

THE VIBRATIONAL SPECTRA OF VINYLMETHYLHALOSILANES  
 $\text{H}_2\text{C}=\text{CH}(\text{CH}_3)_{3-n}\text{SiX}_n$  ( $n = 1, 2$ ;  $\text{X} = \text{F}, \text{Cl}$ )\* \*\*

R.ŘEŘIČHA<sup>a</sup>, J.ŠTOKR<sup>b</sup>, M.JAKOUBKOVÁ<sup>a</sup>, P.SVOBODA<sup>a</sup> and V.CHVALOVSKÝ<sup>a</sup>

<sup>a</sup> Institute of Chemical Process Fundamentals,

Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát and

<sup>b</sup> Institute of Macromolecular Chemistry,

Czechoslovak Academy of Sciences, 162 06 Prague 6

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The infrared spectra ( $4000-200\text{ cm}^{-1}$ ) of gaseous and liquid or dissolved samples of vinyl-dimethylfluorosilane ( $\text{C}_4\text{H}_9\text{SiF}$ , *I*), vinylmethyldifluorosilane ( $\text{C}_3\text{H}_6\text{SiF}_2$ , *II*), and of the chloro-analogs ( $\text{C}_4\text{H}_9\text{SiCl}$ , *III* and  $\text{C}_3\text{H}_6\text{SiCl}_2$ , *IV*) were measured together with the laser Raman spectra of the liquids ( $1700-100\text{ cm}^{-1}$ ). The 70 eV mass spectra of *I* and *II* were also recorded. The assignment was carried out only for bands above  $500\text{ cm}^{-1}$ ; it indicated presence of rotamers.

Existence of pairs of stable rotamers with the *skew* (antiperiplanar) and *cis* (synplanar) conformations has been already predicted<sup>1</sup> for all molecules which represent the combinations of a  $sp^3$ -hybridized asymmetric top (e.g. secondary, tertiary, and quaternary carbon atoms) and a  $sp^2$ -hybridized frame (e.g. vinyl group).

As far as we know, no attempt to recognize rotamers in silicon series had been made though many substituted vinylsilanes were synthesized. For instance, the IR spectra of both liquid *III* and *IV* had been published<sup>2</sup> in figures ( $3200-400\text{ cm}^{-1}$ ), however, the assignment<sup>3</sup> was not carried out below  $900\text{ cm}^{-1}$ . The only exception had been identification<sup>4</sup> of absorptions by the Si-Cl stretching vibration ( $477$  for *III*,  $462$  and  $562\text{ cm}^{-1}$  for *IV*). The tabulated Raman spectrum without polarizations had been quoted<sup>5</sup> only for *III* but without warranty for its purity.

The aim of this work was to re-examine the published spectra of *III*, *IV* and to interpret our spectra of *I-IV* especially in the  $900-500\text{ cm}^{-1}$  region.

## EXPERIMENTAL

*I* and *II* were prepared by reaction of *III* and *IV* with  $\text{SbF}_3$  respectively, their physical constants and detailed synthesis had been published<sup>6</sup> elsewhere. Purity of *I* and *II* was checked by gas-liquid chromatography and mass spectrometry. According to these methods, the content of the parent chloro compounds was less than 0.1 mol. %. The mass spectra were measured on a LKB spectrometer, model GC-MS 9000 at 70 and 13 eV, the temperature of inlet system being  $150^\circ\text{C}$ , that of ion source  $270^\circ\text{C}$ . Ten peaks at 70 eV are collected in the decreasing order of intensities (in per cent of height of the base peak).

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*I* (m.w. = 104):  $m/e = 89$  (100), 63 (51), 47 (31), 77(21), 104 (17), 49 (9·6), 90 (8·9), 76(5·6), 62 (4·4), 91 (3·9);  $m^{++} = 44·6$  ( $89^+ \rightarrow 63^+ + 26$ ).

*II* (m.w. = 108):  $m/e = 93$  (100), 81 (55), 108 (53), 67 (28), 47 (27), 42 (21), 27 (15), 94 (7·9), 89 (7·9), 80 (7·9), 91 (7·5);  $m^{++} = 48·3$  ( $93^+ \rightarrow 67^+ + 26$ ).

The absorption spectra were measured on double-beam spectrometers Beckman IR-7 (700 to 200  $\text{cm}^{-1}$ , CsI-prism/grating optics) and Zeiss (Jena) UR-20 (4000–400  $\text{cm}^{-1}$ , prisms LiF, NaCl, KBr). Spectra of gases were taken in a 10 cm cell with KRS-5 or KBr windows. A droplet of liquid sample was introduced into the cell during flushing it with dried nitrogen. Then, both stopcocks were turned off and the sample was allowed to evaporate. *II* (b.p. 25°C) was cooled

TABLE I

Assignment of the Strongest Bands in Vinyl dimethylfluorosilane *I*, ( $\text{cm}^{-1}$ )<sup>a</sup>

Infrared		Raman		Tentative assignment
gas <sup>b</sup>	type(I)	liq.	I (dep.)	
1 933	asym. (w)	NM	NM	2 x wag. =CH <sub>2</sub>
1 603	PQR (m)	1 598	7 (0·4)	stretching C=C
1 409	PQR (s)	1 410	11 (0·5)	asym. def. SiMe <sub>2</sub> + sciss. =CH <sub>2</sub>
(1 270)	sh ↓ (?)	1 275	11 (0·4)	in-plane def. =C-H
1 265	(s)			sym. def. SiMe <sub>2</sub>
1 220	sharp (s)			in-plane def. =C-H
(1 078)	(m)			rocking =CH <sub>2</sub> ?
1 013	(s)			} twisting HC=CH
1 007	(s)			
963	PQR (s)			wagging =CH <sub>2</sub>
950	sh ↑ (?)			?
895	PQR (vs)			} stretching Si-F
(878)	(vs)			
850	PQR (vs)			} rocking SiMe <sub>2</sub>
799	PQR (vs)	794	4 (1·0)	
774	(vs)	768	1-2 (p ?)	} asym. stretch. SiC <sub>3</sub>
709	PQR (s)			
(700)	sh ↑ (?)	699	7 (0·7)	
(608)	(w)	610	100 (0·32)	sym. stretch. SiC <sub>3</sub>
522	(s)			o-o-p def. =C-H
395	PQR (s)	396	7 (p ?)	} skeletal def.
369	sh ↑ (?)	369	11 (0·5)	
275	PQR (s)	271	14 (dp ?)	
		258	11 (p ?)	
NM	NM	193	33 (0·87)	

<sup>a</sup> Meaning of abbreviations: NM = not measured, d = doublet, sh ↑ or sh ↓ = shoulder on the preceding or following band, o-o-p = out-of-plane, Me = methyl; <sup>b</sup> wave number in parentheses is for liquid or solution in CS<sub>2</sub>. The band center is given for PQR-bands.

in a glass baloon before introduction. This procedure usually offered a high concentration at which the weakest bands were recorded. Pressure in the cell was then gradually decreased by evacuation so that the absolute pressures were not known. After all measurements, moist air was introduced into the cell and the bands of hydrolytic products were identified. IR spectra of liquids were measured as capillary films between KBr plates, for *II*, moreover, a cold solution in  $\text{CS}_2$  was investigated in an incompletely filled 0.1 cm KBr cell. The instruments were calibrated with water vapour,  $\text{CO}_2$ , and 10  $\mu$  polystyrene film, spectra of *III* and *IV* also with gaseous HCl formed by their hydrolysis. The Raman spectra with polarizations were measured with He—Ne laser excitation at room temperature in the  $1700\text{--}100\text{ cm}^{-1}$  region, for *II* in a cooled cell at  $-55^\circ\text{C}$ . Accuracy of readings was  $\pm 2\text{ cm}^{-1}$ .

## RESULTS

The survey spectra of *I* and *II* are in Figs 1, 2, the assignments for *I*–*IV* are in Tables I–IV. The IR bands of hydrolytic product in gaseous and liquid *I*–*IV* are collected in Table V.

The strongest Raman lines (polarized) of vinylfluorosilanes are  $610(0.32)$  for *I*,  $641(0.40)$  for *II*, and  $692\text{ cm}^{-1}(0.28)$  for vinyltrifluorosilane<sup>7</sup>. The same trend we observed for the series of ethylmethylfluorosilanes  $\text{C}_2\text{H}_5(\text{CH}_3)_{3-n}\text{SiF}_n$  ( $n = 1, 2, 3$ )<sup>6</sup>:

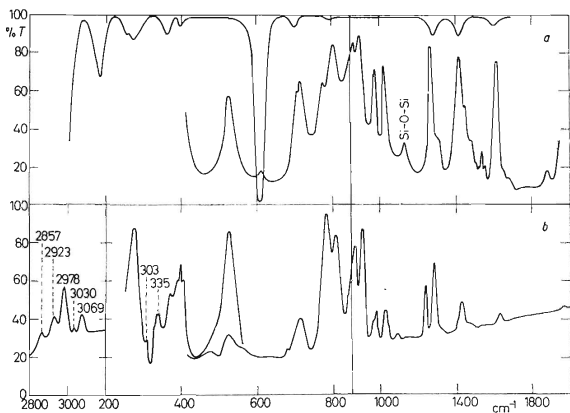


FIG. 1

The Vibrational Spectra of Vinyl dimethyl fluorosilane (*I*) in Different States (*a*, *b*)  
*a* Laser Raman spectrum (upper) and IR spectrum (lower) of liquid. *b* Infrared spectrum of gas.

600 (0.36), 625 (0.33), and  $705\text{ cm}^{-1}$  (0.34) respectively. It follows from this fact that no specific band has to be expected for the stretching vibration of the Si—C bond because all (Si—C)<sub>4-n</sub> bonds ( $n = 1, 2$ ) are vibrationally coupled. The mentioned polarized Raman lines must correspond to the totally symmetrical mode and the remaining out-of-phase Si—C stretching frequencies should be found above the respective in-phase fundamental and below  $900\text{ cm}^{-1}$ .

The rocking vibration of methyl groups attached to silicon atom ( $850\text{--}800\text{ cm}^{-1}$ )<sup>8</sup> and possible existence of rotamers, along with the above mentioned fact, can cause a rather complex pattern of IR spectra in the  $900\text{--}600\text{ cm}^{-1}$  region. This holds for all the compounds studied except gaseous *I* which has a minimal number of IR bands in this region.

*Vinyldimethylfluorosilane (I)*. For this gas, the absorptions by the vinyl group (C=C stretching, =CH<sub>2</sub> scissoring and wagging, twisting HC=CH, o-o-p and in-plane =C—H deformation) were identified without difficulty, the =CH<sub>2</sub> wagging frequency also with the aid of its first overtone at  $1933\text{ cm}^{-1}$ . The Si—F stretching mode was assigned to the strong IR band at  $895\text{ cm}^{-1}$  (cf.<sup>7,9</sup>), the equally intense

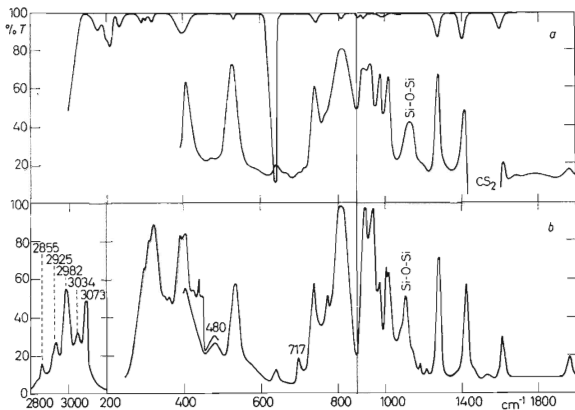


FIG. 2

The Vibrational Spectra of Vinylmethyl difluorosilane (*II*) in Different States (*a*, *b*)

*a* Laser Raman spectrum of liquid at  $-55^{\circ}\text{C}$  (upper) and IR spectrum of a cold solution in  $\text{CS}_2$  (lower). *b* Infrared spectrum of gas.

bands near 850 and 800  $\text{cm}^{-1}$  to the rocking modes of methyls in the  $\text{Si}(\text{CH}_3)_2$  group. The band corresponding to the symmetrical deformation of this grouping (near 1260, *cf.*<sup>8</sup>) could be splitted into a doublet depending on molecular symmetry. The published data<sup>5</sup> for gaseous  $(\text{CH}_3)_2\text{SiFBr}$  ( $C_s$  symmetry) show that the splitting of the 1265  $\text{cm}^{-1}$  band does not exceed 10  $\text{cm}^{-1}$ , the same result we obtained with gaseous  $(\text{CH}_3)_2\text{HSiCl}$  (*cf.*<sup>10</sup>). In the case of gaseous analog *III* no splitting was observed at all and, therefore, we ascribed the unsplit band at 1265  $\text{cm}^{-1}$  to the mentioned vibration.

TABLE II

Assignment of the Strongest Bands in Vinylmethyldifluorosilane *II*, ( $\text{cm}^{-1}$ )<sup>a</sup>

Infrared		Raman		Tentative assignment
gas <sup>b</sup>	type(I)	liq.	I (dep.)	
1 957	asym. (w)	NM	NM	2 x wag. =CH <sub>2</sub>
1 605	PQR ? (m)	1 604	10 (0.43)	stretching C=C
1 413	PQR ? (s)	1 413	15 (0.60)	asym. def. SiMe + sciss. =CH <sub>2</sub>
1 273	PQR ? (s)			sym. def. SiMe
1 218	(w)	1 280	13 (0.50)	in-plane def. =C—H
1 013	(s)			} twisting HC=CH
1 007	(s)			
970	PQR (s)			wagging =CH <sub>2</sub>
933	PQR (vs)			asym. stretch. SiF <sub>2</sub>
894	(vs)			sym. stretching SiF <sub>2</sub>
810	PQR (vs)	812	4 (0.86)	rocking SiMe
770	sh ↑ (?)			} asym. stretch. SiC <sub>2</sub>
734	PQR (s)	745	7 (0.54)	
644	(m)	641	100 (0.40)	sym. stretch. SiC <sub>2</sub>
528	(s)	532	5 (1.0)	o-o-p def. =C—H
434	PQR (m)			} skeletal def.
404	(s)	399	12 (0.83)	
392	(s)			
321	(s)	323	7 (1.0)	
315	sh ↑ (?)	302	6 (dp?)	
297	sh ↑ (?)	292	8 (p ?)	
NM	NM	237 sh ↓	9 (0.75)	} skeletal def.
NM	NM	209	19 (1.0)	
NM	NM	201	17 (p ?)	
NM	NM	177	11 (1.0)	
NM	NM	51	vs (NM)	
NM	NM	35	vs (NM)	

<sup>a,b</sup> For meanings of symbols, see Table I.

The two out-of-phase stretching modes of  $\text{SiC}_3$  grouping can then be identified as the two strong IR absorptions at 774 and 709  $\text{cm}^{-1}$ . Having not calculated the potential energy distribution, we did not try to assign the IR bands of gas below 500  $\text{cm}^{-1}$ . Under these conditions all assumed group frequencies are identified with the exception of the  $=\text{CH}_2$  rocking mode which is weak both in the IR and Raman spectra and masked by the "hydrolytic" band in liquid.

The only case when maxima of *P,R*-envelopes were resolved, is that for the  $\text{C}=\text{C}$  stretching band with the *Q*-branch at 1603  $\text{cm}^{-1}$ . The *P-R* separation was 13  $\text{cm}^{-1}$ , the maxima being 1596 and 1609  $\text{cm}^{-1}$ , respectively. With *I*, on going from gas to

TABLE III

Assignment of the Strongest Bands in Vinyltrimethylchlorosilane III, ( $\text{cm}^{-1}$ )<sup>a</sup>

Infrared		Raman			Tentative assignment
gas <sup>b</sup>	(I)	liq. <sup>c</sup> (I)	liq. <sup>d</sup>	I (dep.) <sup>d</sup>	
1 913	(vw)		NM	NM	2 x wag. $=\text{CH}_2$
1 599	(w)	1 596 (7)	1 599	16 (0.32)	stretching $\text{C}=\text{C}$
1 410	(s)	1 406 (8)	1 410	21 (0.67)	asym. def. $\text{SiMe}_2$
1 383	(m)		1 379	2 (p ?)	scissoring $=\text{CH}_2$
		1 270 (7)	1 275	24 (0.34)	in-plane def. $=\text{C}-\text{H}$
1 260	(vs)				sym. def. $\text{SiMe}_2$
1 010	(s)	1 009 (2)	1 012	4 (1.0)	twisting $\text{HC}=\text{CH}$
958	(s)				wagging $=\text{CH}_2$
844	(vs)		856	2 (?)	rocking $\text{SiMe}_2$
			837	4 (?)	
(820)	(vs)				asym. stretch. $\text{SiC}_3$
797	(vs)	791 (4)	794	7 (?)	rocking $\text{SiMe}_2$
703	(s)	715 (1)	716	15 (0.7)	asym. stretch. $\text{SiC}_3$
		698 (2)	702 <sup>d</sup>		
635	(m)	628 (7)	634	71 (0.32)	sym. stretch. $\text{SiC}_3$
			595	18 (0.2)	? impurity $\text{Si}-\text{O}-\text{Si}$
526	(s)	518 (4)	527	17 (0.45)	o-o-p def. $=\text{CH} + \text{str. SiCl}$
488	(m)	571 (8)	474	91 (0.33)	
		368 (1)	366 sh ↓	16 (0.5)	stretching $\text{Si}-\text{Cl}$
351	(s)	349 (3)	354	36 (0.3)	
240	(vs)				
NM		206 (2)	210	26 (1.0)	skeletal def.
NM			182	65 (1.0)	
NM			105	100 (?)	

<sup>a,b</sup> For meanings of symbols, see Table I; <sup>c</sup> data of Engelhardt<sup>5</sup> with Hg-excitation (4358 Å), intensity scale 0–10; <sup>d</sup> our data with laser. Additional Raman bands: 436 (4, ?), 552 (6, ?), 611 (8, ?), 658 (8.5, ?), 767 (3.5, ?), 806 (6, ?), 1000 (4, dp)  $\text{cm}^{-1}$ .

liquid, there were three remarkable changes in the IR spectra. The band at  $1220\text{ cm}^{-1}$  was shifted to about  $1270\text{ cm}^{-1}$  and it lowered its intensity, the absorption by the Si—F stretching ( $895\text{ cm}^{-1}$  in gas) appeared for liquid at  $878\text{ cm}^{-1}$ , and the bands in the  $780\text{--}700\text{ cm}^{-1}$  region interchanged their intensities.

*Vinylmethyldifluorosilane* (II). On the basis of the preceding results we assigned the bands of II. A general feature of Raman spectra of both I and II is very weak intensity of lines for the Si—F stretching vibration in comparison with corresponding absorptions in the infrared. Also noticeable is the pronounced intensity of Raman lines for the in-phase  $\text{SiC}_2$  stretching vibration caused by presence of fluorine atoms in the molecules (*cf.* vinylchlorosilanes in Table III and IV).

*Vinylchlorosilanes* III and IV. All IR bands of both gases III and IV had simple

TABLE IV  
Assignment of the Strongest Bands in Vinylmethyldichlorosilane IV, ( $\text{cm}^{-1}$ )<sup>a</sup>

Infrared		Raman <sup>c</sup>		Tentative assignment
gas <sup>b</sup>	(I)	liq.	I (dep.)	
1 953	w	NM	NM	2 x wag. =CH <sub>2</sub> stretching C=C
1 610	m	1 600	9 (0.30)	
1 410	s			asym. def. SiMe
(1 382)	m	1 405	12 (0.20)	scissoring =CH <sub>2</sub>
		1 271	15 (0.33)	in-plane def. =C—H
1 267	s			sym. def. Si—Me
1 004	s			twisting HC=CH
973	s			wagging =CH <sub>2</sub>
804	vs			rocking SiMe
(790)	vs			} asym. stretch. SiC <sub>2</sub>
754	vs	748	9 (0.45)	
678	vs	679	18 (0.36)	sym. stretch. SiC <sub>2</sub>
613	m	597	3 (p ?)	} asym. stretch. SiCl <sub>2</sub>
573	vs			
524	} <sup>d</sup> s	521	11 (0.36)	o-o-p def. =C—H
483		479 sh ↓	35 (0.26)	sym. stretch. SiCl <sub>2</sub>
467	s	461	100 (0.21)	} skeletal def.
366	w	367	28 (0.30)	
		341	27 (0.26)	
238	vs	227	34 (0.83)	
NM		201	25 (0.78)	
NM		160	71 (0.82)	

<sup>a,b</sup> For meanings of symbols, see Table I. <sup>c</sup> Additional Raman bands: doublet 546 (7, 0.6) and 558 (8, ?), 640 (2, ?)  $\text{cm}^{-1}$ .

shape with no *PQR*-structure even at higher resolutions so that our spectra generally agreed with the published figures<sup>2</sup> for the liquids. The only change was disappearance of the 820  $\text{cm}^{-1}$  band (liquid *III*) from the spectrum of gas.

The assignment for *III* and *IV* is in agreement with the published data<sup>3</sup> for liquids but ours is more complete. The re-assignments of bands to the *o-o-p* =C—H deformation are collected in Table VI. Comparing our spectra of *III* with those tabulated by Engelhardt<sup>5</sup>, we excluded his IR bands 1182 (vw), 1143 (m), 1120 (w), 752 (m), 562 (s) and also the Raman counterparts at 1148 (3) and 562 (2) as the bands of impurities.

*Note.* The two assignments<sup>7,9</sup> of the fundamental frequencies of vinyltrifluorosilane had been published but with a difference for the =CH<sub>2</sub> wagging mode. For comparison, we measured the IR spectrum of vinyltrifluorosilane in a cooled CS<sub>2</sub> solution. Complete agreement with the data of Crowder and Smyrl<sup>9</sup> was reached: the wagging

TABLE V  
Infrared Bands<sup>a</sup> of Hydrolytic Products in *I–IV* ( $\text{cm}^{-1}$ )

Compound	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>
Gas	1 120–1 100	1 102	1 075	1 100–1 080
Liquid	1 120–1 100	1 130	1 070–1 050	1 130–1 050

<sup>a</sup> Always broad.

TABLE VI  
The Infrared Band of the =C—H *o-o-p* Deformation in Gaseous H<sub>2</sub>C=CH(CH<sub>3</sub>)<sub>*n*-3</sub> SiX<sub>*n*</sub> ( $\text{cm}^{-1}$ )<sup>a</sup>

X / <i>n</i>	1	2	3
F	522	528	542 <sup>b</sup>
Cl	526 <sup>c</sup>	524 <sup>d</sup>	520 <sup>e</sup>

<sup>a</sup> Medium to weak intensity. For vinylsilanes generally<sup>13</sup> in the 580–515  $\text{cm}^{-1}$  region; <sup>b</sup> ref. 7; <sup>c</sup> earlier value<sup>3</sup> 627  $\text{cm}^{-1}$ . Now, presumably obscured by the Si—Cl band; <sup>d</sup> earlier value<sup>3</sup> 602 or 677  $\text{cm}^{-1}$ ; <sup>e</sup> for liquid<sup>4</sup>. Earlier value for liquid was<sup>14</sup> near 611  $\text{cm}^{-1}$ . Not observed in gas<sup>14</sup>.



frequency is that at  $986\text{ cm}^{-1}$ , and not at  $731\text{ cm}^{-1}$  as Durig and Hellams<sup>7</sup> have proposed. In some gaseous samples of vinyltrifluorosilane we also observed a C-type band near  $730\text{ cm}^{-1}$  but of variable intensity, hence we ascribed it to impurities.

## DISCUSSION

It is clear from the second column of Table I that nine bands have an apparent *PQR*-structure. However, eight of these have *P*- and *R*-branches as unresolved shoulders on the prominent central part. The same holds for *II* (Table II). We assume that the blurred *PQR*-structures of bands are also an indirect evidence for presence of rotamers. Their mixtures in vinyl derivatives generally complicated any interpretation of vibrational spectra. For instance, Potts and Nyquist<sup>11</sup> have presented a non-linear correlation between the  $=\text{CH}_2$  wagging frequency of vinyl groups and the Hammett  $\sigma_R$ -constant of their substituents. Using their data and our two wagging frequencies for gaseous *I* and *II* we get for  $(\text{CH}_3)_2\text{SiF}$  and  $\text{CH}_3\text{SiF}_2$  groupings the  $\sigma_R$ -constants about  $(+0.20)$  and  $(+0.26)$ , respectively. It is clear that the  $\sigma_R$ -values obtained must involve a kind of sterical contribution of the substituent which cannot be separated. The plot<sup>11</sup> had been constructed from thirteen compounds, five of which can represent liquid mixtures of rotamers ( $-\text{OCH}_3$ ,  $-\text{OC}_2\text{H}_5$ ,  $-\text{CH}_2\text{Cl}$ ,  $-\text{COOC}_2\text{H}_5$ ,  $-\text{COCH}_3$ ). This possibility had not been known in that time. Now, however, it may serve as an explanation of the non-linearity of the plot and of "a rather bad scatter of the points for the higher values of  $(\sigma_p - \sigma')$ " regardless the sign as it has been pointed out<sup>11</sup>.

In the earlier papers<sup>6,12</sup>, a dependence of molecular dipole moments of liquid  $\text{H}_2\text{C}=\text{CH}(\text{CH}_3)_{3-n}\text{SiX}_n$  ( $n = 0, 1, 2, 3$ ;  $\text{X} = \text{F}, \text{Cl}$ ) on  $n$  has been presented. The experimental points in plots were not "well-behaving" and we believe that presence of rotamers is the main cause for it.

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## REFERENCES

1. Karabatsos G. J., Fenoglio D. J.: *Topics in Stereochem.* 5, 167 (1970).
2. Mironov V. F., Čumajevskij N. A.: *Dokl. Akad. Nauk SSSR* 146, 1117 (1962).
3. Knižek J., Horák M., Chvalovský V.: *This Journal* 28, 3079 (1963).
4. Obreimov I. V., Čumajevskij N. A.: *Ž. Strukt. Chim.* 5, 59 (1964).
5. Engelhardt G.: *Thesis*. Technische Universität, Dresden 1963.
6. Svoboda P., Vaisarová V., Chvalovský V.: *This Journal* 37, 2258 (1972).
7. Durig J. R., Hellams K. L.: *J. Mol. Struct.* 6, 315 (1970).
8. Smith L. A.: *Spectrochim. Acta* 16, 87 (1960).
9. Crowder G. A., Smyrl N.: *J. Chem. Phys.* 53, 4102 (1970).
10. Kriegsmann H., Engelhardt G.: *Z. Anorg. Allgem. Chem.* 310, 320 (1961).

11. Potts W. J., Nyquist R. A.: *Spectrochim. Acta* 15, 679 (1959).
12. Svoboda P., Chvalovský V.: *This Journal* 37, 2253 (1972).
13. Smith L. A.: *Spectrochim. Acta* 19, 849 (1963).
14. Shull E. R., Thursack R. A., Birdsall C. M.: *J. Chem. Phys.* 24, 147 (1956).

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