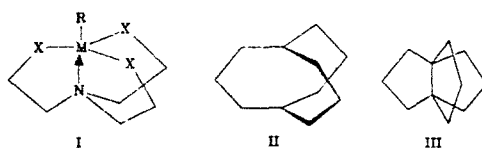


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The results of an investigation of the spin-spin coupling constants of the protons in the $\text{OCH}_2\text{CH}_2\text{N}$ fragments of asymmetric derivatives of metallatranes and the two-dimensional ^1H NMR (NOESY) spectra of 1-substituted 3,6,10-trimethylsilatranes provide evidence in support of a multistep exchange mechanism for conformational transitions, rather than the synchronous conversion of metallatranes in solution.

The study of the structure of metallatranes (I) has been the subject of a large number of publications (see reviews [1-4]). However, the processes associated with the intramolecular dynamics of these compounds have not been adequately studied [5]. Metallatranes may be described as a transitional class of compounds between derivatives of bicyclo[3.3.3]undecane (II) and tricyclo[3.3.3.0]undecane (III) (the latter are also called [3.3.3]propellanes). Therefore, the conformational properties of compounds I, on the one hand, and compounds II and III, on the other hand, should have much in common.



In fact, data from x-ray structural analysis [6-9], NMR [10-13], and calculations [7] attest to the fact that compounds II and III, as well as metallatranes [1-4], exist in a conformation of the "triskelion" type [14] (Fig. 1). Rapid (on the NMR time scale) exchange between enantiomeric conformations A and A' is observed at room temperature in solutions of both metallatranes and derivatives of types II and III. However, it has been demonstrated by theoretical [15] and experimental [13] methods in the case of II and III that the exchange between conformations A and A' takes place according to a multistep exchange mechanism, which includes conformations of types B and B' as transition states. At the same time, a synchronous exchange mechanism, which prohibits transitional conformations B and B', has been postulated for I [5]. The explanation of the fact that the evidence of the conformational transitions in the NMR spectra of metallatranes does not vanish upon freezing on the basis of a synchronous conversion mechanism in [16] is also unsubstantiated, since it is known [14, 15] that in polycyclic systems synchronous processes are, conversely, characterized by a sharp increase in the barrier to interconversion.

In order to clarify the above contradictions, we preliminarily [17, 18] studied the ^1H NMR spectra of asymmetric metallatrane derivatives IV (Table 1). In this case, the protons of the $\text{OCH}_2\text{CH}_2\text{N}$ fragments form a nondegenerate four-spin system of the ABXY type, which makes it possible to study the conformational properties of IVa in solution in greater detail. From Fig. 2 it is seen that the exchange between equally populated enantiomeric conformations A and A' results in the averaging of the vicinal spin-spin coupling constants of the protons. Therefore, the absence of the averaging of these spin-spin coupling constants in the case of derivative IVc and, to a lesser extent, in the case of IVb and IVa, may be attributed to the occurrence of unequally populated conformations of types B and C in the solutions [19]:

$$\Delta p = 10\Delta J_{\text{trans}}, \quad (1)$$

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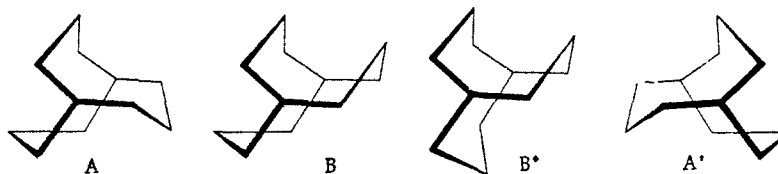


Fig. 1. Multistep mechanism of exchange between enantiomeric triskelion-type conformations A and A' in bicyclo[3.3.3]undecane.

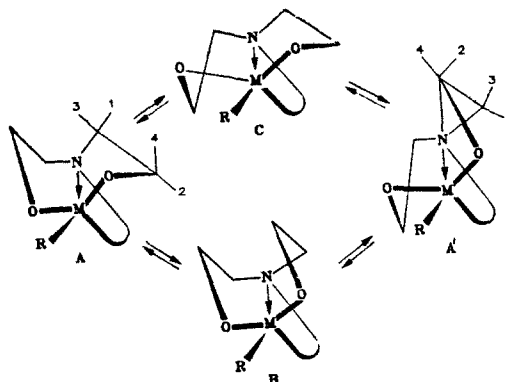
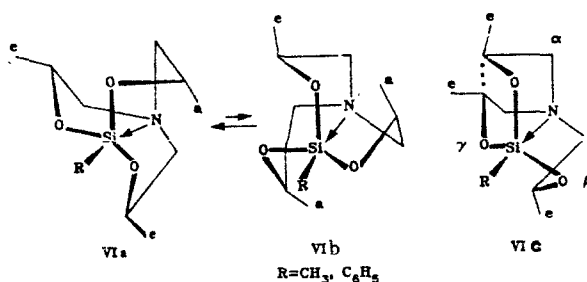


Fig. 2. Conformational transitions in asymmetric analogs of metallotranes.

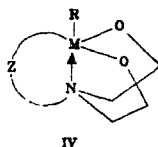
where $\Delta J_{\text{trans}} = J_{1,4} - J_{2,3}$, and Δp is the difference between the populations of conformations B and C (in %). At the same time, using the "R-factor" method [20, 21], we calculated the values of the dihedral angle φ_{ON} formed by the O-C-C and C-C-N planes. A comparison of the data obtained (Table 1) shows that Δp decreases as φ_{ON} decreases. This finding is readily attributed to the decrease in the inequivalence of the conformational energies of B and C as the five-membered rings are flattened. It should be noted that a decrease in Δp does not by any means attest to a decrease in the populations of conformations B and C and that it only points out the equalization of their content. This is indicated, in particular, by the nearly statistical ratio between the diastereomers of the 3,7-dimethyl and 3,7,10-trimethyl derivatives of silatrane and germatrane [5, 22].

The approach just described to the problem under consideration was recently subjected to a critical review [23], since the absence of averaging of the vicinal spin-spin coupling constants may be attributed to the anisochronism of the protons in the $\text{OCH}_2\text{CH}_2\text{N}$ fragments. It should, nevertheless, be noted that chemical anisochronism is specifically a consequence of unequal populating of rotamers and that "pure" magnetic anisochronicity is encountered extremely rarely and only in rigidly immobilized systems [24].



For the purpose of obtaining additional evidence in support of the multistep mechanism of exchange, we studied the structures of 1,3,7,10-tetramethylsilatrane (VI) and 1-phenyl-3,7,10-trimethylsilatrane (VII) in solution. It was previously postulated [23, 25] that in the RRS (or SSR) diastereomer one of the C-methyl groups is oriented predominantly in the axial direction (conformation VIa), since in the case of equatorial orientations for all the methyl groups, the compound should have conformation VIc, which is forbidden according to

TABLE 1. Spin-Spin Coupling Constants of the Protons of the $\text{OCH}_2\text{CH}_2\text{N}$ Fragments in Metallatranes IVa-c*



Compound**	M	R	Solvent	$^1\text{H}, ^1\text{H}$ spin-spin coupling constants, Hz						$\Delta p, \%$	ψ_{ON}
				1,2	1,3	1,4	2,3	2,4	3,4		
IVa	Si	CH_3 $\text{CH}_2=\text{CH}$	CDCl_3	-12,67	4,66	6,99	6,04	4,74	-11,32	9,5	50,9
			CDCl_3	-12,46	4,99	6,85	6,12	5,01	-11,32	7,3	49,8
			C_6H_5	-12,48	4,92	6,80	6,15	4,97	-11,27	6,5	49,9
			CH_2Cl	-12,20	5,48	6,53	6,17	5,38	-11,10	3,6	47,9
IVb	Si	CH_3	CDCl_3	-12,61	4,94	6,58	6,23	5,00	-11,26	3,5	49,6
			CDCl_3	-12,27	4,90	6,36	3,48	5,04	-11,31	1,2	49,7
IVc	Ge	CH_3	$\text{DMSO}-d_6$	-12,49	5,05	6,26	6,40	5,12	-10,94	1,4	49,0
			CDCl_3	-12,41	5,35	6,22	6,49	5,48	-11,45	2,7	48,1
			$\text{DMSO}-d_6$	-12,42	5,57	6,23	6,28	5,64	-11,00	0,5	47,1

*The numbering of the protons is presented in Fig. 2.

**IVa Z = OCOCH_2 , IVb Z = $\text{CH}_2\text{CH}_2\text{CH}_2$, IVc Z = $\text{OCH}_2\text{CH}_2\text{CH}_2$.

the conception of synchronous conversion. Since the evidence of the conversion process in the NMR spectra of metallatranes does not vanish upon freezing, the question of whether there is an axial-equatorial equilibrium for the C-methyl groups or whether the corresponding ring is twisted along the C-C bond cannot be unequivocally resolved by analyzing the spin-spin coupling constants [25] or the ^{13}C chemical shifts [23], i.e., all the arguments in this area are purely speculative. Therefore, we studied the nuclear Overhauser effect (NOE) with the use of the method of two-dimensional NMR spectroscopy (NOESY). In the case of conformation VIc we may expect the appearance of a cross peak between the spatially approaching OCH protons of neighboring rings, which, as a study of Dreiding models shows, cannot be observed in the case of conformation VIa. Despite the fact that the conditions for the observation of the NOE are extremely unfavorable in the latter case (the strong multiplicity and the weak difference between the chemical shifts), this cross peak was found experimentally in the NOESY spectra of compounds VI and VII (Fig. 3). This unequivocally proves the existence of the RRS isomers of compounds VI and VII in conformation VIc and, therefore, proves that the conversion of the metallatranes proceeds according to a multistep exchange mechanism, rather than a synchronous mechanism. It should be noted that the system of cross peaks in the NOESY spectra permits the unequivocal assignment of the signals to three inequivalent semicycles in space (Table 2).

EXPERIMENTAL

The ^1H NMR spectra of compounds IV and VI were recorded on a Bruker WM-360 spectrometer (the working frequency was 360 MHz), and the diameter of the ampuls was 5 mm. The solvent (CDCl_3) was dried over molecular sieves 4 Å. The solutions were purged by argon before measurement of the NOE. The spin-spin coupling constants for the $\text{OCH}_2\text{CH}_2\text{N}$ fragments were obtained by iteration analysis of the spectrum (an ABXY system) with the use of the PANIC program. The mean-square (RMS) deviation did not exceed 0.05 Hz.

The NOESY spectra were obtained with the use of a three-pulse ($90^\circ-t_1-90^\circ-\tau_m-90^\circ-t_2$)_N sequence and a mixing time $\tau_m = 0.8$ sec. The time τ_m was allowed to vary randomly over the course of the experiment in a 10% range in order to suppress the coherent transfer of magnetization. Here t_1 and t_2 are the periods of evolution and observation of the signals. A data matrix containing 256×1024 points was broad up to the dimensions 512×1024 , which correspond to a resolution of 2.4 Hz per point. Before Fourier transformation, the data

matrix was multiplied in the t_1 and t_2 directions by the functions $\sin\left[\frac{t_1(\pi-\varphi)}{t_{s_1}} + \varphi\right]$ (for

the t_1 direction) and $\sin^2\left[\frac{t_2(\pi-\varphi)}{t_{s_2}} + \varphi\right]$ (for the t_2 direction), where t_{s_1} and t_{s_2} were chosen

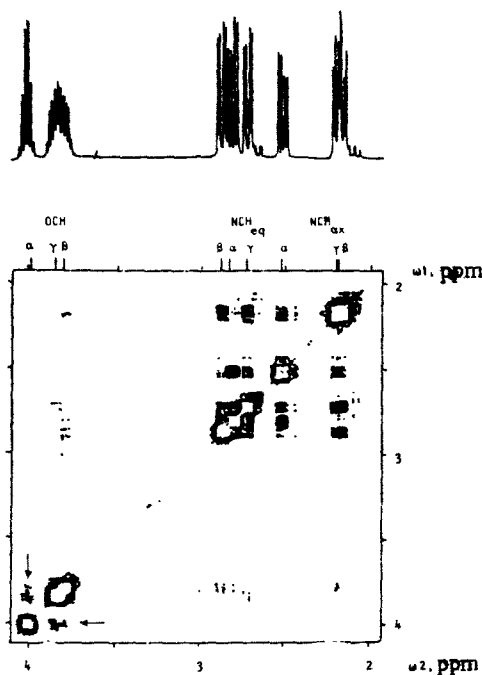


Fig. 3. NOESY spectrum of the RRS diastereomer of 1,3,7,10-tetramethylsilatrane in CDCl_3 at 303°K . The arrows point out the cross peaks which attest to the spatial approach of the OCH protons of the α and γ semicycles. The assignment of the signals is indicated in the upper part of the figure.

TABLE 2. Chemical Shifts of the Protons in 1-R-3,7,10-Trimethylsilatranes VI and VII at 303°K

Compound	R	Isomer	δ , ppm*			
			OCH	NCH_e	NCH_a	CCH_3
VI	CH_3^{**}	RRR	3.73	2.64	2.06	1.03
		RRS (α)	3.98	2.77	2.49	1.08
		(β)	3.76	2.82	2.14	1.04
		(γ)	3.82	2.69	2.15	1.02
VII	$\text{C}_6\text{H}_5^{***}$	RRR	3.81	2.81	2.22	0.99
		RRS (α)	4.01	2.97	2.63	1.07
		(β)	3.85	3.03	2.24	1.01
		(γ)	3.87	2.88	2.29	0.97

*Compound VI in CDCl_3 and compound VII in $(\text{CD}_3)_2\text{CO}$.

**In the case of RRR, $\delta(\text{SiCH}_3) = -0.22$ ppm; in the case of RRS, $\delta(\text{SiCH}_3) = -0.19$ ppm.

*** $\delta(\text{H}_o) = 7.50$ ppm, $\delta(\text{H}_{m,p}) = 6.95$ ppm.

in such a manner that the functions would take on zero values for the last experimental points in both directions. The phase shifts φ in the t_1 and t_2 directions were $\pi/16$ and $\pi/4$.

LITERATURE CITED

1. M. G. Voronkov and V. P. Baryshok, *J. Organomet. Chem.*, **239**, 199 (1982).
2. M. G. Voronkov, V. M. Dyakov, and S. V. Kirpichenko, *J. Organomet. Chem.*, **233**, 1 (1982).
3. V. F. Sidorkin, V. A. Pestunovich, and M. G. Voronkov, *Usp. Khim.*, **49**, 748 (1980).
4. M. G. Voronkov and V. M. D'yakov, *Silatranes* [in Russian], Nauka, Novosibirsk (1978).
5. S. N. Tandura, V. A. Pestunovich, M. G. Voronkov, G. I. Zelchan, V. P. Baryshok, and Yu. A. Lukina, *Dokl. Akad. Nauk SSSR*, **235**, 406 (1977).
6. A. H. J. Wang, R. J. Missavage, S. R. Byrn, and I. C. Paul, *J. Am. Chem. Soc.*, **94**, 7100 (1972).
7. P. Murray-Rust, J. Murray-Rust, and C. I. F. Watt, *Tetrahedron*, **36**, 2799 (1980).
8. N. J. Leonard, J. C. Coll, A. H. Wang, R. J. Missavage, and I. C. Paul, *J. Am. Chem. Soc.*, **93**, 4628 (1971).

9. R. W. Alder, R. B. Sessions, J. M. Mellor, and M. F. Rawlins, *J. Chem. Soc., Chem. Comm.*, 747 (1977).
10. J. C. Coll, D. R. Crist, M. C. G. Barrio, and N. J. Leonard, *J. Am. Chem. Soc.*, 94, 7092 (1972).
11. R. W. Alder, R. J. Arrowsmith, A. Casson, R. B. Sessions, E. Heilbronner, B. Kovac, H. Huber, and M. Taagepera, *J. Am. Chem. Soc.*, 105, 6137 (1983).
12. M. Doyle, W. Parker, P. A. Gunn, J. Martin, and D. D. MacNicol, *Tetrah. Lett.*, 3619 (1970).
13. H. Maggio, H. E. Simmons, and J. K. Kouba, *J. Am. Chem. Soc.*, 103, 1573 (1981).
14. J. Dale, in: *Topics in Stereochemistry*, N. L. Allinger and E. L. Eliel (eds.), Vol. 9, Wiley, New York (1979), p. 263.
15. E. Osawa, *J. Am. Chem. Soc.*, 101, 5523 (1979).
16. V. A. Pestunovich, M. G. Voronkov, G. I. Zelchan, É. Ya. Lukevits, L. I. Libert, A. N. Egorochkin, and A. I. Burov, *Khim. Geterotsikl. Soedin.*, No. 2, 339 (1970).
17. É. Kupche (Kupce), É. Liepin'sh (Liepins), A. Lapsina, G. Zelchan, and É. Lukevits, (Lukevics), *J. Organomet. Chem.*, 251, 15 (1983).
18. É. Kupche, in: *Synthesis and Investigation of Biologically Active Compounds. Abstracts of Reports to the Eighth Conference on Young Scientists [in Russian]*, Riga (1984), p. 108.
19. É. Kupche (Kupce), É. Liepin'sh (Liepins), and É. Lukevits (Lukevics), *J. Organomet. Chem.*, 248, 131 (1983).
20. J. B. Lambert, *J. Am. Chem. Soc.*, 89, 1836 (1967).
21. J. B. Lambert, *Acc. Chem. Res.*, 4, 87 (1971).
22. S. N. Tandura, S. N. Gurkova, A. I. Gusev, and N. V. Alekseev, in: *Structure of Biologically Active Compounds of Germanium with an Expanded Coordination Sphere. Review Information. Organometallic Compounds and Their Application Series [in Russian]*, NIITÉKhim, Moscow (1983).
23. S. N. Tandura, M. G. Voronkov, A. V. Kisin, N. V. Alekseev, E. E. Shestakov, Z. A. Ovchinnikova, and V. P. Baryshok, *Zh. Obshch. Khim.*, 2012 (1984).
24. M. Nogradi, *Stereochemistry, Basic Concepts and Applications*, Pergamon Press (1981).
25. S. N. Tandura, "Investigation of silatranes by ^1H , ^{13}C , ^{14}N , ^{19}F , and ^{29}Si NMR spectroscopy," Author's Abstract of Dissertation for the Degree of Candidate of Chemical Sciences, Irkutsk (1977).