

ORGANOSILICON COMPOUNDS. LXXIV.*

THE EFFECT OF STRUCTURE
ON THE BASICITY OF SOME DIMETHYLAMINOSILANES

Z. PAČL**, M. JAKOUBKOVÁ, Z. PAPOUŠKOVÁ and V. CHVALOVSKÝ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, Prague-Suchdol*

Received June 9th, 1970

A series of dimethylaminosilanes of the types $(C_2H_5)_4-nSi[N(CH_3)_2]_n$ and $RR'_3-nSi[N(CH_3)_2]_n$ ($n = 1-4$, $R = CH_2=CH-$, $p-(CH_3)_2HSiC_6H_5-$, H and $R' = CH_3-$ and C_2H_5-) was prepared. The relative basicities of the nitrogen atoms in these compounds were determined by infrared spectroscopy. The $\Delta\nu$ values of the hydrogen bonds of deuteriochloroform (pyrrole) with the dimethylaminosilanes studied are interpreted in terms of a ($p \rightarrow d$) π nature of the silicon-nitrogen bond and of the inductive and steric effects of the substituents.

A relatively low basicity of the nitrogen atom bonded to silicon have been already observed¹⁻⁵. This phenomenon is usually accounted for by a ($p \rightarrow d$) π nature of the silicon-nitrogen bond. On the other hand, little interest has been shown for a systematic measurement of such model series of alkylaminosilanes that would enable to examine how the nature of the silicon-nitrogen bond is affected by different number of the nitrogen atoms bonded to the same silicon atom and further whether and how the nature of this bond depends on other substituents capable of π -interaction with the $3d$ orbitals of the silicon. In this work the relative basicities of the nitrogen of these compounds, expressed as frequency shifts, $\Delta\nu$, of the IR absorption bands of stretching vibrations of the X-H bonds due to the formation of the hydrogen bonds $X-H \cdots N$, were employed as the main criterion of the nature of the silicon-nitrogen bond.

With this aim we prepared the following series of (dimethylamino)silanes: ethyl-(dimethylamino)silanes $(C_2H_5)_{4-n}Si[N(CH_3)_2]_n$ ($n = 1-4$) and $(C_2H_5)_{3-n}HSi.[N(CH_3)_2]_n$ ($n = 1-3$), vinylmethyl(dimethylamino)silanes $(CH_2=CH)(CH_3)_{3-n}.Si[N(CH_3)_2]_n$ ($n = 1-3$) and $[(p\text{-dimethylsilyl})phenyl]methyl(dimethylamino)-$

* Part LXXIII: This Journal 36, 1587 (1971).

** Present address: Research Institute of Inorganic Chemistry, Ústí n/L.

silanes $[p\text{-}(\text{CH}_3)_2\text{HSi}]_n\text{C}_6\text{H}_4\text{Si}(\text{CH}_3)_{3-n}[\text{N}(\text{CH}_3)_2]_n$ ($n = 1-3$, along with phenyltris(dimethylamino)silane and tris(dimethylamino)chlorosilane.

EXPERIMENTAL

Compounds Used

The *dimethylaminosilanes* were prepared by reaction of appropriate chlorosilanes with dimethylamine (Fluka AG, Buchs SG) in cyclohexane (Lachema, Brno). Most of the chlorosilanes used were commercial products (VCHZ Synthesia, Lučební závody, Kolín), which were redistilled before use. Their purity was checked by glc and IR spectroscopy, and by determining their indices of refraction.

Triethylchlorosilane and *diethylchlorosilane* were prepared by a common Grignard synthesis^{6,7} from diethyldichlorosilane and ethyldichlorosilane, resp., and ethylmagnesium bromide in 22% and 34% yield, resp. *Vinyl dimethylchlorosilane* was prepared by the reaction of dimethyldichlorosilane with vinylmagnesium chloride in tetrahydrofuran. The product was slightly contaminated with divinyl dimethylsilane⁸ (approx. 5%). The [*p*-dimethylsilyl]phenylmethylchlorosilanes were prepared earlier⁹ in our laboratory. The compounds were distilled before use. Physical properties of the organochlorosilanes prepared are summarized in Table I. Their purity was checked by glc and the IR and NMR spectroscopy. Due to a low stability of the silicon-nitrogen bond, all the operations were carried out under the atmosphere of dry nitrogen.

The *ethyl(dimethyl)aminosilanes* were prepared by reactions of appropriate ethylchlorosilanes with an excess of dimethylamine in cyclohexane. Except ethyltris(dimethylamino)silane, the procedure described below was followed.

Diethylbis(dimethylamino)silane. A 500 ml three-necked flask equipped with a mechanical stirrer, a dropping funnel and a dry ice-ethanol cooler was charged with a solution of 50 ml (34 g, 0.75 mol) of dimethylamine in 150 ml of cyclohexane. Then a solution of 20 g (0.13 mol) of diethyldichlorosilane in 50 ml of cyclohexane was added with stirring over a period of 1–2 hours. The reaction mixture was then boiled for 4–5 hours, using the dry ice-ethanol cooler in order to avoid a loss of the excess dimethylamine, till the temperature of the reaction mixture reached the boiling point of cyclohexane. When cooled down, the liquid phase was separated from the precipitated dimethylamine hydrochloride by filtration through a glass frit using an overpressure of dry nitrogen. The cyclohexane was distilled off and the raw product fractionated under reduced pressure, yielding the pure diethyl(dimethylamino)silane, b.p. 62–62.5°C/15 Torr.

Ethyltris(dimethylamino)silane was prepared similarly. However, the obtained product contained 4.3% of chlorine. Eighteen grams of the compound, together with 15 ml of dimethylamine and 50 ml of cyclohexane were therefore heated in a sealed glass ampule for 5 hours to 100°C. After dimethylamine hydrochloride and cyclohexane had been removed, the fractionation of the residue afforded the pure ethyltris(dimethylamino)silane, b.p. 66–67°C/12 Torr.

The *vinyl(dimethylamino)silanes* were prepared similarly as the ethyl(dimethylamino)silanes, by reaction of the appropriate vinylchlorosilanes with an excess of dimethylamine in cyclohexane^{12,13}.

The [*p*-dimethylsilyl]phenylmethyl(dimethylamino)silanes, too, were obtained in the same way⁹. The reaction of (*p*-dimethylsilyl)phenyltrichlorosilane with dimethylamine carried out in the usual way gave a product containing 12% of chlorine. A mixture of 9 g of this compound, 15 ml of dimethylamine and 30 ml of cyclohexane was therefore heated in a sealed glass ampule for

6 hours to 100°C. After the usual work-up, the desired (*p*-dimethylsilyl)phenyltris(dimethylamino)silane was obtained by fractional distillation.

Phenyltris(dimethylamino)silane. A 500 ml three-necked flask, equipped with a mechanical stirrer, a dropping funnel and a dry ice-ethanol condenser was charged with a solution of 50 ml (34 g, 0.75 mol) of dimethylamine in 150 ml of cyclohexane. Then a solution of 20 g (0.09 mol) of phenyltrichlorosilane in 50 ml of cyclohexane was dropwise added with stirring over an 1-hour period. After the usual work-up the fractional distillation of the residue yielded a product, b.p. 103–104°C, containing 11.92% of chlorine (*i.e.* predominantly phenylchlorobis(dimethylamino)silane). A mixture of 15 g of this compound, 25 ml of dimethylamine and 40 ml of cyclohexane was heated in a sealed glass ampule for 6 hours to 100°C. The usual work-up afforded the pure phenyltris(dimethylamino)silane.

Tetrakis(dimethylamino)silane. The reaction of 18 g (0.11 mol) of silicon tetrachloride with 60 ml (41 g, 0.91 mol) of dimethylamine in cyclohexane yielded a compound boiling 74–75°C/20 Torr which was assigned as chlorotris(dimethylamino)silane on the basis of its elemental analysis and infrared spectrum. A mixture of 12 g of this compound, 30 ml of dimethylamine and 30 ml of benzene was heated in a sealed glass ampule for 6 hours⁶. After the usual work-up the fractionation of the residue afforded 6 g of the pure tetrakis(dimethylamino)silane, b.p. 72–73°C/12 Torr.

The physical constants and elemental analyses of the dimethylaminosilanes prepared are summarized in Table II.

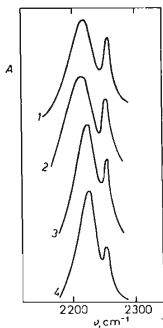


FIG. 1

Infrared Spectra of Hydrogen Bonds between Deuteriochloroform and $(C_2H_5)_{4-n} \cdot Si[N(CH_3)_2]_n$.

1 $n = 1$, 2 $n = 2$, 3 $n = 3$, 4 $n = 4$.

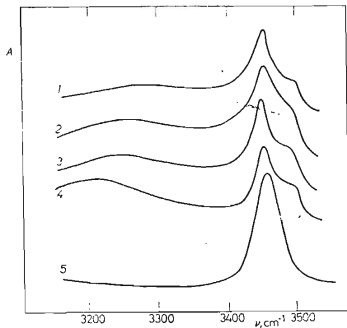


FIG. 2

Infrared Spectra of Hydrogen Bonds between Pyrrole and Some Proton Acceptors

1 $C_6H_5Si[N(CH_3)_2]_3$, 2 $p-(CH_3)_2HSi \cdot C_6H_4Si[N(CH_3)_2]_3$, 3 $p-(CH_3)_2HSiC_6H_4 \cdot SiCH_3[N(CH_3)_2]_2$, 4 $p-(CH_3)_2HSiC_6H_4 \cdot Si(CH_3)_2N(CH_3)_2$, 5 benzene.

TABLE I
Physical Constants of Chlorosilanes Used

Compound	B.p., °C/Torr		n_D^{20}		M.w.	Calculated/Found % Cl	Yield %
	found	lit.	found	lit.			
Vinyldimethylchlorosilane	82	82-82.5 ¹⁰	1.4162	1.4141 ^{10 a}	120.7	29.39 28.54	—
Diethyldichlorosilane	129-130	129 ¹¹	1.4319	1.4309 ¹¹	157.1	45.13 45.29	—
Triethylchlorosilane	146-146.5	146 ⁶	1.4315	1.4299 ^{6 a}	150.7	23.52 22.87	22
Diethylchlorosilane	98-99	99.7 ⁷	1.4169	1.4133 ^{7 a}	122.7	28.90 28.13	34
[<i>p</i> -(Dimethylsilyl)phenyl]-dimethyl- chlorosilane	107-108/7	—	—	—	228.88	15.49 15.62	30
[<i>p</i> -(Dimethylsilyl)phenyl]-methyl- dichlorosilane	100/2	—	—	—	249.31	28.45 28.50	28
[<i>p</i> -(Dimethylsilyl)phenyl]-tri- chlorosilane	102/2	—	—	—	269.73	39.44 39.53	29

^a n_D^{25} .

TABLE II
Physical Constants of (Dimethylamino)silanes

Compound	B.P., °C (Torr)		n_D^{20}		d_4^{20}		M.W.	Calculated/Found			Yield %
	found	lit.	found	lit.	found	lit.		% C	% H	% N	
Ethyltris(dimethylamino)silane	66-7 (12)	—	1.4399	—	0.876	—	189.3	50.71 50.68	12.25 12.11	22.22 21.9	70
Diethylbis(dimethylamino)silane	62-62.5 (15)	—	1.4362	—	0.837	—	174.3	55.08 55.49	12.72 12.67	16.08 16.2	84
Triethyl(dimethylamino)silane	56-56.5 (17)	166-7 ¹⁵	1.4311	1.4325 ¹⁵	0.801	0.8044 ^{15 a}	159.2	60.30 60.83	13.28 13.14	8.79 8.7	86
Tris(dimethylamino)silane	62 (45)	142 ¹⁶	1.4271	—	0.833	0.850 ^{16 a}	161.3	44.67 44.42	11.87 11.62	26.05 24.8	84
Ethylbis(dimethylamino)silane	48-49 (30)	—	1.4232	—	0.819	—	146.3	49.25 49.31	12.40 12.55	19.25 19.3	81
Diethyl(dimethylamino)silane	57 (60)	—	1.4183	—	0.778	—	131.3	54.89 55.37	13.05 13.34	10.67 10.3	67
Vinyl(dimethyl(dimethylamino)silane	52 (100)	107 ¹²	1.4177	1.4170 ^{12 b}	0.763	0.773 ^{12 c}	129.2	55.73 56.80	11.70 11.35	10.84 10.1	58
Vinylmethylbis(dimethylamino)silane	66 (47)	83 ¹² (100)	1.4351	1.4337 ^{12 b}	0.828	0.824 ^{12 c}	158.2	53.10 53.06	11.47 11.24	17.71 17.6	71
Vinyltris(dimethylamino)silane	69 (18)	82 ¹² (30)	1.4467	1.4447 ^{12 b}	0.866 ^d	0.863 ^{12 c}	187.2	51.28 50.93	11.31 11.50	22.45 22.3	75
Tetraakis(dimethylamino)silane	72-73 (12)	72-75 ¹⁴ (13)	1.4427	1.4436 ¹⁴	0.882 ^d	0.885 ¹⁴	204.3	47.01 46.65	11.84 11.69	27.41 27.2	55

Tris(dimethylamino)- chlorosilane	81 (30)	62-63 ¹⁴ (12)	1-4410	1-4417 ¹⁴	0-971 ^d	0-975 ¹⁴	195-7	36-85 37-44	9-28 9-45	21-49 21-95	64
Phenyltris(dimethylamino)- silane	121 (8)	—	1-5039	—	0-966 ^d	—	237-3	60-68 60-43	9-77 9-82	17-71 17-5	69
[(<i>p</i> -Dimethylsilyl)phenyl]di- methyl(dimethylamino)silane	100 (0-5)	—	1-5012	—	0-903 ^d	—	237-3	60-68 60-35	9-77 9-57	5-90 5-8	75
[(<i>p</i> -Dimethylsilyl)phenyl]me- thylbis(dimethylamino)silane	106 (0-5)	—	1-5034	—	0-920 ^d	—	266-3	58-58 58-24	9-84 9-76	10-54 10-7	82
[(Dimethylsilyl)phenyl]tris- (dimethylamino)silane	120 (0-3)	—	1-5058	—	0-938 ^d	—	295-4	56-87 56-75	10-23 10-41	14-23 13-9	68

^a d_{4}^{20} , ^b n_{D}^{25} , ^c d_{4}^{25} , ^d d_{4}^{23} .

Infrared Spectra

The infrared spectra of the above compounds were taken on a Zeiss Model UR 20 spectrophotometer (Zeiss, Jena) using the usual procedure described elsewhere¹⁷.

RESULTS

The infrared spectra of the studied compounds (*cf.*¹⁸) were interpreted in accordance with the literature^{19,20}. The spectra of all the (dimethylamino)silanes exhibit a strong absorption in the 760–700 cm^{-1} region, which is characteristic for the stretching vibrations of the Si—N and Si—C bonds. As with the (dimethylamino)germanes¹⁷ these compounds, too, cannot be measured in carbon disulphide, because of the insertion of the solvent into the silicon–nitrogen bond. The selection of suitable proton donors is limited by similar factors¹⁷ as in the case of the analogical germanium compounds. The values of frequency shifts, $\Delta\nu$, originated from the interaction of deuteriochloroform (pyrrole) with the aminosilanes studied are given in Table III. The form of the spectra of the hydrogen bonds of deuteriochloroform with the series of ethyl(dimethylamino)silanes is represented in Fig. 1. The spectra of the phenyl(dimethylamino)silanes interacting with pyrrole are shown in Fig. 2. The absorption band at 3430 cm^{-1} originates from the interaction of the hydrogen of the N—H bond of pyrrole with the aromatic nucleus, as evidenced by the spectrum of the system benzene–pyrrole in this region (curve 5).

TABLE III
Values of $\Delta\nu(\text{cm}^{-1})$ for Some Dimethylaminosilanes

Protonacceptor	2.5M- CDCl_3 0.3M-pyrrole	
$(\text{C}_2\text{H}_5)_3\text{SiN}(\text{CH}_3)_2$	40	257
$(\text{C}_2\text{H}_5)_2\text{Si}[\text{N}(\text{CH}_3)_2]_2$	38	264
$(\text{C}_2\text{H}_5)\text{Si}[\text{N}(\text{CH}_3)_2]_3$	32	236
$\text{Si}[\text{N}(\text{CH}_3)_2]_4$	28	215
$(\text{CH}_2=\text{CH})(\text{CH}_3)_2\text{SiN}(\text{CH}_3)_2$	40	274
$(\text{CH}_2=\text{CH})\text{CH}_3\text{Si}[\text{N}(\text{CH}_3)_2]_2$	31	249
$(\text{CH}_2=\text{CH})\text{Si}[\text{N}(\text{CH}_3)_2]_3$	23	217
$(\text{C}_2\text{H}_5)_2\text{HSi}[\text{N}(\text{CH}_3)_2]$	34	239
$(\text{C}_2\text{H}_5)\text{HSi}[\text{N}(\text{CH}_3)_2]_2$	29	245
$\text{HSi}[\text{N}(\text{CH}_3)_2]_3$	25	212
$p\text{-(CH}_3)_2\text{HSiC}_6\text{H}_4\text{Si}(\text{CH}_3)_2[\text{N}(\text{CH}_3)_2]$	36	283
$p\text{-(CH}_3)_2\text{HSiC}_6\text{H}_4\text{Si}(\text{CH}_3)[\text{N}(\text{CH}_3)_2]_2$	27	246
$p\text{-(CH}_3)_2\text{HSiC}_6\text{H}_4\text{Si}[\text{N}(\text{CH}_3)_2]_3$	24	242
$\text{C}_6\text{H}_5\text{Si}[\text{N}(\text{CH}_3)_2]_3$	21	211

DISCUSSION

Fig. 3 shows the dependence of $\Delta\nu$ (i.e. the difference in wavenumbers of absorption bands of the C—D stretching vibrations of the associated and of the non-associated deuteriochloroform in the system N,N-dimethylamino group—deuteriochloroform) on the number of the dimethylamino groups for all the series of (N,N-dimethylamino)silanes and for the series of ethyl (N,N-dimethylamino)germanes¹⁷. The mono(N,N-dimethylamino)silanes studied are analogous to tertiary aliphatic amines. Of these amines only interaction of triethylamine with deuteriochloroform was studied ($\Delta\nu$ (C—D) was reported²¹ to be here 84 cm^{-1} ; we found the value of 80 cm^{-1}). Even though there are no data available on the frequency shifts for tertiary amines of isosteric structure with the compounds studied by us, we can state that the $\Delta\nu$ value found by us for triethyl(dimethylamino)silane (40 cm^{-1}) is lower than it could be expected on the basis of the electropositive character of silicon. A similar situation arises also for some other series; so, for instance, the relative basicities of ethers measured in similar fashion are higher than those of alkoxysilanes. The lowest basicities are displayed by siloxanes^{3,22,23}. As with the silicon—oxygen bond, here also this finding can be accounted for by a ($p \rightarrow d$) π nature of the silicon—nitrogen bond, which considerably reduces the electron-donor ability of the nitrogen of this bond. A somewhat lower $\Delta\nu$ value for triethyl(dimethylamino)germane¹⁷ (70 cm^{-1}) is indicative of ($p \rightarrow d$) π bonding also in the germanium—nitrogen bond, which is however substantially less developed, as compared with the silicon—nitrogen bond.

If we compare the basicity of triethyl(dimethylamino)silane (I) with that of vinyl-dimethyl(dimethylamino)silane(II), it can be expected that the substitution of ethyl groups for methyl ones should bring about a decrease in the basicity of the latter

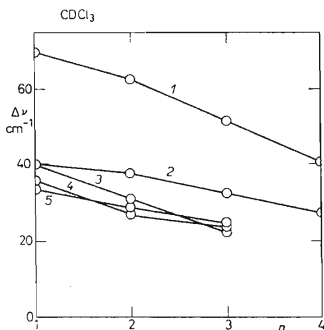


FIG. 3

Dependence of $\Delta\nu$ on the Number of Dimethylamino Groups n in the Molecule of

- 1 $(\text{C}_2\text{H}_5)_4 - n \text{Ge}[\text{N}(\text{CH}_3)_2]_n$, 2 $(\text{C}_2\text{H}_5)_4 - n \cdot \text{Si}[\text{N}(\text{CH}_3)_2]_n$, 3 $(\text{CH}_2=\text{CH})(\text{CH}_3)_{3-n}\text{Si} \cdot [\text{N}(\text{CH}_3)_2]_n$, 4 $[p\text{-(CH}_3)_2\text{HSi}]\text{C}_6\text{H}_4\text{Si} \cdot (\text{CH}_3)_{3-n}[\text{N}(\text{CH}_3)_2]_n$, 5 $(\text{C}_2\text{H}_5)_3 - n \text{HSi} \cdot [\text{N}(\text{CH}_3)_2]_n$.

compound, as a result of the lower +I effect of the methyl group. Also the vinyl group should act, due to its electronegative nature, in similar way. However, this is not the case; the $\Delta\nu$ values for both compounds are practically identical. This fact may be accounted for by assuming that the nitrogen atom of vinyl(dimethylamino)silane is sterically more accessible, as compared with that of derivative *I*, this effect compensating the lower electropositive inductive effect of methyl groups. With the increasing number of dimethylamino groups and the decreasing number of methyl groups, the steric advantage of vinyl group becomes less significant, the electron-acceptor character of vinyl group becoming predominant factor. As a result, vinyltris(dimethylamino)silane displays lower basicity than isosteric ethyltris(dimethylamino)silane.

On the other hand, on the basis of our results, the basicity of [*p*-dimethylsilyl]phenyl(dimethylamino)silane seems to be lower than that of its aliphatic analogue. This may be due to the electron-withdrawing character and steric effect of bulky (*p*-dimethylsilyl)phenyl group, which both reduce the accessibility of the nitrogen atom.

We found the following order of the relative basicity of tris(dimethylamino)silanes towards deuteriochloroform: $C_2H_5Si[N(CH_3)_2]_3 > HSi[N(CH_3)_2]_3 > [p-(CH_3)_2 \cdot HSi]C_6H_4Si[N(CH_3)_2]_3 > CH_2=CH-Si[N(CH_3)_2]_3 > C_6H_5Si[N(CH_3)_2]_3 > Si[N(CH_3)_2]_3Cl$. This sequence can be best explained in terms of electronic effects of substituents. The most marked effect is exerted by a strongly electronegative chlorine in the last compounds, the basicity of which is so low that only a broadening of the band of the C—D stretching vibration of nonassociated deuteriochloroform is observed (2255 cm^{-1}).

In all of the series of (dimethylamino)silanes as well as in the series of ethyl(dimethylamino)germanes the basicity of the compounds decreases with the increasing number of dimethylamino groups (or with the decreasing number of the ethyl to metal or of the methyl-to-metal bonds) in their molecule. This decrease is likely caused by the -I effect of dimethylamino groups (or by the +I effect of ethyl or methyl groups), similarly as in the case of alkylalkoxysilanes and their carbon and germanium analogues^{23,24}. If the number of dimethylamino groups attached to the central atom is increasing, in particular following the two factors are of special importance.

The first one is the fact that a (*p* → *d*) π bonding capacity of silicon (germanium) is being saturated with increasing number of the electron-donor nitrogen atoms bonded to the central atom²⁵. Consequently, the extent of (*p* → *d*) π bonding in each silicon–nitrogen bond decreases with its increasing number in the molecule. This effect alone should lead to increase in basicity as the number of dimethylamino groups increases. However, the opposing effect of a gradual lowering of electron density on the central atom and on the nitrogen atoms with increasing number of alkyl groups (exhibiting +I effect) and upon the introduction of additional di-

methylamino groups (exhibiting $-I$ effect) appears to be more important, since the net result is a gradual decrease in basicity. From comparison of the slopes of the curves representing the dependence of the basicity on substitution number for the ethyl(dimethylamino)silanes and the ethyl(dimethylamino)germanes (Fig. 3) it is evident that this curve is steeper for the germanium derivatives; this is in accordance with the concept of lower tendency of germanium to $(p \rightarrow d)$ π bond formation with nitrogen, compared to silicon. As the number of dimethylamino groups attached to silicon increases, the extent of $(p \rightarrow d)$ π interaction of each nitrogen with silicon becomes less important and thus the basicity of tetrakis(dimethylamino)germane differs from that of tetrakis(dimethylamino)silane much less than in the case of corresponding mono(dimethylamino) derivatives.

REFERENCES

1. Jarvie A. W., Lewis D.: *J. Chem. Soc.* 1963, 4758.
2. Abel E. W., Armitage D. A., Wiley G. R.: *Trans. Faraday Soc.* 60, 1257 (1964).
3. Abel E. W., Armitage D. A., Brady D. B.: *Trans. Faraday Soc.* 62, 3459 (1966).
4. Plazanet J., Metras F., Marchand A., Valade J.: *Bull. Soc. Chim. France* 1967, 1920.
5. Jakoubková M., Chvalovský V.: *This Journal* 33, 3062 (1968).
6. Curran B. C., Witucki R. M., McCusker P. A.: *J. Am. Chem. Soc.* 72, 4471 (1950).
7. Mac Kenzie C. A., Mills A. P., Scott J. M.: *J. Am. Chem. Soc.* 72, 2032 (1950).
8. Svoboda P.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1969.
9. Mareš F., Plzák Z., Chvalovský V.: *This Journal*, in press.
10. Curry J. W.: *J. Am. Chem. Soc.* 78, 1686 (1956).
11. Sommer L. H., Bailey D. L., Whitmore F. C.: *J. Am. Chem. Soc.* 70, 2869 (1948).
12. Stober M. R., Michael K. W., Speier J. L.: *J. Org. Chem.* 32, 2740 (1967).
13. Schraml J., Pacl Z., Chvalovský V.: *This Journal* 36, 1578 (1971).
14. Breederveld H., Waterman H. I.: *Research* 5, 537 (1952).
15. Andrianov K. A., Golubcov S. A., Semenova E. A.: *Izv. Akad. Nauk SSSR, Otděl. Chim. Nauk* 1958, 47.
16. Aylett B. J., Peterson L. K.: *J. Chem. Soc.* 1964, 3429.
17. Pacl Z., Jakoubková M., Řeřicha R., Chvalovský V.: *This Journal*, in press.
18. Pacl Z.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1970.
19. Bürger H., Sawodny W.: *Spectrochim. Acta* 23A, 2827 (1967).
20. Bürger H., Sawodny W.: *Spectrochim. Acta* 23A, 2841 (1967).
21. Huggins C. M., Pimentel G. C.: *J. Chem. Phys.* 23, 896 (1955).
22. Horák M., Bažant V., Chvalovský V.: *This Journal* 25, 2822 (1960).
23. West R., Whatley L. S., Lake K. J.: *J. Am. Chem. Soc.* 83, 761 (1961).
24. Ulbricht K., Jakoubková M., Chvalovský V.: *This Journal* 33, 1963 (1968).
25. Jaffé H. H.: *J. Phys. Chem.* 58, 185 (1954).

Translated by J. Hetflejš.