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X-RAY ANALYSIS OF 1,3-DIOXA-6-AZA-2-SILACYCLOOCTANE DERIVATIVES

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Summary

X-ray analysis has been conducted on four dioxaazasilacyclooctanes $R_2Si(OCH_2CH_2)_2NR'$ with R = C_6H_5, R' = CH_3 (IV); R = C_6H_5, R' = $(CH_3)_3C$ (V); R = CH_3, R' = C_6H_5 (VI) and R = R' = C_6H_5 (VII). The interatomic distances Si—N measured for these compounds had the values: 2.68 (IV), 3.16 (V), 3.19 (VI) and 3.08 Å (VII), indicating weak nitrogen—silicon interaction and a virtual lack of coordinate Si ← N bonding. The data of other authors and our own evidence suggest that the Si ← N interaction in these compounds is strongly influenced by the electronic effects of Si- and N-substituents and, in particular, by the steric effects of the latter.

Introduction

X-ray analysis of silicon-containing cyclic derivatives of triethanolamine, known as silatranes, $R\overline{Si(OCH_2CH_2)_3N}$ has revealed the existence in their molecules of a trigonal bipyramidal coordinated silicon atom and a transannular donor-acceptor Si ← N bond [1—3], its length being largely determined by the induction constant σ^* of the substituent R [4]. The platinum-silatrane complex appears to represent the only case in which Si ← N bonding is not present [5,6]. The silicon atom in this molecule has tetrahedral coordination, the silicon—nitrogen distance being equal to 2.89(1) Å. The lack of Si ← N bonding is attributed by the authors to the much stronger negative character of the silicon atom as compared to other silatranes, making the interaction with the nitrogen lone pair less attainable, and to the steric effects of the ligand, preventing the formation of a trigonal-bipyramidal environment for the silicon.

Our knowledge is even more scanty as far as the structure of silicon-containing cyclic derivatives of diethanolamine, viz. 1,3-dioxa-6-aza-2-silacyclooctanes with the general formula $R_2Si(OCH_2CH_2)_2NR'$, is concerned. For instance, the structure has been determined for 2,2-diphenyl-1,3-dioxa-6-aza-2-silacyclo-

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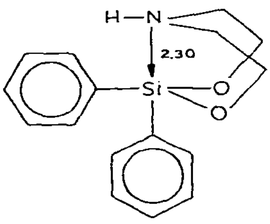

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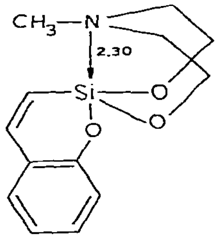

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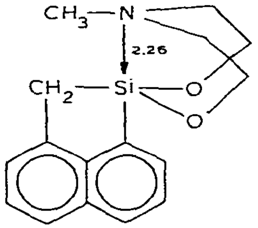
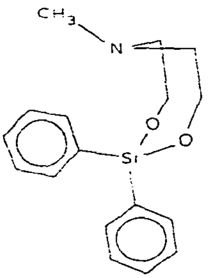


III

octane (I), the molecule of which, formally an eight-membered heterocycle, is bridged by a transannular donor—acceptor Si ← N bond, 2.30 Å long [7]. The Si ← N bond has been also demonstrated in the structurally related molecules 5-methyl-2,8-dioxa-5-aza-1-silacyclooctane-1-spiro-(2′-silachromene) (II) [8] and 5-methyl-2,8-dioxa-5-aza-1-silacyclooctane-1-spiro-1′-silaacenaphthene (III) [9]. The coordinate bond lengths are 2.30 and 2.26 Å, respectively.

In order to gain a better understanding of how electronic and steric factors affect the entire molecular geometry in the compounds of this series as well as the conformation of the heterocycles, we have undertaken an X-ray study of four silicon-containing cyclic derivatives of diethanolamine: 2,2-diphenyl-6-methyl- (IV), 2,2-diphenyl-6-t-butyl- (V), 2,2-dimethyl-6-phenyl- (VI) and 2,2,6-triphenyl-1,3-dioxa-6-aza-2-silacyclooctane (VII).



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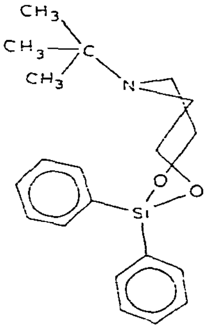

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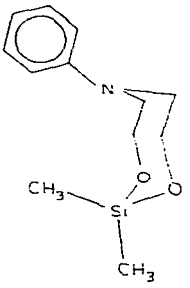
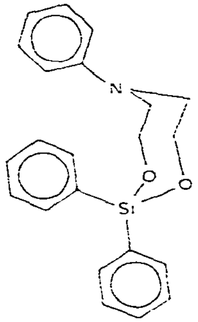


VI



VII

Experimental

The compounds IV—VII were prepared by the reaction of dimethyl- or diphenyldiethoxysilane with the appropriate N-substituted diethanolamine. Single crystals useful for X-ray analysis were obtained by recrystallization from n-hexane. Their main chemical and crystallographic parameters are listed in Table 1.

Integrated intensities of reflections were collected by the θ—2θ scanning technique with Cu-K_α radiation (graphite crystal monochromator) on a Syntex $P2_1$ full-automatic diffractometer. No absorption correction was applied.

The structures IV—VII were solved by direct methods using the MULTAN program [10] and further refined by full-matrix least squares procedure with

TABLE 1

CRYSTAL DATA

Compound	IV	V	VI	VII
Formula	$C_{17}H_{21}O_2NSi$	$C_{20}H_{27}O_2NSi$	$C_{12}H_{19}O_2NSi$	$C_{22}H_{23}O_2NSi$
Formula weight	299.5	341.6	237.4	361.6
Melting point (°)	73	92	102.5	86
Crystal dimensions (mm)	0.2 × 0.25 × 0.38	0.2 × 0.25 × 0.4	0.25 × 0.25 × 0.27	0.1 × 0.15 × 0.3
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$Pc2_1b$	$P2_1/c$	$P2_1/c$
Z	4	4	4	4
a (Å)	9.635(1)	8.767(1)	7.381(1)	11.851(2)
b (Å)	10.189(1)	10.298(2)	9.407(1)	8.870(2)
c (Å)	16.688(2)	20.287(3)	18.810(3)	20.209(4)
β (°)	90	90	96.79(1)	115.42(1)
V (Å^3)	1641.3	1894.7	1296.9	1918.7
μ (Cu K_α) (cm^{-1})	12.6	11.5	14.6	11.8
$d_{calc.}$ (g cm^{-3})	1.21	1.20	1.22	1.25
Number of observed reflections ($I \geqslant 2\sigma_I$)	1300	823	1147	1399
$2\theta_{max}$	150	100	100	100
R	0.062	0.170	0.045	0.068

TABLE 2

ATOMIC COORDINATES (×10^4) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	IV (R = C_6H_5; R′ = CH_3)				V (R = C_6H_5; R′ = $C(CH_3)_3$)			
	Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
R	Si	0935(2)	0487(2)	3183(1)	Si	1515(10)	0001(0)	0544(4)
	O(1)	0186(5)	0017(4)	2362(3)	O(1)	1693(24)	1379(23)	0915(9)
	O(3)	1664(4)	1943(4)	3198(3)	O(3)	0003(23)	−0122(26)	0071(9)
	N	2976(7)	0388(7)	2094(4)	N	−1492(24)	0776(25)	1283(11)
	C(4)	2512(9)	2509(8)	2634(5)	C(4)	−1596(37)	−0274(39)	0208(14)
	C(5)	3294(12)	1750(11)	2149(7)	C(5)	−2190(32)	0901(32)	0655(14)
	C(7)	2097(11)	0107(15)	1455(5)	C(7)	−0797(40)	2022(37)	1415(15)
	C(8)	0780(10)	−0389(9)	1633(4)	C(8)	0638(47)	2265(41)	1124(18)
R′	C(9)	4136(9)	−0470(9)	2113(4)	C(9)	−2472(35)	0286(35)	1814(14)
					C(10)	−1493(30)	0181(38)	2415(15)
					C(11)	−3100(30)	−1142(30)	1634(13)
					C(12)	−3842(33)	1218(33)	1982(13)

TABLE 2 (continued)

	IV ($R = C_6H_5$; $R' = CH_3$)				V ($R = C_6H_5$; $R' = C(CH_3)_3$)			
	Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
R_{ax}	C(10)	−0610(6)	0787(6)	3844(4)	C(13)	3189(29)	−0214(33)	−0060(13)
	C(11)	−1971(7)	0741(8)	3565(4)	C(14)	4102(30)	−1341(33)	−0047(14)
	C(12)	−3060(8)	1036(9)	4079(6)	C(15)	5108(35)	−1407(32)	−0587(15)
	C(13)	−2826(10)	1360(9)	4861(6)	C(16)	5308(34)	−0515(31)	−1036(14)
	C(14)	−1516(10)	1424(8)	5128(5)	C(17)	4382(35)	0573(34)	−1076(15)
	C(15)	−0407(7)	1113(7)	4645(4)	C(18)	3352(35)	0752(39)	−0555(15)
R_{eq}	C(16)	2013(7)	−0774(6)	3679(3)	C(19)	1653(34)	−1380(31)	1178(14)
	C(17)	1672(8)	−2111(8)	3597(4)	C(20)	2508(32)	−1266(31)	1698(14)
	C(18)	2480(9)	−3055(8)	3973(6)	C(21)	2713(35)	−2247(37)	2111(15)
	C(19)	3596(9)	−2724(9)	4438(5)	C(22)	2044(32)	−3399(33)	1990(13)
	C(20)	3943(8)	−1442(9)	4519(4)	C(23)	1227(36)	−3598(37)	1470(16)
	C(21)	3158(7)	−0461(7)	4141(4)	C(24)	0954(32)	−2590(30)	1008(14)

	VI ($R = CH_3$; $R' = C_6H_5$)				VII ($R = R' = C_6H_5$)			
	Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
R	Si	9765(2)	1807(1)	1016(1)	Si	2674(2)	0971(3)	6787(1)
	O(1)	11606(4)	0887(3)	1271(2)	O(1)	2403(5)	2237(6)	6149(3)
	O(3)	8942(4)	2516(3)	1701(2)	O(3)	4151(4)	0775(6)	7368(3)
	N	12776(5)	3660(4)	1960(2)	N	4361(6)	0362(8)	6005(4)
	C(4)	9443(8)	3827(7)	2039(3)	C(4)	4999(8)	−0266(10)	3711(4)
	C(5)	11345(8)	3840(7)	2424(3)	C(5)	5421(7)	0181(9)	6730(5)
C(7)		13845(8)	2346(6)	2010(3)	C(7)	4020(8)	1911(10)	5721(5)
C(8)		13443(7)	1417(6)	1357(4)	C(8)	2678(8)	2316(10)	5537(4)
R′	C(9)	13420(6)	4846(5)	1620(2)	C(9)	3991(8)	−0858(12)	5505(5)
	C(10)	14913(8)	4763(6)	1232(3)	C(10)	4324(8)	−2341(13)	5757(5)
	C(11)	15548(8)	5922(7)	0886(3)	C(11)	3908(11)	−3518(12)	5261(8)
	C(12)	14681(9)	7214(7)	0913(3)	C(12)	3194(13)	−3285(15)	4523(8)
	C(13)	13214(9)	7324(6)	1290(3)	C(13)	2883(10)	−1853(16)	4279(6)
	C(14)	12575(7)	6168(5)	1641(3)	C(14)	3266(8)	−0633(11)	4747(6)
R_{ax}	C(15)	8060(10)	0468(8)	0663(4)	C(15)	1933(8)	1809(9)	7353(5)
					C(16)	0908(9)	2734(11)	7044(5)
					C(17)	0372(9)	3371(11)	7480(7)
					C(18)	0887(10)	3051(12)	8213(6)
					C(19)	1897(9)	2111(12)	8521(5)
					C(20)	2425(8)	1505(9)	8095(5)
R_{eq}	C(16)	10173(12)	3135(8)	0342(4)	C(21)	2004(7)	−0904(10)	6412(5)
					C(22)	1285(8)	−1182(11)	5666(5)
					C(23)	0814(9)	−2606(14)	5415(5)
					C(24)	1052(9)	−3781(12)	5905(6)
					C(25)	1742(9)	−3545(10)	6644(6)
					C(26)	2211(8)	−2102(11)	6889(5)

the aid of the $w = 1/\sigma_{F_0^2}$ weighting scheme. The refinements for non-hydrogen atoms in the molecules IV, VI and VII were carried out in the anisotropic approximation including the positions of hydrogen atoms identified from a difference map and generated from assumed geometries. The silicon atom in compound V was refined in the anisotropic approximation, but the remaining non-hydrogen atoms were refined only in the isotropic approximation, determined by the temperature fluctuations of the molecule (the overall temperature factor

B calculated from Wilson plot is 7.7 Å^2) and limitations of the set of reflections with $I \geqslant 2\sigma_I$.

The final atomic coordinates with their e.s.d.'s in parentheses are listed in Table 2.

Results and discussion

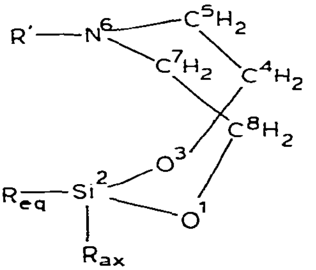
The general structural formula of the 1,3-dioxa-6-aza-2-silacyclooctanes (IV—VII) and the labelling of atoms in the heterocycle are shown in Fig. 1.

Table 3 shows the bond lengths and angles (with e.s.d.'s) in the heterocycles along with their mean values in the substituents of compounds IV—VII.

The transannular donor-acceptor $\mathrm{Si} \leftarrow \mathrm{N}$ interaction occurring in the compounds I—III is similar to that observed in the molecules of silatranes and carbasilatranes. The values of $\mathrm{Si} \leftarrow \mathrm{N}$ bond length in I—III (~2.30 Å) are close to that in the molecule of 1-methyl-2-carbasilatrane, $CH_3—Si(OCH_2CH_2)_2CH_2CH_2CH_2N$, being equal to 2.34 Å [11]. The silicon atom in this compound, like that in I and II, has two carbons and two oxygen atoms as its immediate environment.

In silatranes with the pentacoordinate silicon surrounded by three oxygen atoms located in the equatorial plane of its coordinate polyhedron the $\mathrm{Si} \leftarrow \mathrm{N}$ donor-acceptor bond is shorter. For instance, in the case of 1-phenylsilatrane, $C_6H_5—Si(OCH_2CH_2)_3N$, it has the value 2.13—2.19 Å [3]. Like the platinum-silatrane complex [5,6], compound IV (the silicon—nitrogen distance amounts to 2.68 Å), to say nothing of compounds V—VII (the appropriate distances are still greater and reach the values 3.16, 3.19 and 3.08 Å) are characterized by further weakening of the silicon—nitrogen interaction.

Comparison of the silicon—nitrogen distances in compounds I (2.30 Å), IV (2.68 Å) and V (3.16 Å) revealed that the increase in the values of interatomic distances between silicon and nitrogen is accompanied by changes in the coordinate polyhedron of the silicon atom. The trigonal bipyramid configuration becomes transformed to a tetrahedron, the silicon atom thereby deviates from the equatorial plane of the trigonal bipyramid formed by the atoms O(1) O(3) C(R_{eq}) toward R_{ax} by 0.25, 0.38 and 0.49 Å, respectively. The silicon atom in the present series of compounds (I, IV, V) has identical R substituents, whereas the R′ substituents at the nitrogen are characterized by increasing volume and donor capacity. Despite decrease in the values of the induction constants σ^* of



$R = R_{eq} = R_{ax}$

(IV, $R = C_6H_5$, $R' = CH_3$;

V $R = C_6H_5$, $R' = C(CH_3)_3$,

VI $R = CH_3$, $R' = C_6H_5$;

VII $R = C_6H_5$, $R' = C_6H_5$)

Fig. 1. Numbering of atoms for 1,3-dioxa-6-aza-2-silacyclooctanes.

TABLE 3

INTERATOMIC BOND DISTANCES (Å) AND BOND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	Compound			
	IV	V	VI	VII
Distances				
Si—N	2.68(1)	3.16(2)	3.19(1)	3.08(1)
Si—O(1)	1.62(1)	1.63(2)	1.63(1)	1.63(1)
Si—O(3)	1.64(1)	1.66(2)	1.63(1)	1.65(1)
Si—C(R_{ax})	1.88(1)	1.95(3)	1.85(1)	1.87(1)
Si—C(R_{eq})	1.85(1)	1.95(3)	1.83(1)	1.86(1)
N—C(7)	1.39(1)	1.45(4)	1.46(1)	1.48(1)
N—C(5)	1.42(1)	1.46(4)	1.46(1)	1.47(1)
N—C(R′)	1.42(1)	1.50(4)	1.40(1)	1.42(1)
O(1)—C(8)	1.41(1)	1.37(5)	1.44(1)	1.41(1)
O(3)—C(4)	1.37(1)	1.44(4)	1.42(1)	1.41(1)
C(7)—C(8)	1.40(1)	1.42(5)	1.51(1)	1.51(1)
C(4)—C(5)	1.35(1)	1.62(5)	1.50(1)	1.51(1)
Average C—C in R′	—	1.57(4)	1.38(1)	1.38(1)
Average C—C in R_{ax}	1.38(1)	1.41(4)	—	1.38(1)
Average C—C in R_{eq}	1.39(1)	1.37(5)	—	1.39(1)
Angles				
N—Si—C(R_{ax})	170(1)	167(1)	166(1)	164(1)
O(1)—Si—C(R_{ax})	101(1)	110(1)	105(1)	103(1)
O(3)—Si—C(R_{ax})	101(1)	102(1)	105(1)	104(1)
C(R_{eq})—Si—C(R_{ax})	107(1)	108(1)	112(1)	112(1)
N—Si—O(1)	75(1)	68(1)	68(1)	71(1)
N—Si—O(3)	74(1)	69(1)	69(1)	68(1)
N—Si—C(R_{eq})	82(1)	84(1)	81(1)	84(1)
O(1)—Si—O(3)	118(1)	115(1)	111(1)	115(1)
O(1)—Si—C(R_{eq})	115(1)	108(1)	111(1)	113(1)
O(3)—Si—C(R_{eq})	112(1)	114(1)	112(1)	110(1)
C(7)—N—C(5)	112(1)	106(2)	119(1)	118(1)
C(7)—N—C(R′)	112(1)	113(2)	120(1)	119(1)
C(5)—N—C(R′)	115(1)	118(2)	119(1)	120(1)
Si—N—C(R′)	126(1)	139(2)	116(1)	115(1)
Si—N—C(7)	95(1)	88(2)	85(2)	85(1)
Si—N—C(5)	94(1)	86(2)	84(1)	88(1)
Si—O(1)—C(8)	129(1)	132(2)	126(1)	133(1)
Si—O(3)—C(4)	129(1)	132(2)	128(1)	126(1)
O(1)—C(8)—C(7)	117(1)	128(3)	113(1)	113(1)
O(3)—C(4)—C(5)	120(1)	110(3)	114(1)	112(1)
C(8)—C(7)—N	118(1)	117(3)	113(1)	113(1)
C(4)—C(5)—N	118(1)	109(2)	114(1)	112(1)
Average C—C—C in R′	—	108(3)	120(1)	120(1)
Average C—C—C in R_{ax}	120(1)	120(3)	—	120(1)
Average C—C—C in R_{ax}	120(1)	120(3)	—	120(1)

R′ substituents and, hence, stronger donor properties of the nitrogen atom, the donor-acceptor interaction Si ← N is weakened and the lengthening of the silicon—nitrogen distance in this series (2.30, 2.68 and 3.16 Å, respectively) appears to be correlated with the values of steric constants E_S for R′ substituents (0, 1.24 and 2.78 respectively [12]). Consequently, higher values of the silicon—nitrogen distances in this case are mainly determined by the steric effects of substituents which prevail over electronic effects.

It follows from the comparison of molecular structures IV and VI that, although the steric hindrance between the R_{eq} and R′ substituents is equal, the Si—N distances have the values 2.68 and 3.19 Å. Such remarkable variation of the interatomic distances (~0.5 Å) should be attributed to the electronic effects of the substituents. In contrast to compound IV, compound VI has a phenyl group attached to the nitrogen and p—π interaction takes place involving the nitrogen lone pair electrons in the π-electronic system of the phenyl ring. This eliminates the possibility of Si ← N donor-acceptor bond formation, as evidenced by the high value of the silicon—nitrogen distance (3.19 Å). The same holds true for compound VII. Conjugation of the nitrogen atom with the phenyl ring of the R′ substituent in both VI and VII is equally accompanied by shortening of the N—C(R′) bond, as compared with N—C(5) and N—C(7), by 0.06 Å (see Table 3).

The comparison of structures I and V demonstrates that in the case of V the Si ← N donor-acceptor bonding does not occur owing to the presence of a bulky substituent at the nitrogen atom (the volume of the t-butyl group is ~70 $Å^3$).

Although the nitrogen atom in the molecules VI and VII has sp^2 hybridization, the bonds are not strictly planar, as the nitrogen deviates from the plane formed by the atoms C(7), C(5) and C(R′) toward the silicon atom by 0.12 and 0.16 Å, respectively.

The compounds I—VII, as compared with silatranes, are characterized by somewhat shorter Si—O and Si—C bond lengths, the C—O, C—C and C—N distances remaining unaltered.

The eight-membered heterocycles of compounds IV—VII vary as to their conformation (see the structural formulae). Molecule IV is in the boat-boat (BB) conformation, VI and VII are in the chair-chair (CC) conformation, and V is in the transition state, all due to the different degrees of Si—N interaction. Upon transition from the BB to the CC conformation the obtuse angles Si—N—C(5) and Si—N—C(7) become acute (see Table 3).

The molecules in the crystals are packed according to the Van der Waals distances.

References

1 J.W. Turley and F.P. Boer, J. Amer. Chem. Soc., 90 (1968) 4026.

2 Ya.Ya. Bleidelis, A.A. Kemme, G.I. Zelchan and M.G. Voronkov, Khim. Geteroc. Soed., (1973) 617.

3 L. Parkany, J. Nagy and K. Simon, J. Organometal. Chem., 101 (1975) 11.

4 A.A. Kemme, Ya.Ya. Bleidelis, V.A. Pestunovich, V.P. Baryshok and M.G. Voronkov, Dokl. Akad. Nauk SSSR, 243 (1978) 688.

5 C. Eaborn, K.J. Odell, A. Pidcock and G.R. Scollary, J. Chem. Soc., Chem. Commun., (1976) 317.

6 G.R. Skollary, Aust. J. Chem., 30 (1977) 1007.

7 J.J. Daly and F. Sanz, J. Chem. Soc., Dalton Trans., (1974) 2051.

8 O.A. D'yachenko, L.O. Atovmyan, S.M. Aldoshin, T.L. Krasnova, V.V. Stepanov, E.A. Chernishev, A.G. Popov and V.V. Antipova, Izvest. Akad. Nauk SSSR, Ser. Khim., (1974) 2648.

9 O.A. D'yachenko, L.O. Atovmyan, S.M. Aldoshin, N.G. Komalenkova, A.G. Popov, V.V. Antipova and E.A. Chernishov, Izvest. Akad. Nauk SSSR, Ser. Khim., (1975) 1081.

10 G. Germain, P. Main and M.M. Woolfson, Acta Cryst. A, 27 (1971) 368.

11 F.P. Boer and J.W. Turley, J. Amer. Chem. Soc., 91 (1969) 4134.

12 S.H. Unger and C. Hansch in R.W. Taft (Ed.), Progress in Physical Organic Chemistry, Vol. 12, J. Wiley and Sons, New York, 1976.