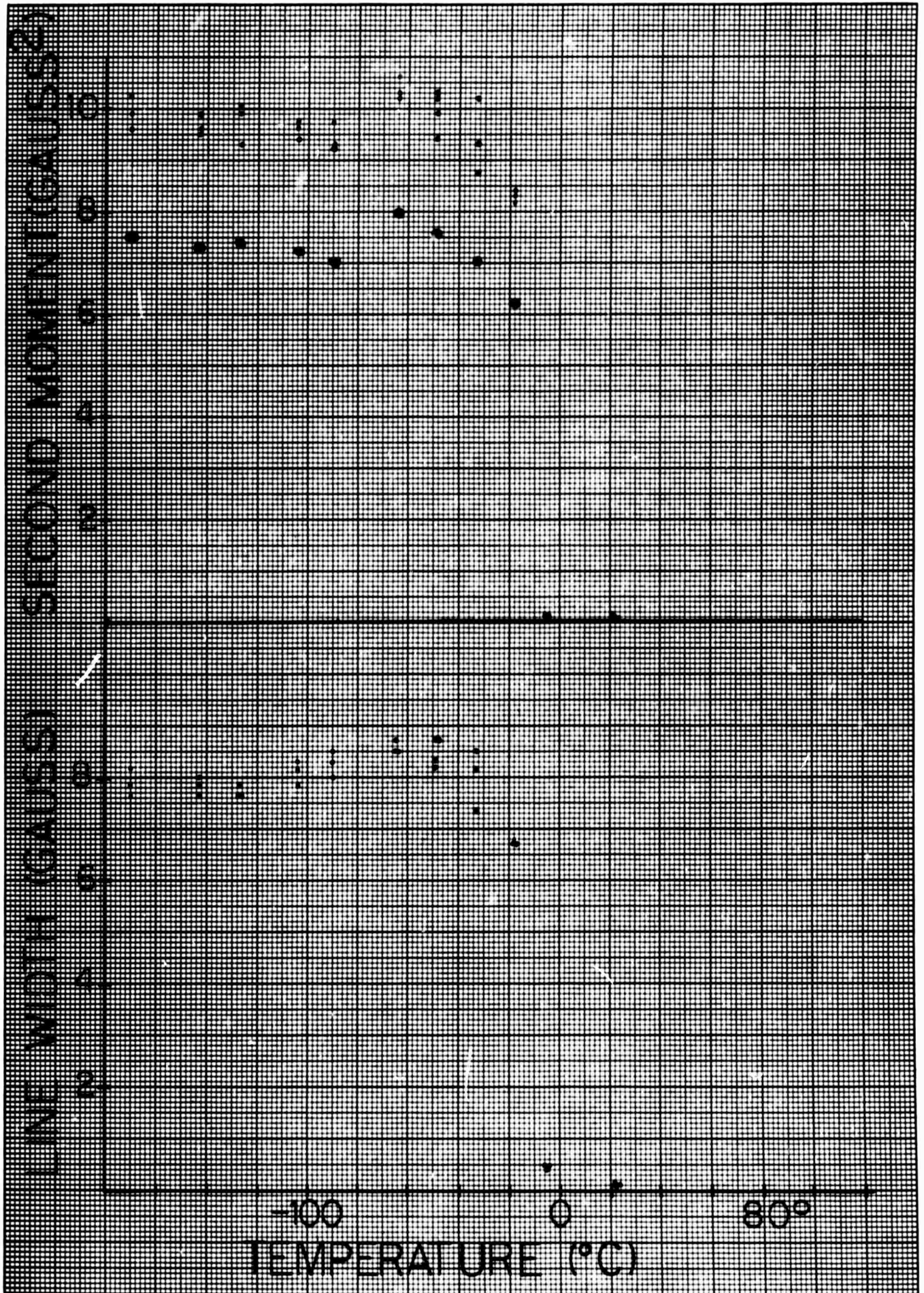
Second moments, before and after correction for
modulation broadening

Compound	Temperature (°C)	Average value of the second moment	
		uncorrected (Gauss ²)	corrected (Gauss ²)
V	+12,2	$(2,8 \pm 0,1) \cdot 10^{-3}$	$(2,5 \pm 0,1) \cdot 10^{-3}$
	-7,6	$(4,4 \pm 0,3) \cdot 10^{-3}$	$(4,1 \pm 0,3) \cdot 10^{-3}$
	-31,0	$(4,1 \pm 0,5) \cdot 10^{-3}$	$(3,7 \pm 0,5) \cdot 10^{-3}$
	-57,0	$(3,4 \pm 0,3) \cdot 10^{-3}$	$(2,4 \pm 0,3) \cdot 10^{-3}$
	-82,0	$10,46 \pm 0,11$	$9,09 \pm 0,11$
	-111,0	$10,64 \pm 0,25$	$9,27 \pm 0,25$
	-140,5	$10,71 \pm 0,20$	$9,34 \pm 0,20$
	-163,8	$11,34 \pm 0,23$	$9,97 \pm 0,23$
VI	+46,2	$3,24 \pm 0,08$	$4,20 \pm 0,08$
	+17,0	$4,14 \pm 0,33$	$4,10 \pm 0,33$
	-6,4	$5,92 \pm 0,18$	$5,82 \pm 0,18$
	-31,0	$5,84 \pm 0,14$	$5,80 \pm 0,14$
	-65,6	$7,57 \pm 0,25$	$7,21 \pm 0,25$
	-95,7	$9,59 \pm 0,55$	$9,23 \pm 0,55$
	-133,7	$9,64 \pm 0,15$	$9,48 \pm 0,15$
	-162,4	$10,41 \pm 0,05$	$10,25 \pm 0,05$

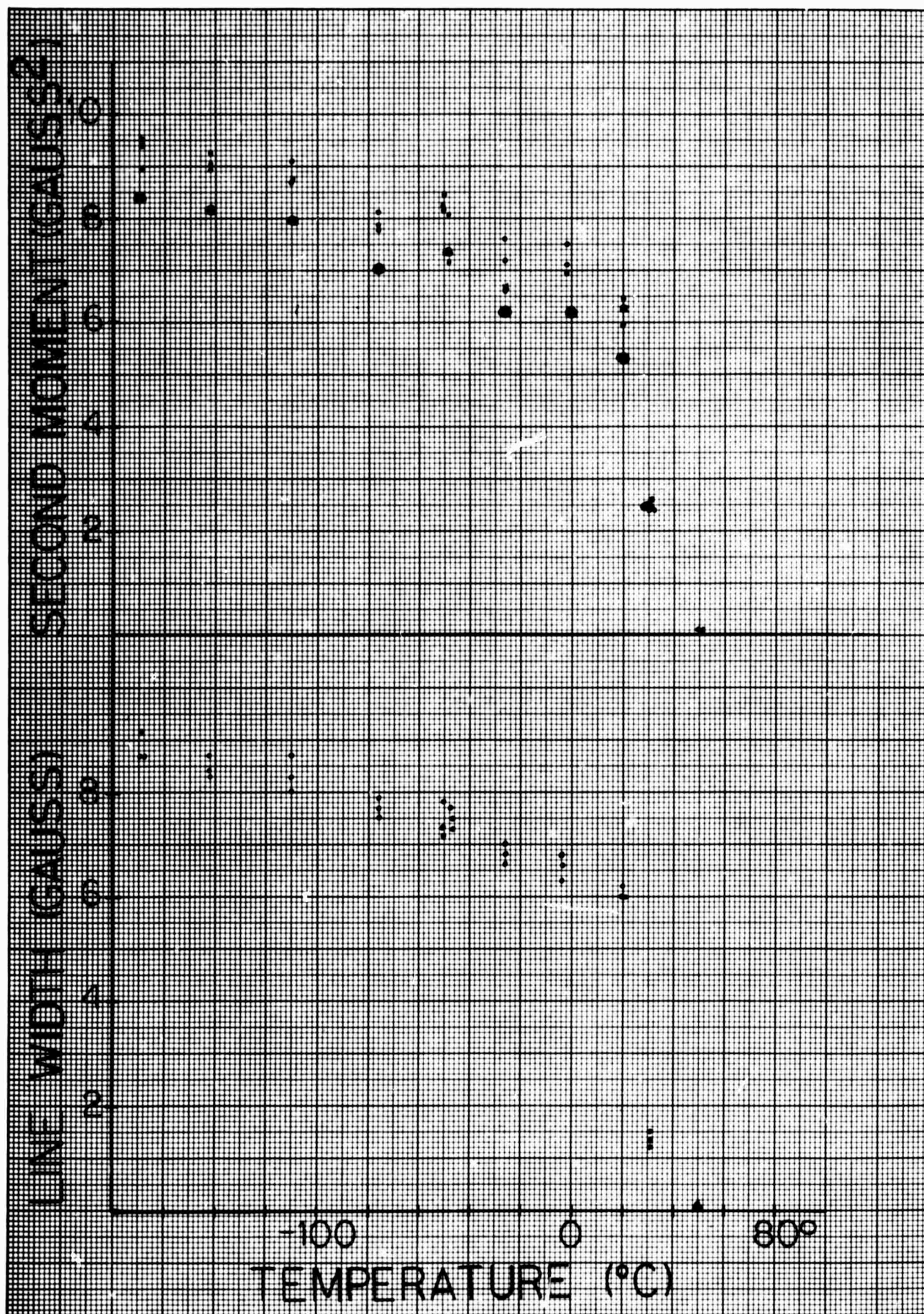
Compound I $(\text{Ph}_2\text{C}=\text{N})_2\text{SiMe}_2$



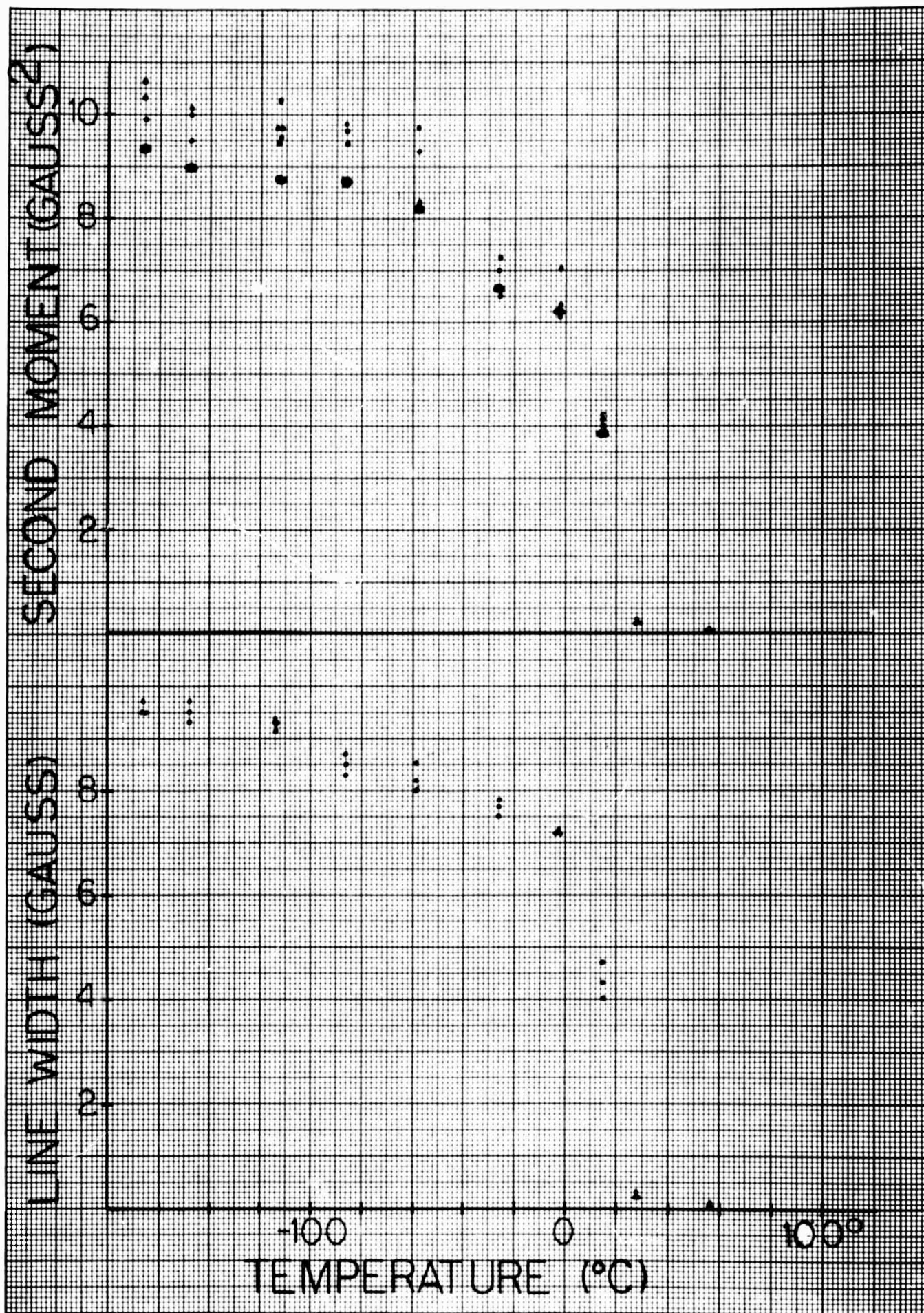
Compound II $(\text{Ph}_2\text{C}=\text{N})_3\text{SiMe}$



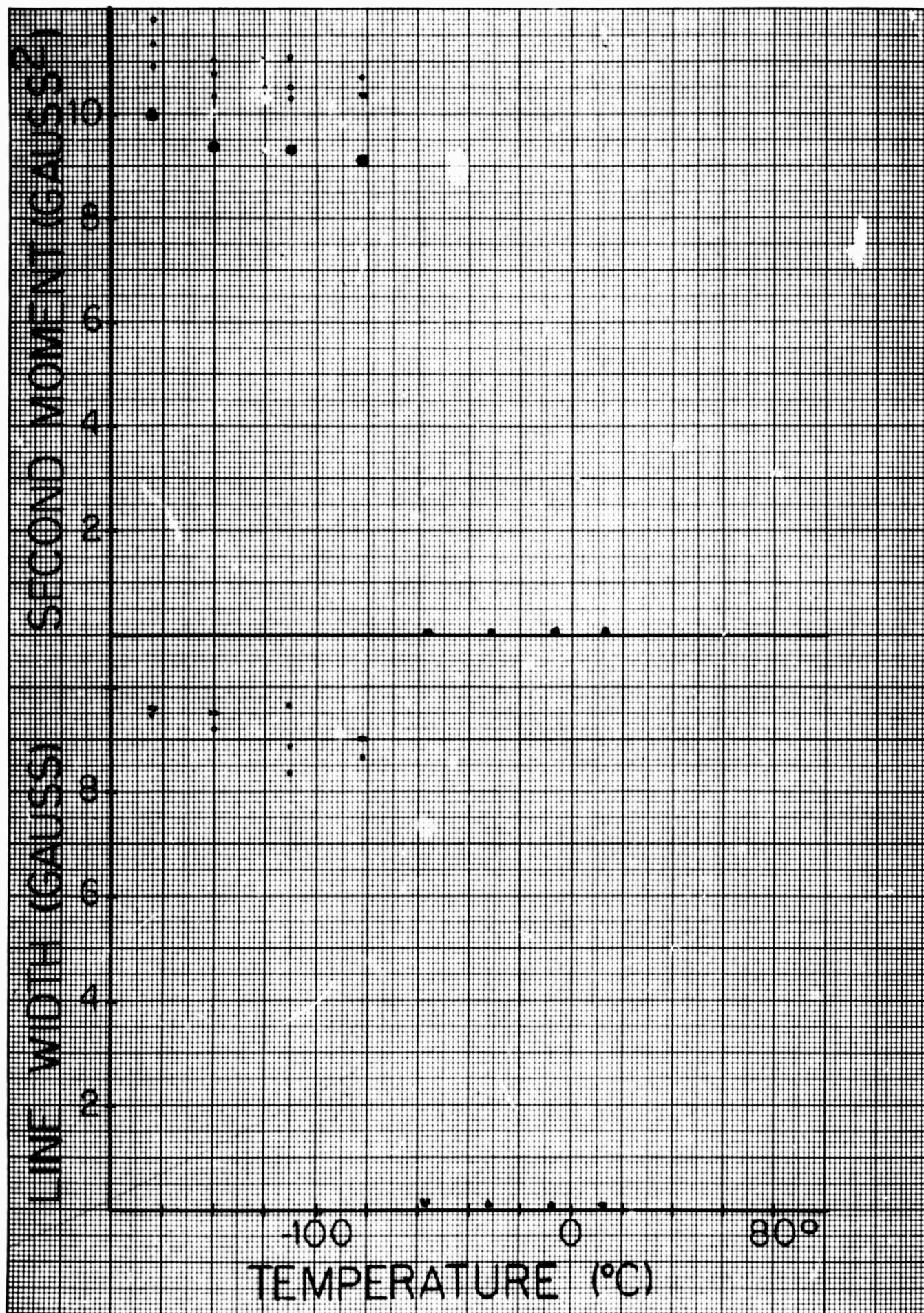
Compound III $(\text{Ph}_2\text{C}=\text{N})_2\text{SiPh}_2$



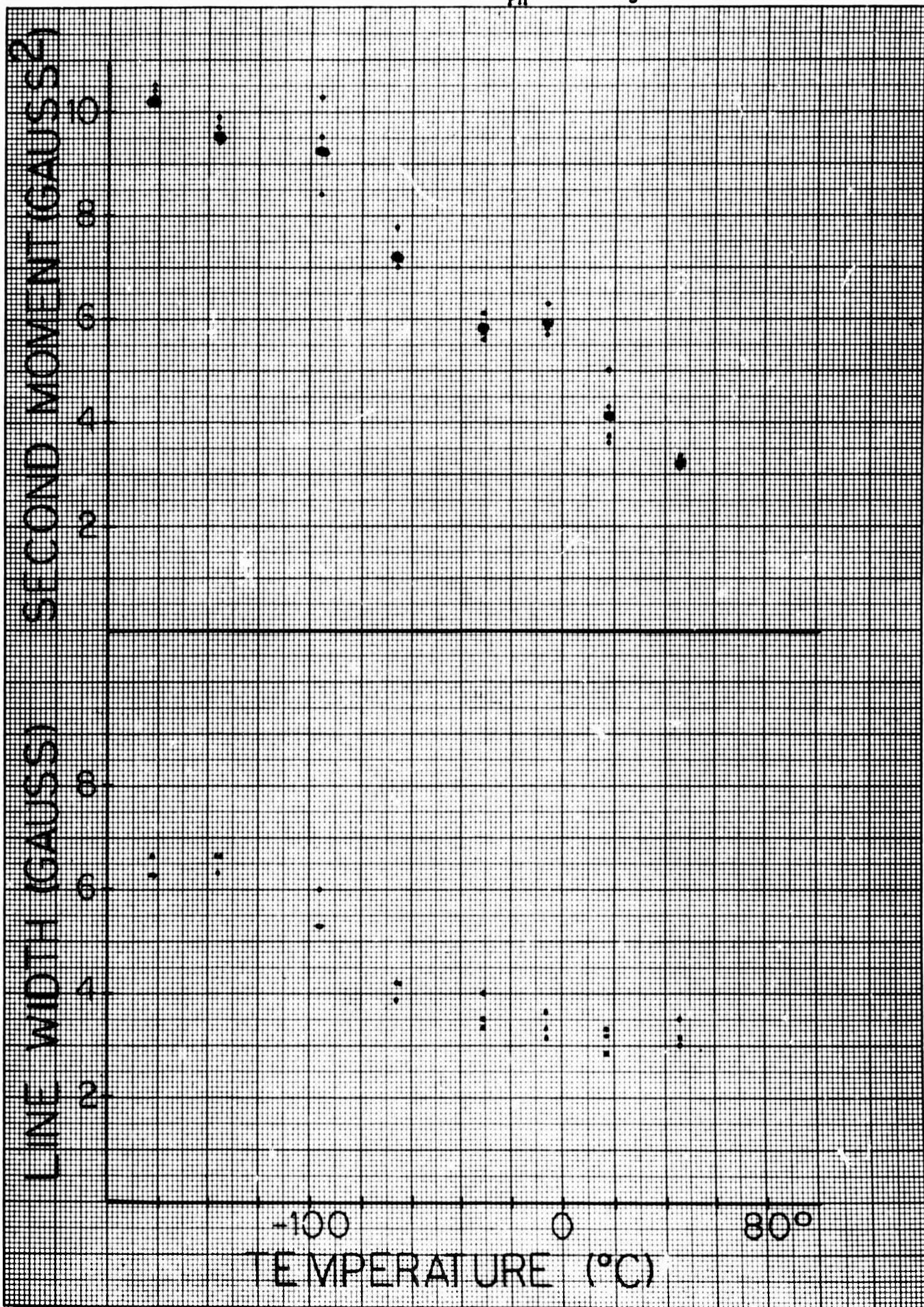
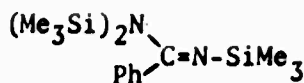
Compound IV $(\text{Ph}_2\text{C}=\text{N})_3\text{SiPh}$



Compound V $\text{Ph}_3\text{C-N=CPh}_2$



Compound VI



Theoretical calculations

Theoretical approximations of the measured line shape were calculated for compounds with less than five interacting spins. Mathematical difficulties with multispin systems limit this method to simple molecules. In cases of more complicated compounds, the theoretical calculation of second moments remains the only way of interpreting the observed broad-line NMR data. A formula derived by van Vleck⁵ is used for the calculation of the second moments of rigid configurations, and is modified for certain types of motions. Following are the formulas for the second moments of polycrystalline materials, and for different types of motion considering proton resonance and interaction of protons with nitrogen atoms:

$$\langle H_2 \rangle^2 = \frac{6}{5} I(I+1) g^2 \mu_0^2 N^{-1} \sum_{jk} r_{jk}^{-6} + \frac{4}{15} \mu_0^2 N^{-1} \sum_{jf} I_f(I_f+1) g_f^2 r_{jf}^{-6}$$

where the symbols are defined as follows:

N = number of nuclei at resonance within in the group, in which the line broadening interactions are considered to take place.

g, I = nuclear g -factor and spin for nucleus at resonance

g_f, I_f = nuclear g -factors and spins for other nuclei in the sample.

rigid configuration: $A = \langle H_2 \rangle^2 = 715.6 N^{-1} \sum_{fk} r_{fk}^{-6} + 22.15 N^{-1} \sum_{jk} r_{jk}^{-6}$

rotation around one axis: $B = \langle H_2 \rangle^2 = \frac{1}{4} \cdot A$

(axis perpendicular to projection plane of the protons)

rotation around two axes, which enclose an angle ϵ and one of which is perpendicular to the projection plane of the protons:

$$C = \langle H_2 \rangle^2 = \left(\frac{3}{2} \cos^2 \epsilon - 1/2 \right)^2 \cdot B$$

The following internuclear distances were used during the calculations:

C-Si	: 1.90Å	C _{ar} -H	: 1.084Å	C _{ar} -C _{al}	: 1.525Å
C=N	: 1.36Å	C _{al} -H	: 1.101Å	H-H _{ar} (ortho)	: 2.479Å
N-Si	: 1.74Å	C=C _{ar}	: 1.395Å	H-H _{ar} (meta)	: 4.296Å
N-H _{methyl}	: 4.03Å	H-H _{methyl}	: 1.802Å	H-H _{ar} (para)	: 4.958Å
N-H _{ar} (ortho)	: 4.08Å				

The internal interaction of nitrogen and protons in the investigated N-silyl-benzophenone imines is small because of the large N-H-distances. Therefore it can be neglected.

Application of the above-mentioned formulas and interatomic distances yielded the following second moments for isolated groups:

	monosubstituted phenyl group (Gauss ²)	methyl group (Gauss ²)
rigid	2.56	21.8
rotation around one axis	1.28 (C ₂ -type)	5.45 (C ₃ -type)
rotation around two axis	0.02 (ε = 60°)	0.604 (ε = 70.5°)

Those parts of the second moments of compounds I - VI which are due to internal motion are obtained by addition of the different contributions of protons in the methyl and phenyl groups. The assumption is made that the methyl groups start rotating earlier than the more bulky phenyl groups. Table XII shows the second moments caused by interaction of protons in the same molecule.

Three problems remain unsolved:

- (1) No reliable structure determination of benzophenone is known. Only

an older one is found in the literature⁶. Simple geometric considerations show that the distance between the ortho-ortho' protons should be only 0.77Å, if the bond angle at the ketone group is assumed to be 120° and the phenyl groups are in one plane. (This would be the most favorable case for resonance between the C=N-system and the phenyl groups.) The ortho-ortho' interproton distance is 3.04Å, if the planes of the phenyl rings include an angle of 90°. At such a distance, the interaction can be neglected as a second order contribution to the second moment. This was done.

(2) The structures of the compounds I-VI are unknown. Therefore not only an accurate calculation of intermolecular contributions to the second moments becomes impossible, but even a rough estimate. It is known that in compounds containing aromatic systems the intermolecular part of the second moments often far exceeds the internal part. To attempt a calculation on arbitrary assumptions about possible arrangements of the molecule in the crystal lattice seems to be worthless.

(3) The uncertainty about bond angles of the C=N-Si arrangement gives rise to additional questions. Angles between 180° and 120° were discussed earlier¹, and the latter value was considered the more likely. Both cases are considered in Table XII. An angle of 180° has a different effect on the rotational contribution of the benzophenone portion to the second moments of I-IV during rotations around two axes.

Table XII

Internal contribution to second moments of the compounds

	I	II	III	IV	V	VI
(all values given in [Gauss ²])						
rigid configuration	7.0	4.2	2.56	2.56	2.56	18.8
rotation around one axis	3.23	2.72				14.8 9.6 5.0
	(methyl groups only)					
	1.13	1.22	1.28	1.28	1.28	
	(phenyl groups also)					
rotation around two axes	2.11	2.29				3.63 2.27 0.91
	(methyl groups only)					
	0.155	0.073	0.482	0.218	0.09	3.24 1.87 0.51
	(C=N-Si-angle : 180°)					
	0.629	0.646	0.908	0.760		3.44 2.07 0.71
	(C=N-Si-angle : 120°)					
	(phenyl groups also rotating)					

Discussion

A comparison of the experimental results shown on the plots of line width and second moments against temperature indicates that a transition in compounds I and II occurs at a lower temperature than the transition in III and IV. Hence the earlier assumption seems to be reasonable, that the motion of methyl groups bound to silicon needs less activation energy than the motion of phenyl groups. Looking at the constitution 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. The latter contains only one phenyl ring 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 motion begins at the opposite end of the molecule.

In contrast to the silicon compounds, 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 below 3 Gauss, and also the second moment stayed over 3 Gauss. A transition is observed between -80°C and -100°C in this case.

The second moments obtained from the NMR spectra taken between -160°C and -170°C are not at all in agreement with the calculated ones for a rigid configuration. This is not surprising, because no intermolecular interaction was taken into account (as discussed in section IV). The difference between experimental and calculated second moments increases from I and II to III, IV and V. 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 temperature⁷.

On the other hand, the experimental values at higher temperatures are larger than all the calculated second moments for compound 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.

An interesting observation was made with IV, which may be worth mentioning. A narrow line (with a line width of 0.08 Gauss at -31.0°C) appeared at higher temperatures superimposed upon the broad line.

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DOCUMENT CONTROL DATA - R & D

Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified

1. ORIGINATING ACTIVITY (Corporate author) Mallinckrodt Laboratory, Dept. of Chemistry Harvard University Cambridge, Massachusetts		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
1. REPORT TITLE I. SYNTHESSES OF IRON AND COBALT COMPLEXES WITH LIGANDS CONTAINING SILICON-NITROGEN BONDS, II. INTERNAL MOTIONS OF N-ORGANOSILYL KETIMINES			
4. DESCRIPTIVE NOTES (Type of report and, inclusive dates) Interim technical report			
3. AUTHOR(S) (First name, middle initial, last name) Friedrich Wilhelm Kuepper			
6. REPORT DATE August 1968	7a. TOTAL NO. OF PAGES 39	7b. NO. OF REFS 12	
8a. CONTRACT OR GRANT NO ARPA SD-88	9a. ORIGINATOR'S REPORT NUMBER(S) Technical Report No. ARPA 35		
b. PROJECT NO	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
c.			
d.			
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11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
13. ABSTRACT <p>This report presents results on two research programs, one on inorganic synthesis and one on structural study by means of broad-line NMR, which were pursued simultaneously during the year ending August 31, 1968. The first had to do with the synthesis of compounds of the transition metals containing organosilicon groups. Organosilyl amines were used as electron donor ligands to form six new stable coordination compounds of iron and cobalt. All previous attempts (extending over the past 7 years) to do this had failed; the present success stems from a thorough study of the equilibrium considerations and the choice of a polar solvent for the reactions. The chemical behavior of the six new compounds is now being examined by Chang Kira, a graduate student in the Program.</p> <p>The second project concerned the structures and behavior of five new compounds prepared last year, all with C=N-Si linkages (plus one additional compound with C=N-C linkage, for comparison). Earlier examination of the UV absorption spectra of these compounds had shown that there is little $d\pi - p\pi$ interaction between the nitrogen and silicon, because the C=N-Si sequence is not linear but bent at an angle of 120°. It was expected that such an inflection also would hinder intramolecular motion, and that some distinctions between the several compounds would appear in their proton magnetic resonances as solids. The spectra were obtained, and calculation of line widths and second moments showed that intramolecular motion in all five organosilicon compounds was indeed hindered more than in the organic compound, and that one of the five (the only one which had an Si-N-C=N-Si structure) had a much more persistent restriction of motion with rise of temperature than the others.</p>			