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CHROMATOGRAPHY OF ORGANOMETALLIC AND ORGANOMETALLOIDAL DERIVATIVES OF AMINO ALCOHOLS

III. DIALKANOLAMINE DERIVATIVES

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SUMMARY

The retention behaviour of 25 derivatives of dialkanolamines and diethylene glycol on Apiezon L and OV-225 has been investigated. It was found that organosilicon derivatives have no transannular N → Si bond under gas–liquid chromatographic conditions. As in the case of atranes, the chromatographic behaviour of boron-containing derivatives of diethanolamine indicates a stronger transannular interaction when compared with the silicon compounds. It is shown by quantum-chemical calculations that the charge distribution in derivatives of dialkanolamines is similar to that observed in atranes. This indicates that the strong solute–sorbent interaction of atranes is due mainly to a specifically favourable conformation which facilitates the attraction of oxygen atoms to alternatively charged centres on the stationary phase.

INTRODUCTION

Previous publications in this series[1,2] discussed the chromatographic properties of atranes, triethanolamine derivatives of boron, silicon, germanium and tin. The chromatographic behaviour of these compounds failed to agree with the simple additive scheme and the difference between the calculated and experimental values of retention indices ($\delta I_{N \to M}$) could be indicative of a transannular bond between the nitrogen atoms and the element in atrane existing under gas–liquid chromatographic (GLC) conditions.

Information is available that diethanolamine derivatives may or may not have such a transannular N → M bond depending on the substituent[3,4]. This bond tends to be less strong than in the corresponding derivatives of triethanolamine. Several organosilicon derivatives of diethanolamine have been shown to occur in solution as an equilibrium of two forms, one of which has the intra-complex N → Si bond, whereas the other fails to do so[4]. It was therefore of interest to study the gas chromatographic properties of dialkanolamine derivatives on Apiezon L and OV-225, which is the subject of this paper.

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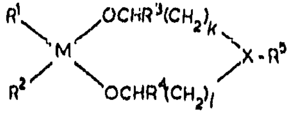
TABLE I

RETENTION PARAMETERS OF COMPOUNDS OF GENERAL FORMULA



No.	*M*	*X*	*k*	*l*	R^1	R^2	R^3	R^4	R^5	*I*		*ΔI*	$\delta I_{X \to M}$	
										*A**	*C**		*A**	*C**
1	Si	O	1	1	C_6H_5	CH_3	H	H	–	1557	2127	560	80	60
2	Si	O	1	1	C_6H_5	C_3H_7	H	H	–	1700	2232	532	20	−30
3	Si	O	1	1	C_6H_5	C_6H_5	H	H	–	2110	2838	728	50	0
4	Si	N	1	1	CH_3	CH_3	H	H	C_6H_5	1724	2247	523	150	140
5	Si	N	1	1	C_6H_5	CH_3	H	H	CH_3	1632	2160	528	60	50
6	Si	N	1	1	C_6H_5	CH_3	H	H	C_6H_5	2260	3020	760	110	130
7	Si	N	1	1	C_6H_5	CH_3O	H	H	CH_3	1701	2370	669	10	140
8	Si	N	1	1	C_6H_5	C_2H_5O	H	H	CH_3	1711	2289	578	−80	−40
9	Si	N	1	1	C_6H_5	C_2H_5O	H	H	CH_3	2182	3015	833	30	45
10	Si	N	1	1	C_6H_5	C_6H_5	H	H	CH_3	2179	2921	742	30	30
11	Si	N	1	1	C_6H_5	C_6H_5	H	H	C_2H_5	2219	2957	738	−30	−30
12	Si	N	1	1	C_6H_5	C_6H_5	H	H	C_3H_7	2277	2986	709	−70	−100
13	Si	N	1	1	C_6H_5	C_6H_5	H	H	C_4H_9	2357	3076	719	−90	−115
14	Si	N	1	1	C_6H_5	C_6H_5	H	H	$C(CH_3)_3$	2353	3066	713	0	20
15	Si	N	1	1	C_6H_5	C_6H_5	H	H	C_6H_5	2750	3649	899	20	−20
16	Si	N	1	1	C_6H_5	C_6H_5	H	H	NH_2	2179	3098	919	−80	−90
17	Si	N	1	1	p-CH_3-C_6H_4	p-CH_3-C_6H_4	H	H	CH_3	2350	3081	731	0	−10
18	Si	N	1	1	C_6H_5	CH_3	CH_3	H	CH_3	1609	2089	480	0	−40
19	Si	N	1	1	C_6H_5	C_6H_5	CH_3	H	CH_3	2148	2842	694	−40	−70
20	Si	N	1	1	C_6H_5	C_6H_5	CH_3	CH_3	CH_3	2127	2755	628	−100	−170
21	B	N	1	1	C_6H_5	–	H	H	CH_3	1943	3313	1370	470	1303
22	B	N	1	1	C_6H_5	–	H	H	$C(CH_3)_3$	1944	3076	1132	270	906
23	B	N	1	1	C_6H_5	–	CH_3	CH_3	CH_3	1886	3141	1255	340	1091
24	B	N	1	2	C_6H_5	–	H	H	CH_3	2061	3330	1269	490	1220
25	B	N	2	2	C_6H_5	–	H	H	CH_3	2054	3253	1199	380	1043

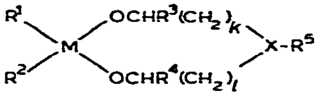
* A = Apiezon L; C = OV-225.

EXPERIMENTAL

The measurement of retention indices were conducted on a Chrom-4 chromatograph at 200°C as described earlier[1,2], using Apiezon L and OV-225 as stationary phases, 80–100-mesh Chromosorb W HP as the solid support and 1.2 m × 3 mm I.D. glass columns. The quantum-chemical calculations were carried out using the CNDO 2 program[5]. Compounds 1–3 (Table I) were obtained by reaction of the corresponding diorganyldiethoxysilanes with diethylene glycol. Similarly, compounds 4–20 were obtained by the reaction of diethoxy- or dimethoxysilanes and diethanolamines, whereas compounds 24–25 were synthesized by reaction of dialkanolamines with phenylboric acid in dioxan solution.

RESULTS AND DISCUSSION

The title compounds have the general formula



where R^1 = alkyl, aryl; R^2 = alkyl, alkoxyl, aryl; R^3,R^4 = H, methyl; R^5 = H, alkyl, phenyl; M = Si, B; X = O, N; and $k,l = 1$ or 2.

Their retention parameters are summarized in Table I. Unlike the trialkanolamine derivatives studied earlier, organosilicon derivatives of dialkanolamines are characterized by low, sometimes negative, values of $\delta I_{X \to M}$. This provides evidence that the above compounds in the chromatographic system appear to possess no intra-complex bond. This conclusion is supported by the comparison of $\delta I_{X \to M}$ values in organosilicon derivatives of dialkanolamines and the corresponding diethylene glycol derivatives (compounds 1–3), which have been shown to have no bond of this type.

It can be assumed that the intra-complex N → Si bond is stabler at low temperatures[6,7]. So, if this gain in stability is appreciable, the values of $\delta I_{N \to Si}$ are expected to increase with decreasing temperature. We estimated $\delta I_{N \to Si}$ values for compound 10 at various temperatures. The transannular bond in this compound, existing both as crystals and in solution, is due to the electron-donor character of the methyl group on the nitrogen atom and the electron-acceptor properties of phenyl radicals[3,4]. Nevertheless, the data presented in Table II demonstrate that with decreasing temperature (down to 160°C) the values of $\delta I_{N \to Si}$ fail to increase, and a slight decrease in the values is even observed. These data suggest that diethanolamine derivatives during GLC at 160–250°C exist in the form without an intra-complex bond.

Boron derivatives, unlike the organosilicon derivatives of dialkanolamines, are characterized by high values of $\delta I_{N \to M}$ comparable to those of boratranes. The relationship of these values to the number of six-membered rings in the molecule is roughly the same for the derivatives of di- and trialkanolamines (Fig. 1). Organoboron derivatives of dialkanolamines resemble boratranes with respect to other physico-chemical properties, *e.g.*, melting points and solubility in organic solvents. The high melting points are apparently responsible for the asymmetric peaks observed in these compounds despite the fact that the temperature of the injection port

TABLE II

RETENTION INDICES OF $(C_6H_5)_2Si(OCH_2CH_2)_2$-$NCH_3$ AS A FUNCTION OF TEMPERATURE

Temperature (°C)	*I*	$\delta I/10°C$	$\delta I_{N \to Si}$
250	2521	10.2	70
200	2470	12.0	20
180	2446	11.5	0
160	2423		−30

of the chromatograph was kept at 350–400°C and the samples were injected as dilute solutions.

The replacement of a secondary with a tertiary amino group usually brings about an increase in retention indices by 70–150 units, depending on the polarity of the stationary phase used. Our experimental conditions provided a reliable identification of compounds with retention indices up to 4000. However, our attempts to perform chromatographic analyses of boron compounds with $R^5 = H$ were unsuccessful. The explanation probably lies in the low thermal stability of these compounds, as evidenced by experiments using a short column (50 cm).

Thus, as with atranes, the chromatographic behaviour of boron-containing derivatives of diethanolamine indicates a stronger transannular interaction than with silicon compounds, apparently because the migration of the unshared electron pair on the nitrogen atom to the *p* orbital of boron is preferred to the *d* orbital of silicon.

An analysis of retention data in earlier publications suggests that the association of atranes with the stationary phase molecules involves oxygen atoms of the atrane backbone. It is to be expected that if the steric hindrances for various derivatives are roughly similar, the solute–sorbent association will be determined primarily by the atoms carrying the greatest absolute charge. To test this assumption, quantum-chemical calculations were conducted for several compounds (Table III). The results obtained show that the charges are most conspicuous on the silicon atom and the oxygen atoms directly bound to it. It should be noted, however, that the silicon atom

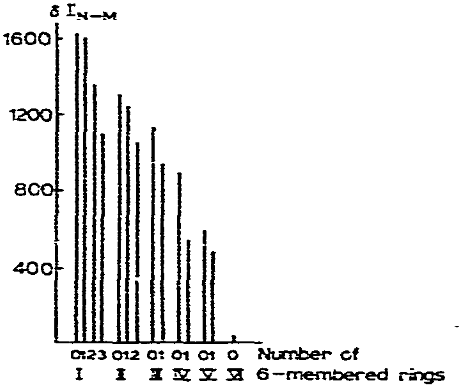
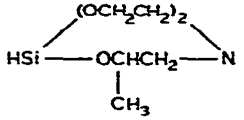
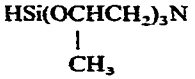
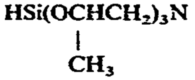
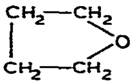


Fig. 1. Relationship between δI_{N-M} and number of 6-membered rings in the molecule. I = B derivatives of triethanolamine; II = B derivatives of diethanolamine, $R^1 = C_6H_5$; III = Ge derivatives of triethanolamine, $R^1 = C_6H_5$; IV = Si derivatives of triethanolamine, $R^1 = C_6H_5$; V = Si derivatives of triethanolamine, $R^1 = CH_3$; VI = Si derivatives of diethanolamine, $R^1 = R^5 = CH_3$, $R^2 = C_6H_5$.

TABLE III

CHARGE DISTRIBUTION IN ATRANE MOLECULES ACCORDING TO QUANTUM-CHEMICAL CALCULATIONS

Compound	*Charge*		
	Si	*O*	*R_1*
$HSi(OCH_2CH_2)_3N$	+0.478	−0.296 −0.296 −0.296	−0.121
	+0.472	−0.302 −0.290 −0.290	−0.118
 $HSi(OCH(CH_3)CH_2)_3N$	+0.468	−0.310 −0.309 −0.307	−0.124
 $HSi(OCH(CH_3)CH_2)_3N$	+0.463	−0.302 −0.302 −0.302	−0.120
$CH_3Si(OCH_2CH_2)_3N$	+0.440	−0.291 −0.291 −0.291	−0.058
$C_2H_5Si(OCH_2CH_2)_3N$	+0.438	−0.288 −0.288 −0.291	−0.054
$CH_2{=}CHSi(OCH_2CH_2)_3N$	+0.438	−0.293 −0.293 −0.293	−0.067
	+0.435	−0.289 −0.293 −0.293	−0.057
$CH_3OSi(OCH_2CH_2)_3N$	+0.576	−0.291 −0.294 −0.294	−0.195
$(CH_3)_2Si(OCH_2CH_2)_2NCH_3$	+0.522	−0.281 −0.281 −0.279	−0.032
	+0.522 (C′)	−0.236	

is strongly shielded by other atoms and is therefore unlikely to participate directly in the formation of an associate. At the same time, a certain contribution is provided by the substituent on the silicon atom, which explains our attempts to relate the charge values over sterically accessible atoms to chromatographic characteristics:

$$\Delta I_{OV\text{-}225} = -4404 + 2772 q_{R_1} + 5837 q_O \; (r = 0.98;\ \sigma = 39)$$
$$\delta I_{N-Si} = -9882 + 2232 q_{R_1} + 11936 q_O \; (r = 0.96;\ \sigma = 83)$$

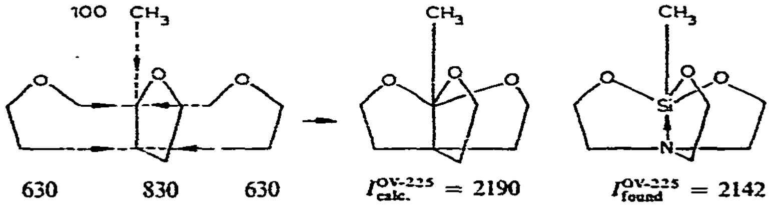
where q_{R_1} and q_O are the charges on the R_1 and oxygen atoms, respectively.

Further, as evidenced by quantum-chemical calculations, the charges on all remaining atoms in the estimated molecules show little dependence on the character of the substituent on the silicon atom. It is evident, therefore, that they cannot be responsible for the different chromatographic behaviour of particular compounds and therefore were neglected.

The present model for explaining the chromatographic properties of compounds appears to be more general in character than the models proposed in our earlier work[1]. It permits, for instance, the assessment of the sequence of elution for diastereoisomeric atranes as well as the calculation of $\delta I_{N \rightarrow Si}$ values for 1-hydrosilatrane, which cannot be achieved with previously proposed equations.

Nevertheless, the quantum-chemical calculations applied to a diethanolamine derivative gave a charge distribution pattern in the molecule (Table III) similar to that observed in atranes. Dialkanolamine derivatives are characterized by small $\delta I_{N \rightarrow M}$ values, suggesting that the strong solute–sorbent association in the case of atranes in due mainly to the charges on the oxygen atoms being in a specifically favourable environment to participate in intermolecular interactions. Unlike organosilicon derivatives of diethanolamine, atrane molecules exhibit enhanced conformational rigidity. In the molecules carrying a transannular bond, oxygen atoms are incorporated in the 5- and 6-membered rings, forming a constant protrusion which facilitates their attraction by the alternatively charged centres of the stationary phase. On the other hand, molecules without a transannular bond permit a variety of energetically equivalent conformations, only some of which are suitable for the specific intermolecular interaction.

This interpretation of the strong chromatographic retention is supported by a certain similarity between the atrane system and the corresponding cyclic ethers. The excessive negative charge on the oxygen atom in tetrahydrofuran is only slightly lower than that on the oxygen atom in atranes (Table III). The additive scheme can be useful for the calculation of retention indices in the hypothetical system, the carbon analogue of 1-methylsilatrane. The retention index of tetrahydrofuran on OV-225 is about 830 at 200°C; hence for the 1-methylsilatrane analogue it should be 830 + (2·630) + 100 = 2190, which is in good agreement with the experimental value[1].



$I_{calc.}^{OV-225} = 2190$ $I_{found}^{OV-225} = 2142$

We therefore think that the high $\delta I_{N \rightarrow M}$ values found for intra-complex ethers are due mainly to the formation of 5- and 6-membered oxygen-containing heterocycles having a conformation that is favourable for intermolecular interactions. If such a conformation predominates, other (secondary) factors come into play, *e.g.*, the electron density distribution and the steric environment of the oxygen atoms.

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