The Conformation of Tris(dimethylimoniomethyl)methide Diperchlorate in the Crystal and in Solution

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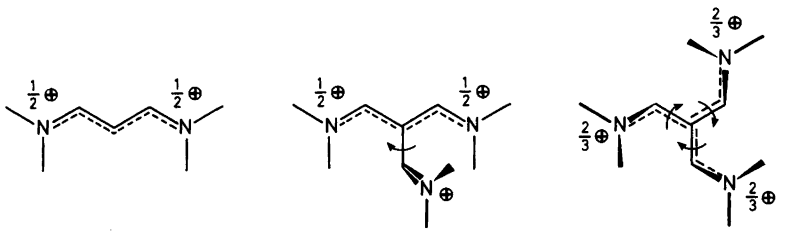
The crystal structure of the diperchlorate of this Y-shaped cyanine dication reveals a propeller-like C_3 conformation with relatively short CN bonds (~1.30 Å) and long CC bonds (~1.42 Å). NMR-spectroscopy confirms the presence of the C_3 conformer in solution and excludes the presence of a second conformer of lower symmetry. The two *N*-methyl signals coalesce at 170 °C (300 MHz, DMSO-d_6). The calculated rotational barrier, 94.1 kJ mol^{-1}, is lower than expected on the basis of the CN double bond character.

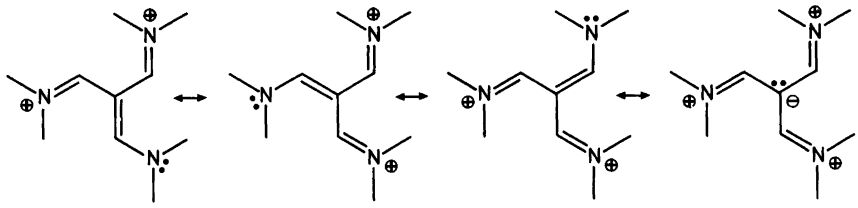
The simplest cyanine dyes are tetramethylamidinium homologues like the bis(dimethylamino)trimethinium salts. They are known to have a strong preference for the linear all-*anti* conformation **1**, both in the crystal and in solution.[1] Related homologues of hexamethylguanidinium have a triple-branched or Y-structure, and the question arises whether two of the branches will retain a cyanine-like planar stretched conformation **2**, leaving the third branch as a non-coplanar substituent, or whether conformation **3**, with all branches turned somewhat less out of the plane in a propeller-like fashion, will be preferred. There is the additional question of how molecule **3** should best be described in terms of the four mesomeric structures **3a, 3b, 3c** and **3d**. Finally, it is of particular interest to examine how the double-bond character in **2** and **3** is reflected in the observed lengths of the CN and CC bonds and in the rotational barriers in the same bonds.

If in our example, the tris(dimethylimoniomethyl)methide dication, only the propeller conformation **3** were populated, the site exchange of geminal NCH_3 groups would be the only process observable by dynamic NMR spectroscopy (DNMR), yielding a value for the CN rotational barrier but none for the CC barrier. Co-population of the unsymmetric conformation **2** makes possible the exchange between the two, giving a value for the (presumably lower) CC rotational barrier of the "propeller" **3**. This must equal the CC rotational barrier in the planar cyanine part of conformation **2**. By further cooling, the barrier in the substituent CC bond in **2** might



1 **2** **3**

Scheme 1.



Scheme 2. **3a** **3b** **3c** **3d**

also become observable, unless the substituent is exactly perpendicular to the "cyanine" part. In such a mixture of **2** and **3** it would, however, be impossible to tell in which CN bond and in which conformer the geminal NCH_3 exchange really takes place at high temperature, since all other interconversions involving the CC bonds would occur more rapidly.

Some related branched cyanine dyestuffs of more complex structure having indoline end groups have been reported by Reichardt and coworkers.[2-4] The crystal structure of one of these[3] reveals a symmetric propeller analogous to **3**, with a slight rotation (13°) about only the three CC bonds next to the central carbon, and with all molecules of the same crystal having the same chirality. In another case[4] a substituted cyanine-type conformation analogous to **2** is found for two different salts (I^- and BF_4^- counter ions); the rotation of the "substituent chain" out of the "cyanine plane" is now considerable (41° and 32°, respectively) and is again concentrated in the CC bond closest to the central carbon. However, the NMR signals of the latter in solution are not split in accordance with this low symmetry even at −90 °C, which suggests a propeller symmetry for the dissolved molecule also in this case. Rotational barriers within the propeller conformation alone cannot be determined for these molecules by DNMR, since the constitutional symmetry is too low to permit site exchange.

To exploit the possibilities of DNMR spectroscopy, we have started a systematic study of the series of chemically simpler *N*-methylated guanidinium homologues. Only the lowest member (**2** or **3**) is a known compound,[5,6] for which we prefer the simpler name tris(dimethylimoniomethyl) methide dication based on the most symmetric mesomeric formula **3d**, instead of 1-dimethylamino-2,2-bis(dimethylimonimethyl)-ethylene dication[5], based on an unsymmetric formula such as **3a**. The results of X-ray and DNMR studies of this compound are reported below. The synthesis of several higher homologues having branches of equal or different lengths, and either one or two cationic charges, has been accomplished for the first time and will be reported later.

Crystal structure determination

The crystals of $(C_{10}H_{21}N_3)^{++}$. $2ClO_4^-$ are monoclinic with cell dimensions a = 13.375(4), b = 19.037(8) and c = 13.894(4) Å; β = 104.85(2)°, space group $P2_1/n$ and Z = 8 (D_x = 1.48 gcm^{-3}, D_m = 1.46 gcm^{-3}). With $2\theta_{max}$ = 50° and Mo$K\alpha$ radiation, 3691 independent reflections [$I > 2.5\sigma(I)$] were recorded on an automatic diffractometer at ca. −150 °C. No corrections for absorption or secondary extinction were applied (crystal size 0.4×0.5×0.2 mm). The structure was solved by direct methods[7] and refined by the least-squares technique. Anisotropic thermal parameters were introduced for non-hydrogen atoms. Hydrogen atom positions were calculated and refined with isotropic temperature factors. The maximum r.m.s. amplitudes of thermal vibration range from 0.26 to 0.52 Å for the perchlorate oxygen atoms (for other atoms from 0.19 to 0.30 Å). The final R-value was 6.4% (R_w = 6.1%) for 3681 observed reflections. Final fractional coordinates with estimated standard deviations for the non-hydrogen atoms are listed in Table 1. Bond distances, bond angles and torsion angles with estimated standard deviations may be found in Table 2. Fig. 1 is a perspective drawing of the two independent cations in the asymmetric unit (accidentally of opposite chirality) showing the numbering of atoms. Fig. 2 is a stereoscopic view of the centrosymmetric unit cell contents.

Lists of thermal parameters, hydrogen atom coordinates, and observed and calculated structure factors are available from one of the authors (P.G.) on request.

Table 1. Final fractional coordinates (e.s.d.'s in parentheses) and equivalent temperature factors for non-hydrogen atoms.

Atom	*x*	*y*	*z*	U_{eq} [a]
Cl1	0.64370(11)	0.13338(8)	0.54546(10)	0.035
Cl2	0.92969(10)	0.12339(7)	0.08719(10)	0.033
Cl3	0.09260(12)	0.13494(8)	0.59926(11)	0.040
Cl4	0.48187(12)	0.05176(8)	0.15638(11)	0.038
O11	0.6065(3)	0.2013(2)	0.5058(3)	0.052
O12	0.6633(4)	0.1330(2)	0.6513(3)	0.065
O13	0.5663(4)	0.0818(2)	0.5065(4)	0.067
O14	0.7352(4)	0.1162(3)	0.5183(4)	0.089
O21	0.8704(3)	0.1664(2)	0.1365(3)	0.051
O22	0.9181(3)	0.1488(2)	−0.126(3)	0.052
O23	0.8941(4)	0.0520(2)	0.0840(4)	0.071
O24	1.0358(3)	0.1266(3)	0.1409(3)	0.060
O31	0.1629(5)	0.1589(4)	0.6833(4)	0.120
O32	0.1148(4)	0.1577(4)	0.5112(4)	0.115
O33	0.1131(6)	0.0611(3)	0.5983(6)	0.162
O34	−0.0128(4)	0.1408(3)	0.5949(4)	0.090
O41	0.5067(4)	0.0759(2)	0.2571(3)	0.054
O42	0.4686(5)	0.0225(3)	0.1563(4)	0.106
O43	0.3884(4)	0.0799(4)	0.1015(3)	0.119
O44	0.5628(4)	0.0638(3)	0.1091(4)	0.083
C1	0.3056(4)	0.1044(3)	0.3582(4)	0.027
C2	0.2572(5)	0.0622(3)	0.2748(4)	0.031
N1	0.1832(4)	0.0166(3)	0.2671(4)	0.035
C3	0.1517(5)	0.0288(3)	0.1793(5)	0.052
C4	0.1193(5)	0.0085(4)	0.3390(5)	0.053
C5	0.3219(4)	0.0742(3)	0.4565(4)	0.032
N2	0.3538(4)	0.1059(3)	0.5400(3)	0.034
C6	0.3867(5)	0.0638(4)	0.6331(4)	0.053
C7	0.3603(5)	0.1815(3)	0.5574(4)	0.042
C8	0.3684(4)	0.1620(3)	0.3464(4)	0.031
N3	0.3566(4)	0.2035(2)	0.2695(3)	0.033
C9	0.2667(5)	0.2033(3)	0.1829(5)	0.047
C10	0.4398(5)	0.2531(4)	0.2639(5)	0.056
C11	0.3731(4)	0.2216(3)	0.8924(4)	0.026
C12	0.2775(4)	0.1981(3)	0.9088(4)	0.028
N4	0.2401(4)	0.1344(2)	0.9072(3)	0.029
C13	0.2855(5)	0.0709(3)	0.8746(5)	0.047
C14	0.1425(5)	0.1221(3)	0.9338(5)	0.042
C15	0.3855(4)	0.2954(3)	0.8800(4)	0.030
N5	0.3151(4)	0.3407(3)	0.8358(3)	0.034
C16	0.2118(5)	0.3234(4)	0.7742(5)	0.052
C17	0.3397(6)	0.4166(3)	0.8414(5)	0.057
C18	0.4623(5)	0.1799(3)	0.9143(4)	0.031
N6	0.5480(4)	0.1904(2)	0.8887(3)	0.032
C19	0.5610(5)	0.2410(3)	0.8124(5)	0.043
C20	0.6440(5)	0.1513(4)	0.9358(5)	0.058

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Table 2. Bond distances (Å), bond angles (°) and torsion angles (°) with standard deviations.

Distance		Distance	
Cl1 –O11	1.443(5)	Cl1 –O12	1.426(5)
Cl1 –O13	1.429(5)	Cl1 –O14	1.408(6)
Cl2 –O21	1.431(5)	Cl2 –O22	1.439(4)
Cl2 –O23	1.437(5)	Cl2 –O24	1.425(5)
Cl3 –O31	1.377(7)	Cl3 –O32	1.399(6)
Cl3 –O33	1.434(7)	Cl3 –O34	1.400(6)
Cl4 –O41	1.429(5)	Cl4 –O42	1.425(6)
Cl4 –O43	1.394(6)	Cl4 –O44	1.422(6)
C1 –C2	1.421(8)	C1 –C5	1.445(8)
C1 –C8	1.417(8)	C2 –N1	1.300(8)
N1 –C3	1.466(8)	N1 –C4	1.480(9)
C5 –N2	1.281(8)	N2 –C6	1.490(8)
N2 –C7	1.457(8)	C8 –N3	1.306(8)
N3 –C9	1.466(8)	N3 –C10	1.476(9)
C11–C12	1.427(8)	C11–C15	1.430(8)
C11–C18	1.400(8)	C12–N4	1.310(8)
N4 –C13	1.474(8)	N4 –C14	1.464(8)
C15–N5	1.309(8)	N5 –C16	1.464(9)
N5 –C17	1.480(8)	C18–N6	1.301(8)
N6 –C19	1.476(8)	N6 –C20	1.483(8)
Angle		**Angle**	
O11–Cl1 –O12	110.7(3)	O11–Cl1 –O13	109.0(3)
O11–Cl1 –O14	110.1(3)	O12–Cl1 –O13	108.1(3)
O12–Cl1 –O14	109.4(3)	O13–Cl1 –O14	109.5(4)
O21–Cl2 –O22	109.4(3)	O21–Cl2 –O23	109.7(3)
O21–Cl2 –O24	108.9(3)	O22–Cl2 –O23	109.6(3)
O22–Cl2 –O24	109.7(3)	O23–Cl2 –O24	109.5(3)
O31–Cl3 –O32	112.8(4)	O31–Cl3 –O33	104.0(5)
O31–Cl3 –O34	118.2(4)	O32–Cl3 –O33	102.2(5)
O32–Cl3 –O34	112.0(4)	O33–Cl3 –O34	105.7(5)
O41–Cl4 –O42	108.5(3)	O41–Cl4 –O43	111.2(4)
O41–Cl4 –O44	112.8(3)	O42–Cl4 –O43	106.7(4)
O42–Cl4 –O44	105.6(4)	O43–Cl4 –O44	111.6(4)
C2 –C1 –C5	118.2(5)	C2 –C1 –C8	120.2(5)
C5 –C1 –C8	117.8(5)	C1 –C2 –N1	128.4(6)
C2 –N1 –C3	120.8(5)	C2 –N1 –C4	124.9(5)
C3 –N1 –C4	114.1(5)	C1 –C5 –N2	127.1(6)
C5 –N2 –C6	119.2(5)	C5 –N2 –C7	127.5(5)
C6 –N2 –C7	113.3(5)	C1 –C8 –N3	127.8(6)
C8 –N3 –C9	124.9(5)	C8 –N3 –C10	119.7(5)
C9 –N3 –C10	115.4(5)	C12–C11–C15	117.7(5)
C12–C11–C18	122.3(5)	C15–C11–C18	117.7(6)
C11–C12–N4	130.0(6)	C12–N4 –C13	125.3(5)
C12–N4 –C14	120.4(5)	C13–N4 –C14	114.3(5)
C11–C15–N5	127.8(6)	C15–N5 –C16	125.7(6)
C15–N5 –C17	119.7(6)	C16–N5 –C17	114.5(6)
C11–C18–N6	127.9(6)	C18–N6 –C19	124.9(5)
C18–N6 –C20	121.8(5)	C19–N6 –C20	113.3(5)

contd

Table 2. (contd)

Torsion angle	
C5 –C1 –C2 –N1	36.5(7)
C2 –C1 –C5 –N2	–172.1(9)
C8 –C1 –C2 –N1	–165.9(10)
C2 –C1 –C8 –N3	33.8(6)
C8 –C1 –C5 –N2	29.8(6)
C5 –C1 –C8 –N3	–168.5(9)
C1 –C2 –N1 –C3	–172.1(10)
C1 –C2 –N1 –C4	12.4(6)
C1 –C5 –N2 –C6	–167.4(6)
C1 –C5 –N2 –C7	14.3(6)
C1 –C8 –N3 –C9	7.7(6)
C1 –C8 –N3 –C10	–169.4(9)
C15–C11–C12–N4	168.3(9)
C12–C11–C15–N5	–35.5(6)
C18–C11–C12–N4	–29.2(6)
C12–C11–C18–N6	168.1(10)
C18–C11–C15–N5	161.2(9)
C15–C11–C18–N6	–29.4(6)
C11–C12–N4 –C13	–8.3(6)
C11–C12–N4 –C14	175.4(9)
C11–C15–N5 –C16	–11.4(6)
C11–C15–N5 –C17	172.3(9)
C11–C18–N6 –C19	–14.1(6)
C11–C18–N6 –C20	165.7(10)

Discussion of structure

Figs. 1 and 2 show clearly that the organic dication adopts a propeller-like conformation. There are two independent molecules in the asymmetric unit which are practically identical (Table 2). The central carbon is very nearly coplanar with its three neighbouring carbon atoms, and each nitrogen atom forms a perfect plane with its three neighbouring carbon atoms. The twist induced by the steric 1,5-interaction between the *cis-N*-methyl group and an olefinic CH is distributed between a 32° rotation about the CC bond and an 11° rotation about the adjacent CN bond, all six angles having the same sign within one molecule.

The CN bonds are somewhat shorter than in related cyanines (~1.30 Å as opposed to ~1.33 Å, Table 3), and almost as short as in a bis(dimethylimoniomethyl)-substituted 1,3-dinitropropenide chromophore (~1.29 Å).[8] The CC bonds are clearly longer than in related cyanines (~1.42 Å as opposed to ~1.38 Å, Table 3), and almost as long as in the dinitropropenide (~1.44 Å). These bond lengths suggest not only that a superposition of the three mesomeric structures **3a, 3b** and

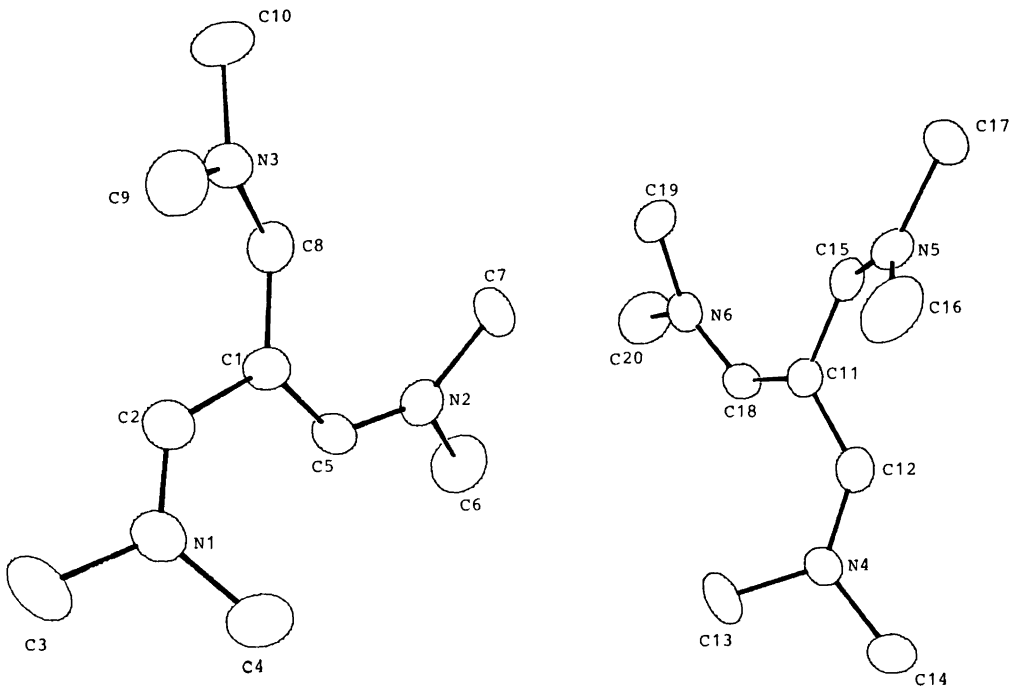


Fig. 1. Perspective drawing of the two independent cations of **3** in the asymmetric unit showing the numbering of atoms.

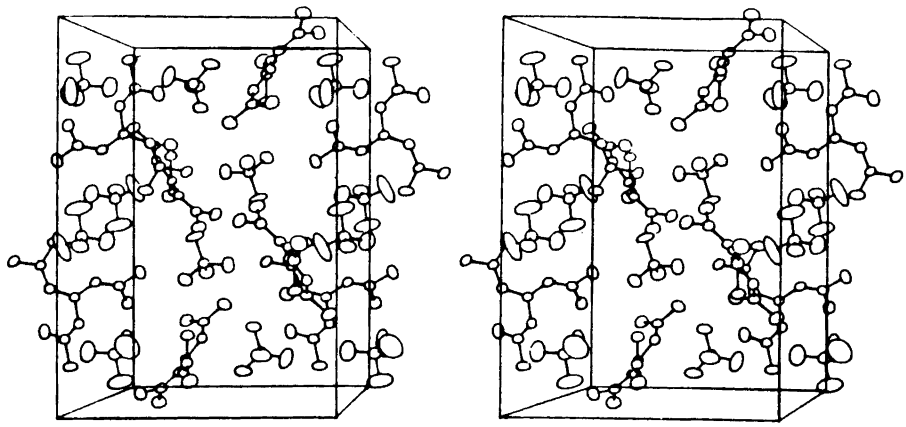


Fig. 2. Stereo view of the unit cell contents.

3c is a fair description of the molecule, but also that structure **3d** alone is an equally good representation. This supports our choice of **3d** as a basis for the nomenclature. A central negative charge can be defended on the basis that for symmetry reasons this 8-π-electron system must have an electron density maximum on the central carbon.

Rotational barriers

The NMR spectra of tris(dimethylimoniomethyl) methide diperchlorate at 20 °C showed sharp ^1H lines [300 MHz, CD_3CN: δ 3.54 (9H), 3.43 (9H), 8.11 (3H)] and ^{13}C lines [75 MHz, CD_3CN: δ 44.3, 50.1, 91.9, 165.5] that correspond to conformation **3**. For dynamic NMR studies, DMSO-d_6

Table 3. Bond lengths and rotational barriers for dication **3** and cyanine cations.

Cation	Bond	Double bond character/%[a]	Observed bond lengths/Å[b]		Theoretical bond lengths/Å[c]	Rotational barriers/kJ mol^{-1}
Tris(dimethylimoniomethyl)methide dication (**3**)	CN	67	1.30[d]		–	94[d]
	CC	33	1.42		–	–
1,3-Bis(dimethylamino)trimethinium cation	CN	50	1.32[e]		1.31	94[j]
	CC	"	1.39		1.38	–
1,5-Bis(dimethylamino)pentamethinium cation	C^1N	50	1.33[f]	1.34[g]	1.32	76[j]
	C^1C^2	"	1.39	1.37	1.38	75[k]
	C^2C^3	"	1.38	1.37	1.38	
1,7-Bis(dimethylamino)heptamethinium cation	C^1N	50	1.32[h]		1.32	65[j]
	C^1C^2	"	1.38		1.37	–
	C^2C^3	"	1.39		1.38	–
	C^3C^4	"	1.37		1.39	–
1,5-Bis(dimethylamino)-2,4-dinitro-pentamethinium cation	C^1N	(100)	1.29[i]		–	–
	C^1C^2	(0)	1.44		–	–

[a]Expected from mesomeric structures without charge separation. [b]Average of reported values. [c]Calcd. for the free cation with NH_2 instead of NMe_2.[9] [d]Diperchlorate, this work. [e]Perchlorate.[10,11] [f]Perchlorate.[12–14] [g]Chloride dihydrate.[15] [h]Chloride tetrahydrate.[16] [i]Perchlorate.[8] [j]Average of $\Delta G^{\ddagger}$ values obtained by DNMR in several solvents.[1] [k]Recalculated[1] from published flash-photolysis data.

was used as solvent. Approaching the coalescence temperature for the methyl proton doublet, slow decomposition took place. As this occurred also with the bis-tetrafluoroborate, it must be due to the instability of the solvent and not of the perchlorate anion. The spectra were nevertheless of sufficiently good quality to locate the coalescence temperature, viz. 170 °C at 300 MHz. The barrier was calculated using the Eyring eqn. ($\Delta\nu$ = 33.3 Hz, $k = \Pi \cdot \Delta\nu/\sqrt{2}$ = 74.0 s^{-1}, $\Delta G^{\ddagger}$ = 94.1 kJ mol^{-1}). This value is strikingly similar to the value of 93.5 kJ mol^{-1} observed[1] for three different salts of the trimethinium cation (**1**) (Table 3). Once again, this demonstrates that there is not necessarily a simple relationship between the double-bond character of the CN bond in the ground state and the rotational barrier in that bond. We have previously reported[1] that the CN rotational barrier in the homologous series of the simple bis(dimethylamino)polymethinium salts decreases rapidly with chain length although the CN bond length remains practically constant (Table 3). Subsequently, *ab initio* calculations by Sæbø and Almlöf[9] reproduced the constant bond lengths along the series (Table 3), and these authors found it necessary to allow full geometry relaxation of the 90° rotated forms in order to reproduce the observed trend of decreasing barriers.

On cooling a CD_3CN solution to −30 °C or a CD_3CN/CD_3OD solution to −40 °C, no tendency to broadening and further splitting of the NMR signals has been observed. Thus, the propeller-like crystal conformation **3** seems to be the only one, also in solution. Even if we assume a rotational barrier in the CC bond as low as 40 kJ mol^{-1}, an incipient broadening should have been observable at −40 °C.

Experimental

The diperchlorate of tris(dimethylimoniomethyl) methide, m.p. 223–225 °C, was prepared by Vilsmeyer formylation of bromoacetic acid, following the procedure of Arnold.[6] The bis(tetrafluoroborate), m.p. 196–198 °C, was prepared in an analogous manner, using $NaBF_4$ instead of $NaClO_4$ to precipitate the organic salt.

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