Synthesis, Stereochemistry, and Crystal and Molecular Structure of endo-3-Methyl-exo-3-hydroxy-3-silabicyclo[3.2.1]octane

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The structure of the title compound was determined by an X-ray diffraction study. The crystals are mono-clinic, $a = 21.733(2)$, $b = 10.328(1)$, $c = 8.587(2)$ Å, $\beta = 105.39(1)°$, space group $C2/c$, $Z = 8$. The structure was solved by direct methods from diffractometer data and refined to an R value of 0.053. The silacyclohexane ring in this bicyclic system adopts a chair conformation which is substantially flattened at the silicon end. The endo-disposition of the 3-methyl substituent was confirmed by this study. The bond angles and distances are in close agreement with those in endo-3-methyl-3-silabicyclo[3.2.1]-octane as determined by molecular mechanics calculations and gas-phase electron diffraction.

Both the stereochemical changes that occur at silicon in a chemical reaction and the conformational shape of silicon heterocycles have been of concern to us. Based upon this interest we have synthesized the parent ring system, 3-silabicyclo[3.2.1]octane (SBO) and several derivatives which involve substituent variation about the silicon centre.[1] Analogous heterocycles which contain nitrogen, oxygen, phosphorus, sulphur, or other elements with non-bonding electrons are necessarily more complex with respect to their conformational analysis.

In 1972 two independent reports by Allinger [2] and by Oullette [3] appeared which described the molecular mechanics calculations on a variety of acyclic and cyclic silanes, including silacyclohexane derivatives. Subsequently, Oullette carried out force field calculations on 1-, 2-, 3-, and 4-methylsilacyclo-hexane, several t-butylsilacyclohexanes, and 3-silabicyclo-[3.2.1]octane.[4] The 3,3-dimethyl, endo-3-methyl, and exo-3-methyl derivatives of SBO were also examined. These cal-culations revealed intriguing conformational preferences. For example, the methyl group in 1-methylsilacyclohexane is biased in an axial position (by 0.2 kcal mol⁻¹) and a 1-t-butyl substituent favoured an equatorial position by just 1.28 kcal mol⁻¹. However, no experimental verification of these cal-culations were available at that time. Recently, we have experimentally determined the equilibrium constants for the isomerization in 3-methyl-3-silabicyclo[3.2.1]octane (MSBO) [1] and in 2-methyl-2-silabicyclo[2.2.1]heptane.[5] In collaboration with Hilderbrandt and Shen, the molecular structures of SBO and endo-MSBO were established through gas-phase electron diffraction analysis.[6]

During the course of our synthetic work we isolated a crystalline substance by treatment of 3-methoxy-3-methyl-3-silabicyclo[3.2.1]octane (isomer mixture) with silica gel in boiling ethyl acetate.[7] The product, endo-3-methyl-exo-3-hydroxy-3-silabicyclo[3.2.1]octane (I) appeared to crystallize preferentially from the isomer mixture. The isomer assign-ment of the silanol was tentatively made on the basis of the relative chemical shifts of the Si-CH₃ substituent in both the ¹H and ¹³C n.m.r. spectra: δ_H 0.2 (endo-CH₃) and 0.02 (exo-CH₃); δ_C 3.2 (endo-CH₃) and 1.7 (exo-CH₃) p.p.m. The exo-CH₃ absorption in the ¹H and ¹³C n.m.r. spectra has been con-sistently upfield in most cases that we have investigated.[7]

The current X-ray study was undertaken in order to confirm the stereochemical assignments in the silanol and to establish the conformational shape of the ring. Few X-ray crystal structure determinations have been made on silicon hetero-

(1)

and molecular mechanics calculations on MSBO was also of interest to us.

Experimental

Synthesis.—A mixture of exo- and endo-3-methoxy-3-methyl-3-silabicyclo[3.2.1]octane (0.50 g, 2.9 mmol) and silica gel (2 g; Fisher; 28—200 mesh) in ethyl acetate (3 ml) was stirred at reflux temperature for 24 h. Additional silica gel (1 g) was added and the mixture was stirred at reflux for another 36 h. The silica gel was filtered and washed with ethyl acetate and pentane. The combined filtrates were dried (Na₂SO₄) and the solvent was evaporated under a nitrogen purge with warming by an external bath. Bulb-to-bulb distillation of the residue at 50—60 °C (0.5 mmHg) gave a colourless liquid (0.35 g) containing a solid. The product was purified by preparative g.l.c. (5% QF-1 on Chromosorb W, 6 ft × ¼ in column; column temperature 100 °C, He flow rate of 60 ml min⁻¹). The solid silanol was recrystallized from pentane to give a pure sample, m.p. 91—92 °C. The ¹³C n.m.r. spectrum (CDCl₃ solvent) of the endo-methyl-exo-hydroxy-isomer showed peaks at δ 41.3, 34.5, 31.6, 25.7, and 3.2 p.p.m.; the exo-methyl isomer gave the corresponding peaks at δ 41.4, 34.0, 31.4, 25.7, and 1.7 p.p.m. The ¹H n.m.r. spectrum (CDCl₃) showed peaks at δ 2.5 (2 H, m), 1.1—2.0 (6 H, m), 0.7—1.0 (4 H, m), 0.20 (s, endo-methyl), and 0.02 (s, exo-methyl); the OH signal was observed in the δ 1—2.5 region. The i.r. spectrum (CCl₄) showed peaks at 3 670 (w), 3 270br (m), 2 900 (s), 1 440 (m), 1 390 (w), 1 390 (w), 1 250 (s), 1 210 (m), 1 110 (m), 1 010 (m), 980 (m), 890 (s), and 820 (s) cm⁻¹. The silanol gave a satisfactory elemental analysis (Found: C, 61.3; H, 10.1. Calc. for C₈H₁₆OSi: C, 61.5; H, 10.3%).

Crystal Data.—C₈H₁₆SiO, monoclinic, $a = 21.733(2)$, $b = 10.328(1)$, $c = 8.587(2)$ Å, $\beta = 105.39(1)°$, $U = 1\,958.3$ Å³,
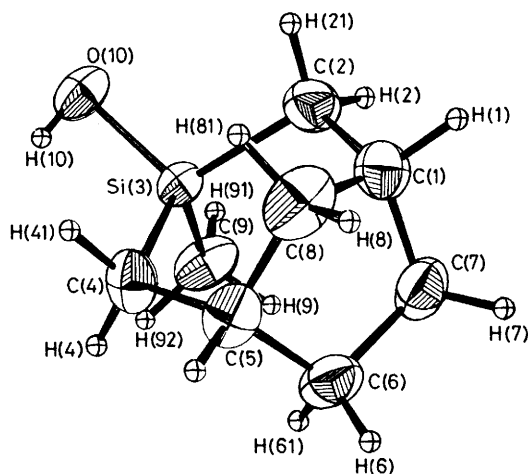
Figure 1. Molecule of endo-3-methyl-exo-3-hydroxy-3-silabicyclo-[3.2.1]octane showing the numbering scheme used

Table 1. Fractional co-ordinates ($\times 10^4$) for non-hydrogen atoms with e.s.d.s in parentheses

Atom	x	y	z
C(1)	1 892(2)	8 131(4)	7 655(6)
C(2)	1 569(2)	9 000(4)	6 190(6)
Si(3)	860(0)	8 229(1)	4 791(1)
C(4)	566(2)	7 012(5)	6 028(5)
C(5)	1 077(2)	6 535(4)	7 505(5)
C(6)	1 632(2)	5 853(4)	7 082(8)
C(7)	2 135(2)	6 871(4)	7 145(7)
C(8)	1 412(3)	7 651(5)	8 526(5)
C(9)	1 044(3)	7 474(5)	2 986(5)
O(10)	318(1)	9 361(2)	4 073(3)

Table 2. Fractional co-ordinates ($\times 10^3$) and U values for hydrogen atoms, with e.s.d.s in parentheses

Atom	x	y	z	U	O.F.
H(1)[C(1)]	236(2)	865(5)	825(7)	0.11(2)	
H(2)[C(2)]	185(2)	928(5)	551(7)	0.10(2)	
H(21)[C(2)]	144(2)	983(5)	644(5)	0.08(1)	
H(4)[C(4)]	45(3)	605(6)	534(8)	0.15(2)	
H(41)[C(4)]	18(2)	735(4)	630(6)	0.08(1)	
H(5)[C(5)]	88(2)	602(3)	808(6)	0.09(1)	
H(6)[C(6)]	176(2)	514(5)	772(7)	0.11(2)	
H(61)[C(6)]	148(2)	548(4)	617(6)	0.06(1)	
H(7)[C(7)]	255(2)	648(4)	791(6)	0.09(1)	
H(71)[C(7)]	218(3)	683(5)	597(8)	0.12(2)	
H(8)[C(8)]	167(2)	849(6)	950(8)	0.11(2)	
H(81)[C(8)]	107(2)	837(4)	869(6)	0.08(1)	
H(9)[C(9)]	145(3)	705(6)	325(8)	0.11(2)	
H(91)[C(9)]	121(4)	804(9)	235(14)	0.21(4)	
H(92)[C(9)]	76(3)	669(7)	248(10)	0.15(3)	
H(10)[O(10)]	4	886	408	0.10	0.40
	9	994	460	0.10	0.40
	2	959	307	0.10	0.20

Table 3. Bond lengths and angles with e.s.d.s in parentheses

(a) Distances (Å)

C(1)–C(2)	1.555(6)	C(5)–C(6)	1.522(6)
C(1)–C(7)	1.523(7)	C(5)–C(8)	1.512(7)
C(1)–C(8)	1.519(7)	C(5)–H(5)	0.91(5)
C(1)–H(1)	1.15(5)	C(6)–C(7)	1.511(7)
C(2)–Si(3)	1.864(4)	C(6)–H(6)	0.92(6)
C(2)–H(2)	0.99(5)	C(6)–H(61)	0.86(4)
C(2)–H(21)	0.94(5)	C(7)–H(7)	1.05(4)
Si(3)–C(4)	1.864(4)	C(7)–H(71)	1.02(6)
Si(3)–C(9)	1.871(4)	C(8)–H(8)	0.89(6)
Si(3)–O(10)	1.657(2)	C(8)–H(81)	1.08(4)
C(4)–C(5)	1.529(6)	C(9)–H(9)	0.96(6)
C(4)–H(4)	1.16(6)	C(9)–H(91)	0.94(11)
C(4)–H(41)	0.99(4)	C(9)–H(92)	1.04(7)
		C(10)–H(10)	0.80

(b) Angles (°)

C(2)–C(1)–C(7)	111.6(4)	C(6)–C(5)–H(5)	112(3)
C(2)–C(1)–C(8)	111.4(4)	C(8)–C(5)–H(5)	111(3)
C(7)–C(1)–C(8)	102.1(4)	C(5)–C(6)–C(7)	106.8(4)
C(2)–C(1)–H(1)	104(3)	C(5)–C(6)–H(6)	113(3)
C(7)–C(1)–H(1)	101(2)	C(7)–C(6)–H(6)	117(3)
C(8)–C(1)–H(1)	126(3)	C(5)–C(6)–H(61)	107(3)
C(1)–C(2)–Si(3)	113.0(3)	C(7)–C(6)–H(61)	116(3)
C(1)–C(2)–H(2)	115(3)	H(6)–C(6)–H(61)	99(4)
Si(3)–C(2)–H(2)	106(3)	C(1)–C(7)–C(6)	107.0(4)
C(1)–C(2)–H(21)	116(3)	C(1)–C(7)–H(7)	116(3)
Si(3)–C(2)–H(21)	107(2)	C(6)–C(7)–H(7)	104(3)
H(2)–C(2)–H(21)	99(4)	C(1)–C(7)–H(71)	118(3)
C(2)–Si(3)–C(4)	105.8(2)	C(6)–C(7)–H(71)	102(3)
C(2)–Si(3)–C(9)	113.0(3)	H(7)–C(7)–H(71)	109(4)
C(4)–Si(3)–C(9)	111.8(2)	C(1)–C(8)–C(5)	104.5(3)
C(2)–Si(3)–O(10)	108.7(2)	C(1)–C(8)–H(8)	100(4)
C(4)–Si(3)–O(10)	111.8(2)	C(5)–C(8)–H(8)	119(4)
C(9)–Si(3)–O(10)	105.8(2)	C(1)–C(8)–H(81)	115(2)
Si(3)–C(4)–C(5)	114.0(3)	C(5)–C(8)–H(81)	111(2)
Si(3)–C(4)–H(4)	111(3)	H(8)–C(8)–H(81)	107(5)
C(5)–C(4)–H(4)	100(3)	Si(3)–C(9)–H(9)	113(4)
Si(3)–C(4)–H(41)	109(3)	Si(3)–C(9)–H(91)	115(6)
C(5)–C(4)–H(41)	113(3)	H(9)–C(9)–H(91)	87(6)
H(4)–C(4)–H(41)	110(4)	Si(3)–C(9)–H(92)	116(4)
C(4)–C(5)–C(6)	113.4(4)	H(9)–C(9)–H(92)	99(5)
C(4)–C(5)–C(8)	111.5(4)	H(91)–C(9)–H(92)	121(7)
C(6)–C(5)–C(8)	101.7(4)	Si(3)–O(10)–H(10)	90
C(4)–C(5)–H(5)	107(3)		

to the hygroscopic nature of the crystals no density measurement was made.)

A crystal of 0.25 × 0.35 × 0.50 mm mounted in a glass capillary was used for intensity measurements on an Enraf–Nonius CAD-4 diffractometer. Cell dimensions and their standard deviations were obtained by least squares refinement of 25 accurately centred reflections. A total of 2 023 reflections (to $\theta < 25°$) was measured by the ω—2θ scan technique, with background counts being taken on each side of the peak. The intensities of three standard reflections showed no significant change during data collection. 1 118 Reflections were considered observed, having $I > 3\sigma(I)$. Lorentz and polarisation corrections were applied as usual. Form factors for non-hydrogen atoms were taken from ref. 8 and for hydrogen atoms from ref. 9. Anomalous terms for silicon were included.[10]

All calculations were carried out on the University of Petroleum and Minerals IBM 3033 computer using SHELX-76 [11] crystallographic programs.

The structure was solved by direct methods. The automatic multi-solution routine of SHELX-76 was used with all the unique reflections to generate a series of E maps, one of which correctly located all the non-hydrogen atomic positions. Full matrix least squares refinement with isotropic temperature factors reduced R to 0.088 for the observed reflections; anisotropic temperature factors reduced R to 0.062. Plausible hydrogen atom positions were located from a difference map, but subsequent attempts at refinement of these positions resulted in an unreasonably short (ca. 0.6 Å) O(10)–H(10) distance. A second difference map was therefore produced,
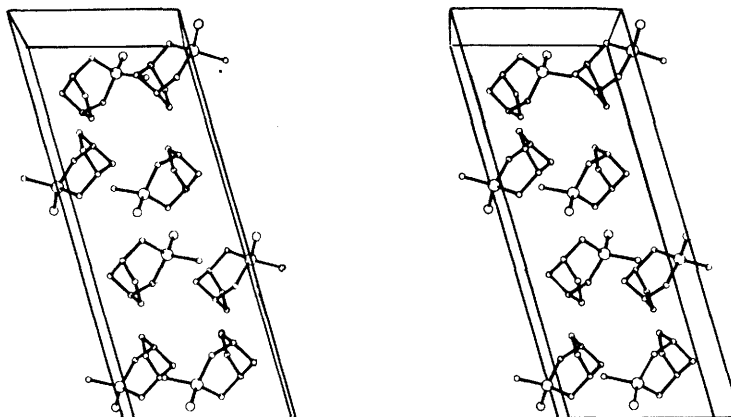
Figure 2. Stereopair showing the packing of molecules

based on all the atomic positions except H(10). Three possible sites for H(10) were identified, including the original position, but attempts to refine them individually resulted in the same outcome as before. H(10) was therefore considered as disordered, and the three positions were assigned occupancy factors of 0.4, 0.4, and 0.2, respectively (Table 2), based on the relative peak heights. The final least squares cycles were run constraining the H(10) positions, and an R value of 0.052 was obtained by refining the remaining hydrogen-atoms isotropically and the non-hydrogen atoms anisotropically. A weighting scheme based on counting statistics was used, with $w = 1.0 \ [\sigma^2(F_0) + 0.0187(F_0)^2]^{-1}$ minimising Δw^2. A final difference map showed no significant features.

Results and Discussion

Figure 1 is an ORTEP [12] drawing illustrating 50% probability ellipsoids for the non-hydrogen atoms and arbitrary spheres of radius 0.1 Å for the hydrogen atoms; Figure 2 shows the packing of the molecules. The atomic co-ordinates of the non-hydrogen and hydrogen atoms are given in Tables 1 and 2, respectively. Interatomic distances and valence angles are listed in Table 3. Anisotropic thermal parameters as well as observed and calculated structure factors are listed in Supplementary Publication No. SUP 23514 (9).*

The first molecular mechanics calculations on MSBO were carried out by Oullette.[4] Subsequently, Hilderbrandt performed a modified force field calculation on these same structures; however, this was optimized to reproduce the observed electron diffraction structures instead of the equilibrium internuclear bond lengths.[6] In general, the two different calculations were in reasonably close agreement. The most noticeable differences were in the torsional angles; for example, in endo-MSBO Oulette found the torsional angles Si⁻C(4)⁻C(5)⁻C(6) and C(1)⁻C(2)⁻Si(3)⁻C(4) to be 63.9 and 21.5°, respectively, whereas Hilderbrandt calculated them to be 58.5 and 30.3°, respectively.

A comparison of the X-ray data for the silanol and the force field calculation by Oullette on endo-MSBO is shown in Table 4. Although the force field calculation on 3,3-dimethyl-3-silabicyclo[3.2.1]octane might be deemed a better model for the silanol (because of the two substituents on the silicon), inspection of Oullette's calculations shows that the data for endo-MSBO and the 3,3-dimethyl derivative to be nearly identical. Also given in this table are Hilderbrandt's cal-

Table 4. Comparison of bond lengths and angles in endo-3-methyl-exo-3-hydroxy-3-silabicyclo[3.2.1]octane with calculated values for endo-MSBO

Distances (Å)	X-Ray		Calc.[4]
C(1)⁻C(2)	1.555 [1.529(6)] *		1.533
C(2)⁻Si(3)	1.864 [1.864(4)]		1.870
C(5)⁻C(6)	1.522 [1.523(7)]		1.530
C(1)⁻C(8)	1.519 [1.512(7)]		1.524
C(6)-C(7)	1.511		1.535

Angles (°)	X-Ray	Calc.[4]	Calc.[6]
C(1)⁻C(2)⁻Si(3)	113.0 [114.0(3)]	113.3	110.5
C(2)⁻Si(3)⁻C(4)	105.8(2)	106.5	107.3
C(2)⁻C(1)⁻C(8)	111.4 [111.5(4)]	111.1	110.0
C(2)⁻C(1)⁻C(7)	111.6 [113.4(4)]	112.4	111.0
C(7)⁻C(1)⁻C(8)	102.1 [101.9(4)]	103.3	104.5
C(1)⁻C(8)⁻C(5)	104.5(3)	103.8	103.9
C(1)⁻C(7)⁻C(6)	107.0 [106.8(4)]	106.4	106.5

Torsional angles (°)	X-Ray	Calc.[4]	Calc.[6]
C(1)⁻C(8)⁻C(5)⁻C(6)	41.6 (39.7)	39.4	36.2
C(8)⁻C(5)⁻C(6)⁻C(7)	27.3 (22.0)	24.3	22.3
Si(3)⁻C(4)⁻C(5)⁻C(6)	61.5 (61.1)	63.9	58.5
C(1)⁻C(7)⁻C(6)⁻C(5)	3.3	0.2	0.0
C(1)⁻C(2)⁻Si(3)⁻C(4)	24.2 (24.5)	21.5	30.3
C(2)⁻C(1)⁻C(8)⁻C(5)	79.6 (79.7)	79.5	82.9

* The value in square brackets represents the distance or angle counterpart due to symmetry.

culated results. The agreement of the X-ray data with Oullette's force field calculations is very good, and uniformly closer than with Hilderbrandt's calculations.

The Si(3)⁻C(2) and Si(3)⁻C(4) distances of 1.864(4) Å are identical, as expected from symmetry and agree closely with the force field calculations.[4] By contrast a ' normal ' Si⁻C bond is given as 1.942 Å.[13]

The seven $(sp^3\text{-}sp^3)$ bonds in the silanol have a mean length of 1.524(6) Å, which agrees well with the 1.530 Å in endo-MSBO and with 1.529(8) Å in exo-3-p-nitrobenzyl-endo-3-phenyl-3-phosphoniabicyclo[3.2.1]octane bromide.[14] However, these bond lengths are appreciably lower than the value of 1.544 (3) Å given in ref. 15, which is based on a large number of studies, not all of them of good accuracy. The mean of 11 valence angles at the tetrahedral atoms in the silanol is 108.8(4)° which agrees well with the ideal value of 109.5°, and with the 107.9° value from force field calculations.[4]

The silacyclohexane ring in the silanol adopts a chair

conformation which is flattened at the silicon end. The flap angles between C(1)–C(2)–C(4)–C(5) and C(2)–Si(3)–C(4) and C(1)–C(8)–C(5) are 157.6 and 111.4°, respectively. The corresponding angles from the electron diffraction structures of *endo*-MSBO are 160.6 and 101.3°, respectively. Also, the dihedral angle between C(1)–C(7)–C(6)–C(5) and C(5)–C(8)–C(1) is 138.7° from *X*-ray data and 146.1° from the electron diffraction study of *endo*-MSBO. A least squares plane calculation shows that C(1)–C(2)–C(4)–C(5) are coplanar and that Si(3) and C(8) are 0.429 and −0.864 Å away from this plane. As mentioned in a previous report [6] the ring flattening in the six-membered ring results from two factors, namely, the substitution of a carbon by silicon and the presence of the C(6)–C(7) bridge, these effects being nearly additive. Thus, the flap angle at the silicon end of the ring is 138.7° in silacyclohexane compared to 130.4° in cyclohexane. The parent hydrocarbon, bicyclo[3.2.1]octane, by contrast, shows a 138.9° angle and SBO itself was measured (electron diffraction) at 145.0°. The presence of the *endo*-methyl substituent in MSBO increases the flap angle further due to steric crowding. The *exo*-hydroxy-group in the silanol serves to diminish the flap angle by 3.0° relative to MSBO.

An examination of intermolecular contacts between non-hydrogen atoms revealed two distances which were significantly less than the sum of the relevant van der Waal's radii.[16] These contacts, both of type O(10) · · · O(10) are of magnitude 2.69 and 2.71 Å, respectively. Clearly, the possibility of hydrogen bonding must be considered in these instances, but the disorder in the H(10) position is not consistent with such a scheme.

References
1 S. E. Cremer and C. Blankenship, *Tetrahedron Lett.*, 1980, 3979.
2 M. T. Tribble and N. L. Allinger, *Tetrahedron*, 1972, **28**, 2147.
3 R. J. Ouellette, D. Baron, F. Stolfo, A. Rosenblum, and P. Weber, *Tetrahedron*, 1972, **28**, 2163.
4 R. J. Ouellette, *J. Am. Chem. Soc.*, 1974, **96**, 2421.
5 S. E. Cremer and C. S. Blankenship, *J. Org. Chem.*, 1982, **47**, 1626.
6 Q. Shen, R. L. Hilderbrandt, C. S. Blankenship, and S. E. Cremer, *J. Organometal. Chem.*, 1981, **214**, 155.
7 C. S. Blankenship, Ph.D. thesis dissertation, Marquette University, 1982.
8 D. T. Cromer and J. B. Mann, *Acta Crystallogr.*, 1968, A24, 321.
9 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
10 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
11 G. M. Sheldrick, SHELX Program for Crystal Structure Determination, University of Cambridge, 1976.
12 C. R. Johnson, ORTEP Report, ORNL-5138, Oak Ridge National Laboratory, 1976.
13 L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 1967, p. 224.
14 Mazhar ul Haque, W. Horne, S. E. Cremer, P. W. Kremer, and J. T. Most, *J. Chem. Soc., Perkin Trans.* 2, 1980, 1467.
15 'Molecular Structures and Dimensions,' eds, O. Kennard, D. G. Watson, F. H. Allen, N. W. Isaacs, W. D. S. Motherwell, R. C. Pattersen, and W. G. Town, Oosthoek, Utrecht, 1972, Vol. A1, PS2.
16 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.