78. Crystal Structure of 4-Trimethyltin-quinuclidinium Perchlorate

by **Margareta Zehnder**

Institut für Anorganische Chemie der Universität, Spitalstrasse 51, CH-4056 Basel, Switzerland

(10.XII.79)

Summary

The crystal structure of 4-trimethyltin-quinuclidinium perchlorate has been determined by direct methods and refined by least squares techniques. Crystals of $C_{10}H_{22}ClNO_4Sn$ are monoclinic, space group $I2/c$ with lattice parameters $a = 29.445(13)$, $b = 18.400(8)$, $c = 11.300(5)$ Å, $\beta = 95.82(5)°$, $V = 6090.65$ Å^3, and two independent molecules ($Z = 16$). Interatomic distances are compared with those of known structures of quinuclidinium chloride and 4-haloquinuclidinium chlorides and perchlorates.

Introduction. – The pK_a-values of quinuclidine and 4-substituted derivatives have been determined by *Grob et al.* [1] and were found to depend strongly on the nature of the substituent in the 4-position. It was therefore of interest to learn whether there is a corresponding change in the bond lengths and angles and in the C(3)...N nonbonded distance[1]) as the substituent is varied. *Kurahashi et al.* [2] have recently solved the X-ray structures of quinuclidinium chloride and of 4-haloquinuclidinium chlorides and perchlorates. This communication describes the crystal structure of 4-trimethyltin-quinuclidinium perchlorate, in which, in contrast to the halogen derivatives, the substituent is a bulky, electron-donating group *(vide infra)*.

Crystallographic Part. – The systematic absences, hkl: $h+k+l=2n+1$, h0l: $h=2n+1$, $l=2n+1$, are compatible with the monoclinic space groups Ic or $I2/c$. Lattice constants are $a = 29.445(13)$, $b = 18.400(8)$, $c = 11.300(5)$ Å, $\beta = 95.82(5)°$, $V = 6090.65$ Å^3, $D_{obs.} = 1.630$, $D_{calc.} = 1.633$ g/cm^3 for $Z = 16$. The intensities of 3963 independent reflexions were collected ($\theta/2\theta$ scan) in the range $2 < \theta < 27°$ with a *Philips*-PW-1100 diffractometer equipped with a fine-focus molybdenum tube and a graphite monochromator (MoK_α, $\lambda = 0.71069$ Å). No absorption correction was made. Since the *Patterson* map could not be interpreted, the structure was solved by direct methods with the program SHELX-76 [3], assuming the space group to be $I2/c$. Scattering factors for neutral atoms (except H-atoms) and terms for anomalous dispersion were taken from *Cromer et al.* [4]. Scattering factors for H-atoms are from [5]. 1770 reflexions with $(F_0) > 3\sigma(F_0)$ were used in the anisotropic refinement. All parameters converged and a subsequent difference *Fourier* map led to the location of all H-atoms. The final R-index is 0.038 ($R = \sum ||F_0| - |F_c|| / \sum |F_0|$). Atomic positional and thermal parameters are listed in *Table 1*, positional parameters of H-atoms in *Table 2*, while interatomic distances and bond angles are given in *Table 3*.

[1]) The numbering is that of the *Figure*.

0018-019X/80/3/0750-04$01.00/0

Table 1. *Positional and thermal parameters of the nonhydrogen atoms and their standard deviations.* The temperature factors are of the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^*)]$. The general positions are: $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}) \pm (x,y,z),\ (x,-y,\frac{1}{2}+z)$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cation									
Sn	0.0890(1)	0.5507(1)	0.0164(1)	0.0724(8)	0.0684(8)	0.0465(6)	−0.0010(7)	−0.0028(5)	−0.0014(8)
C(1)	0.2098(6)	0.6790(9)	0.1635(15)	0.1130(9)	0.0497(9)	0.0572(9)	−0.0035(9)	0.0113(9)	−0.0124(9)
C(2)	0.1621(6)	0.6607(9)	0.1092(15)	0.0923(9)	0.0547(9)	0.0634(9)	0.0006(9)	−0.0053(9)	0.0046(9)
C(3)	0.1569(6)	0.5807(8)	0.0803(12)	0.0786(9)	0.0454(9)	0.0321(8)	0.0067(7)	0.0185(8)	0.0093(9)
C(4)	0.1917(6)	0.5636(9)	−0.0091(12)	0.0885(9)	0.0743(9)	0.0373(9)	0.0059(9)	0.0032(8)	0.0004(9)
C(5)	0.2391(6)	0.5887(9)	0.0322(13)	0.0809(9)	0.0828(9)	0.0555(9)	−0.0066(9)	0.0209(9)	−0.0060(9)
C(6)	0.2236(5)	0.5534(9)	0.2317(12)	0.0795(9)	0.0642(8)	0.0426(9)	−0.0027(9)	0.0008(9)	−0.0111(9)
C(7)	0.1739(5)	0.5391(9)	0.1946(12)	0.0838(9)	0.0617(9)	0.0369(8)	0.0078(9)	0.0031(8)	0.0048(9)
C(8)	0.0861(7)	0.4347(8)	0.0028(15)	0.1127(9)	0.0868(9)	0.0619(9)	0.0118(9)	−0.0110(9)	−0.0359(9)
C(9)	0.0429(7)	0.5871(15)	0.1347(19)	0.0838(9)	0.1528(9)	0.1063(9)	0.0032(9)	0.0184(9)	0.0172(9)
C(10)	0.0710(8)	0.6019(11)	−0.1529(16)	0.1459(9)	0.0792(9)	0.0739(9)	0.0232(9)	−0.0445(9)	−0.0004(9)
N	0.2396(6)	0.6138(8)	0.1586(11)	0.0673(9)	0.0708(9)	0.0506(8)	−0.0002(7)	0.0012(8)	−0.0052(9)
Anion									
Cl	0.2791(1)	0.1629(2)	0.4297(3)	0.0743(3)	0.0657(3)	0.0617(2)	0.0098(2)	0.0059(2)	−0.0046(3)
O(1)	0.3056(4)	0.1556(7)	0.3335(10)	0.1290(9)	0.1176(9)	0.1076(8)	0.0189(8)	0.0632(8)	0.0085(8)
O(2)	0.2497(4)	0.1024(6)	0.4330(9)	0.0924(8)	0.0736(8)	0.1018(8)	0.0100(7)	0.0139(7)	−0.0165(7)
O(3)	0.2510(4)	0.2254(6)	0.4145(10)	0.1289(9)	0.0661(8)	0.1176(9)	−0.0037(7)	0.0212(8)	0.0163(8)
O(4)	0.3091(4)	0.1656(9)	0.5318(11)	0.1259(9)	0.2066(9)	0.0928(9)	0.0237(9)	−0.0416(8)	−0.0418(9)
Cation									
Sn′	0.4523(1)	0.3380(1)	0.5284(1)	0.0761(7)	0.0705(7)	0.0449(5)	−0.0012(6)	0.0018(5)	0.0047(7)
C(1′)	0.3183(5)	0.3673(9)	0.3068(12)	0.0501(9)	0.0981(9)	0.0527(8)	−0.0036(8)	0.0043(8)	−0.0023(9)
C(2′)	0.3543(5)	0.3605(9)	0.4140(12)	0.0964(9)	0.0580(9)	0.0405(8)	−0.0055(8)	0.0067(7)	−0.0101(9)
C(3′)	0.4005(4)	0.3450(7)	0.3778(10)	0.0483(9)	0.0609(9)	0.0422(7)	−0.0015(7)	0.0045(6)	0.0053(8)
C(4′)	0.3973(6)	0.2751(8)	0.3051(13)	0.0680(10)	0.0674(9)	0.0540(9)	−0.0164(8)	0.0067(8)	0.0063(9)
C(5′)	0.3633(6)	0.2832(9)	0.1963(14)	0.0921(9)	0.0535(9)	0.0636(9)	−0.0077(8)	0.0064(9)	−0.0095(9)
C(6′)	0.3767(6)	0.4136(9)	0.1891(13)	0.0769(9)	0.0640(9)	0.0522(9)	−0.0036(8)	0.0076(8)	−0.0118(9)
C(7′)	0.4129(5)	0.4086(6)	0.2945(11)	0.0711(9)	0.0533(9)	0.0530(9)	0.0028(7)	0.0031(7)	−0.0053(8)
C(8′)	0.4298(9)	0.2577(9)	0.6510(19)	0.1494(9)	0.1005(9)	0.0770(9)	0.0391(9)	0.0062(9)	−0.0096(9)
C(9′)	0.5139(7)	0.3056(15)	0.4692(20)	0.0847(9)	0.1476(10)	0.1325(9)	0.0007(9)	−0.0172(9)	0.0111(9)
C(10′)	0.4611(11)	0.4461(9)	0.6020(20)	0.1632(10)	0.0871(10)	0.1068(9)	−0.0261(9)	−0.0048(9)	−0.0462(9)
N′	0.3418(4)	0.3564(7)	0.1964(9)	0.0718(8)	0.0773(9)	0.0365(6)	−0.0024(6)	0.0036(6)	0.0011(7)
Anion									
Cl′	−0.1509(2)	0.8902(3)	−0.6547(3)	0.0774(3)	0.0830(3)	0.0625(3)	0.0192(2)	0.0006(2)	0.0002(3)
O(1′)	0.3947(5)	0.6044(9)	0.3640(12)	0.0816(9)	0.2984(11)	0.1332(9)	0.0283(9)	−0.0022(9)	−0.0189(9)
O(2′)	0.3284(5)	0.5469(8)	0.3843(14)	0.1703(9)	0.0999(9)	0.2105(9)	−0.0233(9)	0.0461(9)	−0.0310(9)
O(3′)	0.3353(8)	0.6623(8)	0.4113(14)	0.2295(9)	0.0710(9)	0.1832(10)	−0.0001(9)	0.1224(9)	0.0654(9)
O(4′)	0.3346(5)	0.6225(9)	0.2307(11)	0.1538(9)	0.2156(9)	0.0616(8)	0.0650(9)	−0.0327(8)	−0.1261(9)

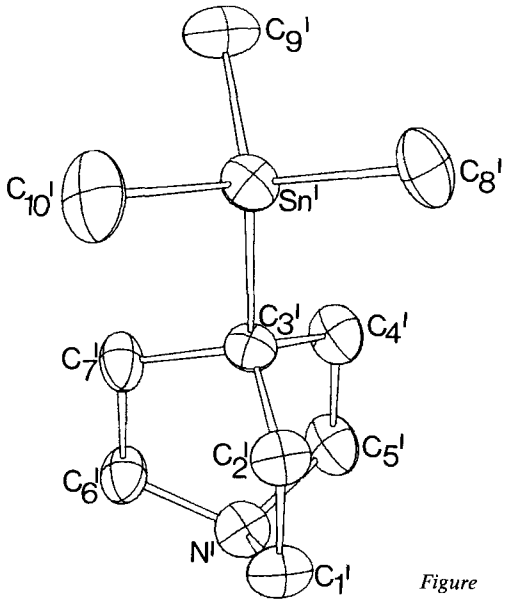
Table 2. *Positional parameters assigned to H-atoms*

	Atom	x	y	z		Atom	x	y	z
C(1)	H(1)	0.2083	0.6961	0.2097	C(1′)	H(1′)	0.2972	0.4250	0.2978
	H(1*)	0.2229	0.7109	0.1220		H(1′*)	0.2939	0.3370	0.3010
C(2)	H(2)	0.1363	0.6698	0.1434	C(2′)	H(2′)	0.3543	0.3177	0.4422
	H(2*)	0.1532	0.6785	0.0883		H(2′*)	0.3613	0.4058	0.4357
C(4)	H(4)	0.1799	0.5825	−0.0329	C(4′)	H(4′)	0.3973	0.2751	0.3051
	H(4*)	0.1919	0.5097	−0.0043		H(4′*)	0.4205	0.2626	0.2852
C(5)	H(5)	0.2641	0.5491	0.0258	C(5′)	H(5′)	0.3404	0.2565	0.2060
	H(5*)	0.2490	0.6294	0.0077		H(5′*)	0.3833	0.2748	0.1235
C(6)	H(6)	0.2581	0.9942	0.2817	C(6′)	H(6′)	0.3946	0.4085	0.1382
	H(6*)	0.2362	0.5657	0.2921		H(6′*)	0.3587	0.4567	0.1918
C(7)	H(7)	0.1644	0.4810	0.1643	C(7′)	H(7′)	0.4429	0.3989	0.2743
	H(7*)	0.1540	0.5474	0.2272		H(7′*)	0.4122	0.4665	0.3396
C(8)	H(8)	0.0556	0.4319	−0.0098	C(8′)	H(8′)	0.4442	0.2465	0.6764
	H(8*)	0.1116	0.3964	0.0202		H(8′*)	0.4063	0.2064	0.5642
	H(8**)	0.1097	0.4290	−0.0264		H(8′**)	0.3944	0.2711	0.6688
C(9)	H(9)	−0.0008	0.5592	0.0830	C(9′)	H(9′)	0.5453	0.2956	0.4917
	H(9*)	0.0345	0.6365	0.1038		H(9′*)	0.5236	0.3290	0.4268
	H(9**)	0.0498	0.5744	0.1621		H(9′**)	0.5121	0.2618	0.4455
C(10)	H(10)	0.0391	0.6030	−0.1385	C(10′)	H(10′)	0.4943	0.4558	0.6125
	H(10*)	0.0909	0.5896	−0.2389		H(10′*)	0.4309	0.4442	0.6203
	H(10**)	0.0654	0.6536	−0.1338		H(10′**)	0.4556	0.5040	0.5367
N	H(N)	0.2706	0.6257	0.1956	N′	H(N′)	0.3146	0.3570	0.1360

Table 3. *Bond distances and selected bond angles in the cation*

Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Angle (°)
N–C(1)	1.484(24)	N–C(1′)	1.500(19)	C(1)–N–C(5)	109.6(1.4)
C(1)–C(2)	1.502(27)	C(1′)–C(2′)	1.533(19)	C(5)–N–C(6)	108.1(1.3)
C(2)–C(3)	1.512(22)	C(2′)–C(3′)	1.488(20)	C(1)–N–C(6)	110.3(1.4)
C(3)–C(4)	1.545(22)	C(3′)–C(4′)	1.525(20)	C(2)–C(3)–C(4)	106.6(1.3)
C(4)–C(5)	1.494(25)	C(4′)–C(5′)	1.513(22)	C(4)–C(3)–C(7)	104.3(1.2)
C(5)–N	1.503(21)	C(5′)–N′	1.489(21)	C(2)–C(3)–C(7)	106.0(1.1)
N–C(6)	1.498(23)	N–C(6′)	1.479(21)	Sn–C(3)–C(2)	114.3(1.0)
C(6)–C(7)	1.480(23)	C(6′)–C(7′)	1.518(20)	Sn–C(3)–C(4)	113.3(0.9)
C(3)–C(7)	1.549(19)	C(3′)–C(7′)	1.567(19)	Sn–C(3)–C(7)	112.6(1.0)
C(3)–Sn	2.119(14)	C(3′)–Sn′	2.171(11)	C(1′)–N′–C(5′)	110.7(1.2)
C(8)–Sn	2.126(18)	C(8′)–Sn′	2.175(24)	C(5′)–N′–C(6′)	110.2(1.2)
C(9)–Sn	2.131(27)	C(9′)–Sn′	2.082(22)	C(1′)–N′–C(6′)	109.5(1.2)
C(10)–Sn	2.157(21)	C(10′)–Sn′	2.162(22)	C(2′)–C(3′)–C(4′)	107.6(1.2)
C(3)–N	2.550	C(3′)–N′	2.554	C(4′)–C(3′)–C(7′)	108.1(1.0)
				C(2′)–C(3′)–C(7′)	107.3(1.2)
				Sn′–C(3′)–C(2′)	112.6(0.8)
				Sn′–C(3′)–C(4′)	1118.(0.9)
				Sn′–C(3′)–C(7′)	109.2(0.8)

Discussion. – An ORTEP-plot of a 4-trimethyl-quinuclidinium cation is shown in the *Figure*. In contrast to quinuclidinium chloride and its halogen derivatives the molecules lacks any crystallographic symmetry. *Table 4* compares average distances of the C(1)–N- and the C(3)–N-bonds in trimethyl-quinuclidinium



Figure

Table 4. *Comparison of average distances in 4-R-quinuclidinium chlorides and perchlorates*[a])

4-R-Quinuclidinium salt		C(1)–N-Distance (Å)	C(3)–N-Distance (Å)
R	Anion		
H	Cl^-	1.508(7)	2.534(8)
F	Cl^-	1.490(7)	2.502(8)
F	ClO_4^-	1.51(2)	2.48(3)
Cl	Cl^-	1.489(9)	2.501(9)
Cl	ClO_4^-	1.504(11)	2.490(10)
Br.	Cl^-	1.501(10)	2.506(10)
Br.	ClO_4^-	1.50(3)	2.49(2)
J	ClO_4^-	1.50(3)	2.55(3)
$Sn(CH_3)_3$	ClO_4^-	1.484(24)	2.550(22)

[a]) Values for quinuclidinium chloride and 4-halo-quinuclidinium chlorides and perchlorates are taken from [2].

perchlorate with those in quinuclidinium chloride and halogen derivatives. No significant variation is observed. In particular, C(3)–N distances in 4-iodoquinuclidinium perchlorate and 4-trimethyltin-quinuclidinium perchlorate are found to be similar, although the pK_a-values are 8.95 and 11.52 respectively [1].

The author is grateful to Professor *C.A. Grob* for having suggested this problem.

REFERENCES

[1] *C.A. Grob, B. Schaub & M.G. Schlageter,* Helv. *63,* 57 (1980).
[2] *M. Kurahashi, P. Engel & W. Nowacki,* Z. Kristallogr. in press; *M. Kurahashi, P. Engel & W. Nowacki,* Z. Kristallogr. in press.
[3] *G.M. Sheldrick,* Göttingen, unpublished.
[4] *D.T. Cromer & J.B. Mann,* Acta crystallogr. A*24,* 321 (1968); *D.T. Cromer & D. Liebermann,* J. chem. Physics *53,* 1891 (1970).
[5] *R.F. Stewart, E.R. Davidson & W.T. Simpson,* J. chem. Physics *42,* 3175 (1965).