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CHROMATOGRAPHY OF ORGANOMETALLIC AND ORGANOMETAL-LOIDAL DERIVATIVES OF AMINO ALCOHOLS

II. GAS CHROMATOGRAPHIC EVIDENCE FOR TRANSANNULAR BONDS IN SOLUTES

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SUMMARY

The applicability of gas chromatography to the resolution of boratranes and germatranes on polar and non-polar stationary phases at 200–250°C has been demonstrated. A remarkably high retention reported earlier for silatranes is also exhibited by boratranes, germatranes and stannatranes. The effects of modification of the atrane framework and of introduction of substituents on retention parameters indicate that the association of atrane molecules with the stationary phase molecules is essentially controlled by the oxygen atoms of the atranes. The difference between experimental and theoretical values of retention indices has been correlated with some physical and chemical properties of transannular bonds, and can be used as a criterion of the presence of such a bond in solute molecules under gas–liquid chromatographic conditions.

INTRODUCTION

We have reported previously[1] that silatranes possess sufficient volatility and thermal stability to be resolved by gas–liquid chromatography (GLC). The extremely high values of the retention indices (I) and ΔI found for silatranes could not be predicted on the basis of the components of their structures. The observed effects are believed to be due to the presence of transannular $N \rightarrow Si$ bonds. Association of silatranes with the stationary phase is determined by the oxygen atoms of the silatrane ring, as evidenced by the effects of substituents on retention parameters.

To extend our previous investigations we have now studied the chromatographic properties of Si- and C-substituted silatranes, homosilatranes, Ge- and C-substituted germatranes, homogermatranes, 1-(trimethylsilylmethyl)stannatrane, boratrane and its analogues.

EXPERIMENTAL

The retention indices were measured under the same conditions and using the same columns as described previously[1]. As the chromatographic behaviour of the silatranes studied earlier was found to be determined only by the overall polarity of the stationary phase and not by the presence of particular functional groups on it, the present study was restricted to the measurements of I values on columns A (Apiezon L) and C (OV-225). The samples were injected as 1–10% solutions in acetone or benzene, or 0.1–1% solutions in dimethylformamide. Preliminary investigations have shown that germatranes and stannatranes, like silatranes, can be chromatographed at 200–250°C. Conversion of dissolved samples into the vapour phase can be achieved by using injection port temperatures of 270–300°C. Boratranes are characterized by significantly higher melting points and lower volatilities and require an injection port temperature of 380°C. Unlike silatranes and germatranes, boratranes gave wide and asymmetrical peaks resulting in greater errors in the I measurements. Despite the high temperatures used, symmetrical peaks could be obtained only with C-methyl-substituted boratranes whose melting points are lower. Attempts to chromatograph the appropriate molybdenum and vanadium derivatives met with no success and we could not establish whether this was due to their extremely low volatilities or to chemical interaction with the sorbent.

The general procedures for the synthesis of the compounds used can be found in refs. 2 and 3, the synthesis of 19, 20, 26, 27 and 55 (Table I) is described in ref. 4 and compounds 14–17, 24, 34, 38, 40 and 56–60 were prepared by alcoholysis of organotrialkoxysilanes, $R'Si(OR'')_3$, and organotrialkoxygermanes, $R'Ge(OR'')_3$, respectively, using the corresponding amino alcohols. Compounds 18, 21, 22 and 28 were obtained by hydrosilylation of 1-vinylsilatrane (II). Stannatrane (61) was kindly provided by Dr. V. Shiryaev (Moscow).
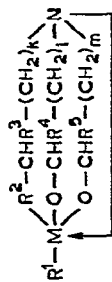
RESULTS AND DISCUSSION

The retention parameters of the compounds studied are listed in Table I along with some previously obtained data[1] presented for the sake of comparison. Even a cursory glance at the data reveals that the retention indices have much higher values than one would expect, taking into account the number of carbon atoms in the molecules and the presence of only one tertiary amino group and three ether groups. The contribution of the transannular $N \rightarrow M$ bond to I can be estimated from the difference between experimental and calculated values, the latter being found according to:
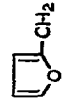
$$\delta I_{N \rightarrow M} = I_{\text{exptl.}} - I_{\text{calc.}} \qquad (1)$$

$\delta I_{N \rightarrow M}$ values are also given in Table I. The values for complex organic compounds are only a rough approximation because of the interactions between the various parts of the solute molecule. Therefore a discrepancy of even 100 units between estimated and experimental values should be considered normal. However, the silatranes studied earlier gave differences of 300–600 I units and 600–1200 I units on the non-polar and polar stationary phase, respectively. The $\delta I_{N \rightarrow M}$ values for bora-
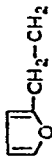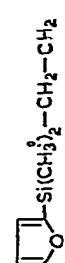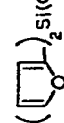
TABLE I

RETENTION PARAMETERS OF DERIVATIVES WITH THE GENERAL FORMULA:

$$R^1-M \underset{O-CHR^5-(CH_2)_m}{\overset{R^2-CHR^3-(CH_2)_k}{\diagdown \! O-CHR^4-(CH_2)_l \! \diagup}} N$$

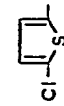| No.	M	k	l	m	R¹	R²	R³	R⁴	R⁵	Stationary phase			$\delta I_{N \to M}$	
										A	C		A	C
										I	I	ΔI	A	C
1	B	1	1	1	—	O	H	H	H	1745	3041	1296	780	1620
2	B	1	1	1	—	O	CH₃	H	H	1716	2952	1236	720	1510
3	B	1	1	1	—	O	CH₃	CH₃	H	1672	2837	1165	660	1430
										1730*	2938*	1208*		
4	B	1	1	1	ſ	O	CH₃	CH₃	CH₃	1632	2726	1094	580	1300
										1694	2836	1142		
5	B	2	1	1	—	O	H	H	H	1770	3104	1334	710	1580
6	B	2	2	1	—	O	H	H	H	1854	2984	1130	690	1360
7	B	2	2	2	—	O	H	H	H	1844	2808	964	580	1090
8	Si	1	1	1	H	O	H	H	H	1487	2597	1110	520	1180
9	Si	1	1	1	CH₃	O	H	H	H	1387	2142	755	300	600
10	Si	1	1	1	C₆H₅	O	H	H	H	2242	3171	929	590	870
11	Si	1	1	1	CH₂=CH	O	H	H	H	1522	2463	941	350	810
12	Si	1	1	1	p-Cl-C₆H₄	O	H	H	H	2343	3547	1201	500	980
13	Si	1	1	1	α-C₁₀H₇	O	H	H	H	2718	4125	1407	600	1250
14	Si	1	1	1	[furyl ring]	O	H	H	H	1996	3317	1324	530	1190
15	Si	1	1	1	[furyl ring]	O	H	H	H	1980	3029	1139	420	910
16	Si	1	1	1	[furyl–CH₂ ring]	O	H	H	H	1963	3097	1134	390	870

TABLE I *(continued)*

No.	M	k	l	m	R¹	R²	R³	R⁴	R⁵	Stationary phase				$\delta I_{N\to M}$	
										A	C			A	C
										I	I	I'	ΔI		
17	Si	1	1	1	furanyl–CH₂–CH₂	O	H	H	H	2020	2953	933	350	620
18	Si	1	1	1	$(C_2H_5)_3Si$–CH₂–CH₂	O	H	H	H	2179	2824	645	360	550
19	Si	1	1	1	furanyl–$Si(CH_3)_2$–CH₂–CH₂	O	H	H	H	2132	2988	856	660	510
20	Si	1	1	1	(furanyl)₂$Si(CH_3)$–CH₂–CH₂	O	H	H	H	2473	3537	1064	150	350
21	Si	1	1	1	(furanyl)₃Si–CH₂–CH₂	O	H	H	H	2778	4068	1290	60	270
22	Si	1	1	1	furanyl–$Si(CH_3)_2$CH₂–CH₂	O	H	H	H	2032	3002	970	110	420
23	Si	1	1	1	methylthiophene	O	H	H	H	2158	3440	1282	490	960
24	Si	1	1	1	thiophene	O	H	H	H	2149	3320	1171	480	900
25	Si	1	1	1	Cl–thiophene	O	H	H	H	2386	3918	1532	670	1440
26	Si	1	1	1	thiophenyl–$Si(CH_3)_2$–CH₂–CH₂	O	H	H	H	2396	3327	931	280	460
27	Si	1	1	1	(thiophenyl)₂$Si(CH_3)$–CH₂–CH₂	O	H	H	H	2946	4136	1190	230	470
28	Si	1	1	1	$(C_6H_5)_2Si(CH_3)CH_2CH_3$	O	H	H	H	2931	4052	1121	250	520
29	Si	1	1	1	H	O	CH₃	CH₃	CH₃	1569	2764	1195	490	1280
										1618	2869	1251		
30	Si	1	1	1	CH₃	O	CH₃	H	H	1380	2077	697	270	550

No.	El.	n	n	n	Substituent	X	R	R	R	1357 / 1381	2004 / 2041	647 / 660	220	440
31	Si	1	1	1	CH₃	O	CH₃	CH₃	H	1357 1381	2004 2041	647 660		
44	Si	2	1	1	CH₂=CH	O	H	H	H	1567	2199	632	310	430
45	Si	2	1	1	Cl-CH₂	O	H	H	H	1826	2722	896	470	760
46	Si	2	1	1	C₆H₅	O	H	H	H	2082	2945	863	340	540
47	Si	2	1	1	p-Br-C₆H₄	O	H	H	H	2383	3339	956	340	520
48	Si	2	1	1	p-Cl-C₆H₄	O	H	H	H	2260	3212	952	320	540
49	Si	2	1	1	CH₂=CH	O	CH₃	CH₃	CH₃	1542	2071	529	200	260
50	Si	2	1	1	C₆H₅	O	CH₃	CH₃	CH₃	2025	2766	741	200	330
51	Si	2	1	1	p-Br-C₆H₅	O	CH₃	CH₃	2244	3140	796 3166	220 822	290	330
52	Si	2	1	1	p-Cl-C₆H₅	O	CH₃	CH₃	CH₃	2253	3004	751	230	310
53	Ge	1	1	1	C₆H₅	O	H	H	H	1274	3487	1213	580	1140
54	Ge	1	1	1	α-C₁₀H₇	O	H	H	H	2833	4264	1431	670	1330
55	Ge	1	1	1	(thiophene)	O	H	H	H	2299	3606	1307	510	1140
56	Ge	1	1	1	C₆H₅	O	CH₃	CH₃	CH₃	2097	3070	973	300	680
32	Si	1	1	1	CH₃	O	CH₃	CH₃	CH₃	2124 1365*	3104 1928 1965	980 563* 600*	180	350
33	Si	1	1	1	CH₃	O	H	H	H	2171	2889	718	500	570
34	Si	1	1	1	CH₃	O	C₆H₅	C₆H₅	H	2779*	3544 3570 3621	765* 791* 842*	500	460
35	Si	1	1	1	C₆H₅	O	H	H	H	2075	3155	1080	380	840
36	Si	1	1	1	C₆H₅	O	CH₃	CH₃	H	2038	3052	1031	320	720
37	Si	1	1	1	C₆H₅	O	CH₃	CH₃	CH₃	2067* 1991 2022	3082* 2945 2980	1015* 954 958	230	580
38	Si	1	1	1	C₆H₅	O	C₆H₅	C₆H₅	H	3253	4595	1342	390	700
39	Si	1	1	1	CH₂=CH	O	H	H	H	2353	3185	832	580	715
40	Si	1	1	1	CH₂=CH	O	C₆H₅	C₆H₅	H	2916*	3849* 3876*	933* 960*	540	590
41	Si	1	1	1	CH₃	CH₂	H	H	H	1425	1909	484	330	450
42	Si	1	1	1	C₆H₅	CH₂	H	H	H	2089	2888	799	420	650
43	Si	2	1	1	CH₃	O	H	H	H	1537	2103	566	380	480
57	Ge	1	1	1	C₆H₅	O	C₆H₅	C₆H₅	H	2816	4116	1300	570	1140
58	Ge	1	1	1	C₆H₅	O	C₆H₅	H	H	3339	4793	1454	430	840
59	Ge	2	1	1	C₆H₅	O	H	H	H	2298	3364	1066	510	910
60	Ge	2	1	1	α-C₁₀H₇	O	H	H	H	2839	4110	1271	580	1080
61	Sn	2	1	1	(CH₃)₃Si-CH₂	O	H	H	H	1689	2695	1006	320	820

* Overlapping of diastereomer peaks resulted in measurement error of about 10 units.

tranes and germatranes are of the same order of magnitude. A comparison of I values of silatranes with those of analogous boratranes showed that the latter are eluted later than the former. The difference in the chromatographic properties of silatranes and boratranes is determined by the nature of the substituents at the carbon atoms. It is largest for unsubstituted compounds and smallest for trimethyl-substituted derivatives. Boratranes are also characterized by large ΔI values. Comparison of retention values found for germanium and silicon derivatives indicates stronger interaction of germatranes with the sorbent. Stannatrane (61) on Apiezon has $\delta I_{N \to M}$ values comparable with silatrane (18), whereas on OV-225 the former has higher values. Since it is impossible to obtain boratranes with substituents at the boron atom, their full comparison with sila- and germatranes was not feasible. Nevertheless, estimation of the average contribution of the N → M fragment to retention gave the sequence B ≫ Ge ≈ Si, which coincides with the order found from nuclear magnetic resonance (NMR) data: $[O = V > O = Mo(OH)] > B \gg CH_3Si \approx CH_3Ge$[5]. This is also supported by our failure to perform chromatographic resolution of derivatives Mo and V.

It had been found earlier that $\delta I_{N \to M}$ in silatranes is correlated with the effective electronegativity of the substituents at the silicon atom. The same is apparently valid for other atranes: the values of $\delta I_{N \to M}$ of Si- and Ge-phenyl-substituted compounds exceed by 200–290 units the corresponding values of methyl-substituted derivatives.

ΔI and $\delta I_{N \to Si}$ values diminish with elongation of the silicon and carbon chain connecting the electron-acceptor substituent with the carbon of the silatrane ring. For the chain consisting of three atoms, $\delta I_{N \to Si}$ approaches the values characteristic of *n*-alkylsilatranes (Fig. 1).
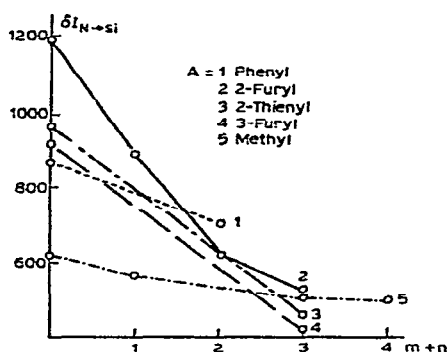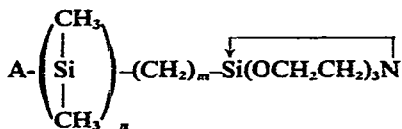

Fig. 1. Dependence of $\delta I_{N \to Si}$ on $m + n$ values in the series of compounds:

$$A-\left(\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}\right)_n -(CH_2)_m-Si(OCH_2CH_2)_3N$$

Introduction of methyl or phenyl substituents into the atrane framework usually leads to lower $\delta I_{N \to M}$ values, the decrease apparently being independent of R^1 and $k + l + m$ (Table II). Similar changes are observed for the chemical shifts in ^{29}Si NMR spectra upon R^3 introduction: when $R^1 = C_6H_5$, the resonances shift to

higher fields, and show almost no dependence on the nature of R^3. An increase in $\delta I_{N \to M}$ upon R^3, R^4, R^5 introduction was observed only for silatranes with $R^1 = H$. The decreases in $\delta I_{N \to M}$ following the introduction of substituents were more pronounced and with increasing number of substituents its values approach $\delta I_{N \to Si}$.

The melting point of silatranes has also been found to drop with increasing number of methyl groups in the rings[2]. However, the dipole moments decrease when $R^1 = CH_3$ and somewhat increase when $R^1 = C_6H_5$ (ref. 6). Hence it appears that changes in $\delta I_{N \to Si}$ values do not follow the changes in polarity, the values decreasing even when the dipole moments increase. This indicates that silatrane retention is determined by the steric accessibility of the oxygen atoms rather than by the high polarity of these molecules. This conclusion is consistent with the suggestion that the oxygen atoms of silatranes participate in hydrogen bonding with chloroform[7]. Substitution of oxygen for a methylene group in the silatrane ring results in a substantial drop in $\delta I_{N \to Si}$ values (by 150 and 220 units, respectively, when $R^1 = CH_3$ and C_6H_5).

Analogues of atranes with a six-membered ring (homosilatranes, homogermatranes) are characterized by lower dipole moment values and greater $N \to M$ bond lengths. $\delta I_{N \to M}$ values diminish with increasing number of six-membered rings in the molecule (Fig. 2). If we assume that the changes of $\delta I_{N \to M}$ alterations are at least roughly similar for boron, silicon and germanium derivatives, the germatranes and particularly silatranes with two and three six-membered cycles would be expected to have very low $\delta I_{N \to M}$ values as a result of their comparatively weak $N \to M$ bonds. This is supported by the failure to synthesize these compounds.
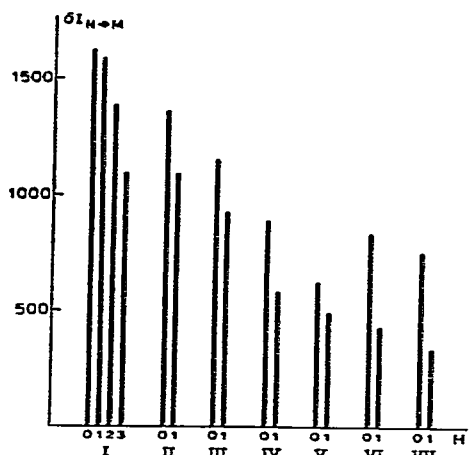

Fig. 2. Dependence of $\delta I_{N \to M}$ on the number of six-membered rings (H). I, M=B; II, M=Ge, $R^1 = \alpha$-$C_{10}H_7$; III, M=Ge, $R^1 = C_6H_5$; IV, M=Si, $R^1 = C_6H_5$; V, M=Si, $R^1 = CH_3$; VI, M=Si, $R^1 = CH = CH_2$; VII, M=Si, $R^1 = C_6H_5$, $R^3 = R^4 = CH_3$.

The experimental values of dipole moments for silatranes are considerably (by 3–6 D) greater than the values calculated using a vector scheme. These findings provide further support for the existence of a transannular bond. The difference between the experimental and estimated dipole moment values μ [2], is correlated with the $\delta I_{N \to M}$ values (Fig. 3). It can be seen that $\delta I_{N \to M}$ values close to zero, i.e., when a transannular bond is absent, correspond to $\Delta \mu$ values ≈ 2–2.5 D.

TABLE II

EFFECTS OF SUBSTITUENTS IN THE ATRANE FRAMEWORK ON $\delta I_{N \to M}$ VALUES

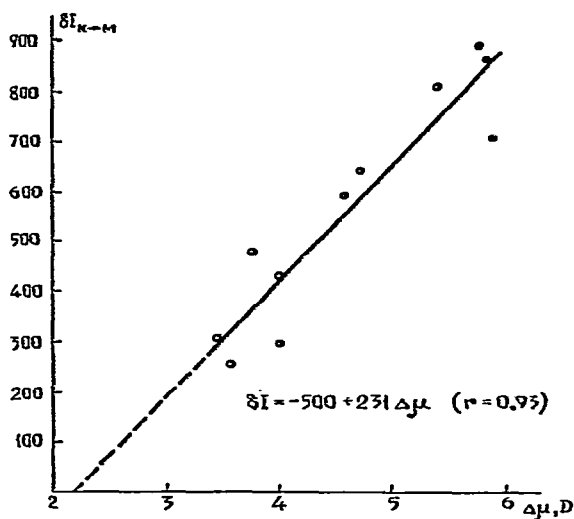| M	$k+l+m$	R^I	Substituent in atrane framework	$\delta I_{N \to M}$ Number of substituents				Mean change of $\delta I_{N \to M}$ values following introduction of a single substituent
				0	1	2	3	
B	3	—	CH$_3$	1620	1510	1430	1300	−107
Si	3	CH$_3$	CH$_3$	600	550	440	350	−83
Si	3	H	CH$_3$	1180			1280	+33
Si	3	C$_6$H$_5$	CH$_3$	870			580	−97
Si	4	CH$_2$=CH	CH$_3$	430		260		−85
Si	4	C$_6$H$_5$	CH$_3$	540		330		−105
Si	4	p-Br-C$_6$H$_4$	CH$_3$	520		290		−115
Si	4	p-Cl-C$_6$H$_4$	CH$_3$	540		310		−115
Ge	3	C$_6$H$_5$	CH$_3$	1140			680	−153
Si	3	CH$_3$	C$_6$H$_5$	600	570	460		−70
Si	3	C$_6$H$_5$	C$_6$H$_5$	870		700		−85
Si	3	CH$_2$=CH	C$_6$H$_5$	810		590		−110
Ge	3	C$_6$H$_5$	C$_6$H$_5$	1140	1140	870		−150

Fig. 3. Dependence of $\delta I_{N \to M}$ on the difference between calculated and experimental values of dipole moments ($\Delta\mu$).
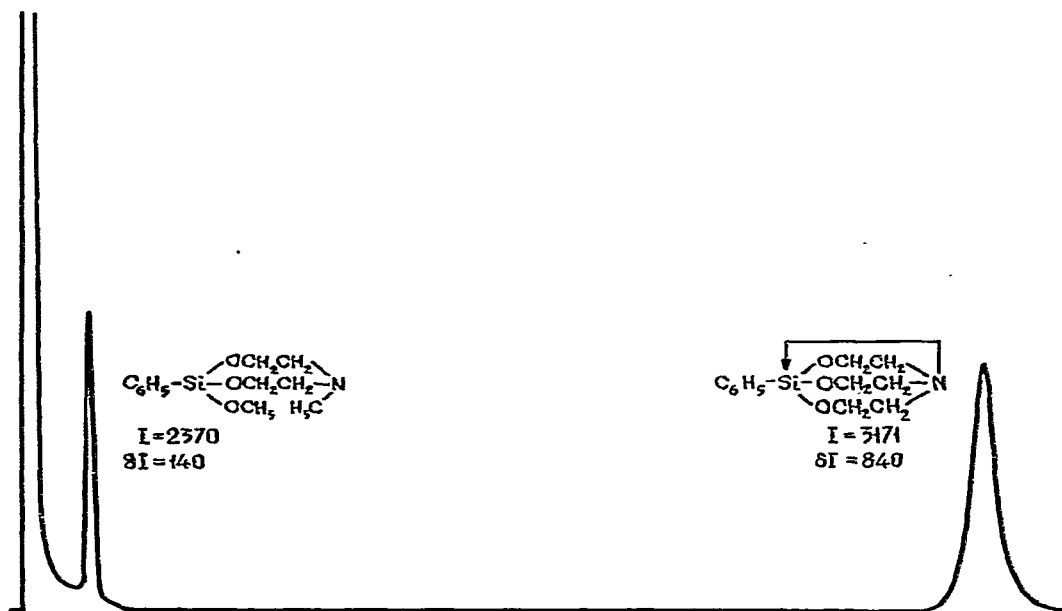

Fig. 4. Chromatogram of di- and triethanolamine derivatives on OV-225 at 200°C.

Another parameter indicative of a transannular bond is the N → M distance. The compounds with similar substituents at silicon exhibit decreasing $\delta I_{N \to M}$ values with increasing distances between the atoms:

		$\delta I_{N \to Si}$	r (Å)
(a)	1-Ethylsilatrane	570	2.21
(b)	1-Methyl-2-carbasilatrane	450	2.34
(c)	1-Phenylsilatrane	870	2.13
(d)	1-Phenyl-3,7-dimethylhomosilatrane	330	2.42

Extrapolation of data for compounds a, b and c, d to values corresponding to $\delta I_{N \to Si} = 0$ shows that such hypothetical substances would have r values of about 2.7 Å. This is in accord with the fact[8] that the silicon derivative with $R^1 = [C_6H_5(CH_3)_2P]_2Pt(Cl)$ has a N → Si distance of 2.89 Å and no transannular bond.

Diethanolamine derivatives similar to atranes are characterized by more labile N→Si bonds. The absence of this bond is quite feasible at the high temperatures of the chromatographic column. Fig. 4 shows a chromatogram of two compounds containing similar structural fragments but differing as to the presence of a N → Si bond. The retention volumes of the two substances differ significantly, and the $\delta I_{N \to Si}$ value of the diethanolamine derivative is considerably lower than that of the corresponding silatrane. Consequently, the accumulated data on the relationship between $\delta I_{N \to M}$ and the structure of amino alcohol derivatives, as well as the physico-chemical characteristics of transannular N → M bonds, enable us to regard this parameter as an indication of the presence of a transannular bond in amino alcohol derivatives under GLC conditions.

REFERENCES

1 V. D. Shatz, V. A. Belikov, G. I. Zelchan, I. I. Solomennikova and E. Lukevics, *J. Chromatogr.*, 174 (1979) 83.
2 M. G. Voronkov and V. M. Dyakov, *Silatranes* (in Russian), Nauka, Novosibirsk, 1978.
3 I. I. Solomennikova, G. I. Zelchan and E. Ya. Lukevics, *Khim. Geterotsikl. Soedin.*, (1977) 1299.
4 E. Ya. Lukevics, S. K. Germane, O. A. Pudova and N. B. Erchak, *Khim.-Farm. Zh.*, 13, No. 10 (1979) 52.
5 V. A. Pestunovich, M. G. Voronkov, G. I. Zelchan, A. F. Lapsinya, E. Ya. Lukevics and L. I. Libert, *Khim. Geterotsikl. Soedin.*, (1970) 348.
6 I. S. Yankovska, I. I. Solomennikova, I. B. Mazheika, G. I. Zelchan and E. Ya. Lukevics, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, (1975) 366.
7 B. A. Chetverikova, V. A. Kogan, G. I. Zelchan, O. A. Osipov and M. G. Voronkov, *Zh.Obshch. Khim.*, 40 (1970) 1282.
8 C. Eaborn, K. J. Odell, A. Pidcock and G. R. Scollary, *J. Chem. Soc., Chem. Commun.*, (1976) 317.