The Conformation of Tris(2-dimethylaminoethenyl)methylium Perchlorate and Tris(3-dimethylimonio-1-propenyl)methide Diperchlorate

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The crystal structures of these two triple-branched cyanine dyes have been determined by X-ray methods. The organic monocation has a propeller-like conformation, while the organic dication is essentially planar with a three-fold symmetry axis, and both have extended planar branches. As expected from superposition of mesomeric structures, and unlike simple cyanines, alternation of double-bond character is observed within each branch. The skeletal valency angles reflect the stronger alternation of π-electron density on the carbon atoms, as also found for simple cyanines.

MAS solid-phase ^{13}C NMR spectra confirm the crystallographic identity of the three branches for the dication, and the non-equivalent environment for closely similar branches in the monocation. In solution, the vicinal ^{1}H coupling constants confirm the all-*anti* conformation for all branches. Dynamic NMR spectroscopy gives for the rotation about the CN bond a lower barrier for the monocation (56.0 kJ mol^{-1}) and a higher barrier for the dication (74.8 kJ mol^{-1}) than for the comparable simple cyanines.

Recently, we reported the crystal structure and NMR studies of the Y-shaped, or branched, cyanine dye, tris(dimethylimoniomethyl)methide diperchlorate, and concluded that it adopts, in the solid, and most likely also in solution, a propeller-like C_3 conformation.[1]

Two homologous symmetric triply branched cyanine dyes, (**1**) and (**2**), have now been synthesized and obtained crystalline as a monocation perchlorate and a dication diperchlorate, respectively.[2] In Fig. 1 these cations are represented with localized single and double bonds in their most symmetric form, chosen as a basis for a simplified nomenclature (**1a** and **2a**). The problem to be discussed in this paper is whether the actual conformation is indeed planar and close to this C_{3h} symmetry with three equivalent all-*anti* branches, or whether these molecules adopt a linear all-*anti* cyanine made up of two branches, the third branch forming a more or less perpendicular substituent (**1c** and **2c**). Additionally, the question arises to what extent the former C_{3h} conformation is better described by a delocalized π-electron system (**1b** and **2b**). In conformations **1c** and **2c** delocalization would be possible only in the planar extended cyanine chromophore.

We now present NMR data for solutions of these branched cyanines, which give only partial information about the conformations, and the crystal structure of both perchlorates, supplemented by magic-angle-spinning NMR spectra.

NMR spectroscopy in solution; rotational barriers

The room-temperature 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra of the perchlorate (**1**) in CD_3CN and the diperchlorate (**2**) in $(CD_3)_2SO$ have already been given.[2]

In the case of the monocation (**1**), the ^{1}H spectrum corresponds to a C_3 symmetry or to the C_{3h} symmetry of planar **1a** or **1b**, with fast exchange

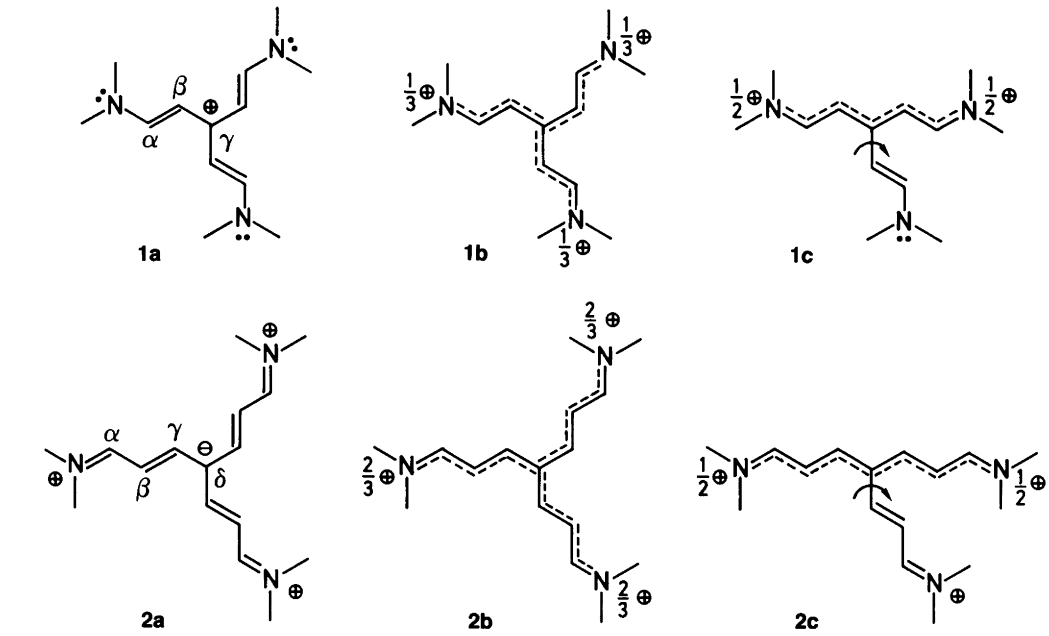

Fig. 1. Possible conformations for monocationic (**1**) and dicationic (**2**) branched cyanines. Variants **a** and **b** differ only in charge distribution.

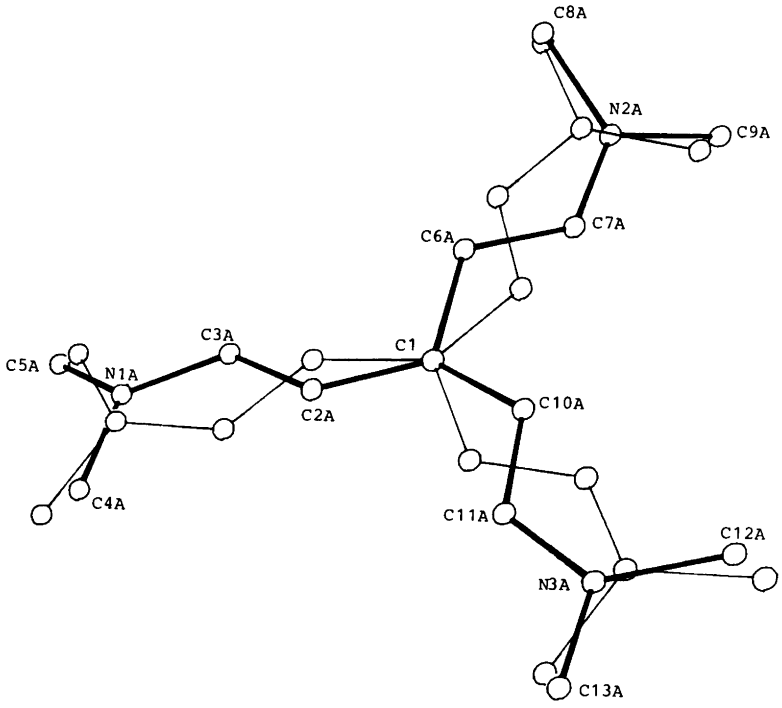

Fig. 2. Drawing of the two independent arrangements **A** and **B** of the disordered cation **1**. The numbering of atoms is shown for **A** only.

Table 1. Final fractional coordinates and equivalent temperature factors with estimated standard deviations for the non-hydrogen atoms of $C_{13}H_{24}N_3^+ \cdot ClO_4^-$ (**1**).

Atom	*x*	*y*	*z*	U_{eq}[a]/*U*
C1	0.41507(19)	0.37577(10)	0.22837(9)	0.049
O1	0.5840(6)	0.3337(3)	0.2543(3)	0.077
O2	0.3202(6)	0.3153(3)	0.1660(3)	0.083
O3	0.3314(6)	0.3849(3)	0.3063(3)	0.086
O4	0.4384(6)	0.4653(3)	0.1903(3)	0.079
C1	0.8420(6)	0.5725(4)	0.4318(3)	0.043
C2A	0.8489(14)	0.5505(8)	0.3410(7)	0.039(3)
C3A	0.9438(11)	0.5937(7)	0.2838(7)	0.040(2)
N1A	0.9719(15)	0.5641(8)	0.1996(7)	0.048(3)
C4A	0.899(2)	0.472(2)	0.165(1)	0.074(5)
C5A	1.0932(18)	0.6089(10)	0.1534(9)	0.055(4)
C6A	0.8882(13)	0.6701(9)	0.4573(8)	0.045(3)
C7A	0.9259(12)	0.6957(8)	0.5463(7)	0.039(2)
N2A	0.9735(19)	0.7796(12)	0.5789(12)	0.062(5)
C8A	0.9816(16)	0.8671(10)	0.5249(8)	0.048(3)
C9A	1.0387(17)	0.7895(10)	0.6738(9)	0.058(4)
C10A	0.7554(13)	0.5200(8)	0.4894(7)	0.043(3)
C11A	0.7052(11)	0.4326(7)	0.4707(7)	0.031(2)
N3A	0.6384(15)	0.3726(11)	0.5274(9)	0.045(4)
C12A	0.6242(17)	0.3948(10)	0.6228(10)	0.054(4)
C13A	0.5623(19)	0.2861(11)	0.4949(10)	0.055(5)
C2B	0.9068(15)	0.5826(9)	0.3465(8)	0.045(3)
C3B	0.8669(13)	0.5199(8)	0.2745(7)	0.046(3)
N1B	0.9175(13)	0.5324(9)	0.1933(6)	0.041(3)
C4B	0.905(2)	0.451(1)	0.136(1)	0.074(6)
C5B	1.0361(19)	0.6073(11)	0.1656(10)	0.056(4)
C6B	0.8850(12)	0.6364(9)	0.5008(8)	0.049(3)
C7B	0.9471(13)	0.7239(8)	0.4892(8)	0.046(3)
N2B	0.9824(18)	0.7878(11)	0.5572(10)	0.054(5)
C8B	1.0561(18)	0.8754(10)	0.5345(8)	0.058(3)
C9B	0.9856(18)	0.7687(10)	0.6507(11)	0.060(4)
C10B	0.7658(14)	0.4824(10)	0.4520(8)	0.047(3)
C11B	0.7121(12)	0.4612(8)	0.5303(7)	0.041(2)
N3B	0.6372(16)	0.3822(11)	0.5497(10)	0.051(5)
C12B	0.5782(17)	0.3692(10)	0.6361(9)	0.058(4)
C13B	0.6103(17)	0.2992(10)	0.4904(9)	0.041(4)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$. (Disordered atoms have isotropic temperature factors).

Table 2. Bond distances (Å), bond angles (°) and torsion angles (°) with estimated standard deviations for $C_{13}H_{24}N_3^+ \cdot ClO_4^-$ (**1**).

Distance		Distance	
Cl–O1	1.455(5)	Cl–O2	1.411(5)
Cl–O3	1.421(5)	Cl–O4	1.423(5)
C1–C2A	1.41(2)	C1–C6A	1.48(2)
C1–C10A	1.39(2)	C2A–C3A	1.36(2)
C3A–N1A	1.38(2)	N1A–C4A	1.50(3)
N1A–C5A	1.40(2)	C6A–C7A	1.38(2)
C7A–N2A	1.33(3)	N2A–C8A	1.50(3)

contd

Table 2. (cont'd)

N2A–C9A	1.46(3)	C10A–C11A	1.33(2)
C11A–N3A	1.36(2)	N3A–C12A	1.49(3)
N3A–C13A	1.43(3)		
C1–C2B	1.45(2)	C1–C6B	1.39(2)
C1–C10B	1.47(2)	C2B–C3B	1.41(2)
C3B–N1B	1.34(2)	N1B–C4B	1.45(3)
N1B–C5B	1.51(2)	C6B–C7B	1.36(2)
C7B–N2B	1.37(2)	N2B–C8B	1.44(3)
N2B–C9B	1.43(3)	C10B–C11B	1.34(2)
C11B–N3B	1.32(2)	N3B–C12B	1.45(2)
N3B–C13B	1.48(3)		

Angle		Angle	
O1–Cl–O2	107.6(3)	O1–Cl–O3	108.4(3)
O1–Cl–O4	108.6(3)	O2–Cl–O3	110.2(3)
O2–Cl–O4	111.5(3)	O3–Cl–O4	110.3(3)
C2A–C1–C6A	115.0(8)	C2A–C1–C10A	124.6(8)
C6A–C1–C10A	118.1(8)	C1–C2A–C3A	127.4(10)
C2A–C3A–N1A	127.5(11)	C3A–N1A–C4A	119.4(12)
C3A–N1A–C5A	121.0(11)	C4A–N1A–C5A	118.5(12)
C1–C6A–C7A	121.0(10)	C6A–C7A–N2A	127.6(13)
C7A–N2A–C8A	125.6(15)	C7A–N2A–C9A	119.6(15)
C8A–N2A–C9A	114.6(14)	C1–C10A–C11A	122.1(10)
C10A–C11A–N3A	125.9(11)	C11A–N3A–C12A	123.6(13)
C11A–N3A–C13A	120.4(12)	C12A–N3A–C13A	115.7(13)
C2B–C1–C6B	121.2(8)	C2B–C1–C10B	118.0(8)
C6B–C1–C10B	119.2(8)	C1–C2B–C3B	123.4(10)
C2B–C3B–N1B	123.6(11)	C3B–N1B–C4B	115.6(12)
C3B–N1B–C5B	127.5(11)	C4B–N1B–C5B	113.7(11)
C1–C6B–C7B	124.2(11)	C6B–C7B–N2B	123.8(12)
C7B–N2B–C8B	116.8(13)	C7B–N2B–C9B	125.6(14)
C8B–N2B–C9B	116.4(13)	C1–C10B–C11B	124.3(11)
C10B–C11B–N3B	126.0(12)	C11B–N3B–C12B	120.7(14)
C11–N3B–C13B	125.6(13)	C12B–N3B–C13B	113.7(13)

Torsion angle	
C6A–C1–C2A–C3A	24.2(11)
C2A–C1–C6A–C7A	−164.9(14)
C10A–C1–C2A–C3A	−173.4(16)
C2A–C1–C10A–C11A	16.5(10)
C10A–C1–C6A–C7A	31.5(10)
C6A–C1–C10A–C11A	178.3(14)
C1–C2A–C3A–N1A	169.1(19)
C2A–C3A–N1A–C4A	−2.8(13)
C2A–C3A–N1A–C5A	−170.6(19)
C1–C6A–C7A–N2A	178.2(19)
C6A–C7A–N2A–C8A	5.6(13)
C6A–C7A–N2A–C9A	−168.6(23)
C1–C10A–C11A–N3A	171.7(18)
C10A–C11A–N3A–C12A	−4.9(12)
C10A–C11A–N3A–C13A	169.3(20)
C6B–C1–C2B–C3B	−179.9(15)
C2B–C1–C6B–C7B	18.7(11)
C10B–C1–C2B–C3B	14.8(11)
C2B–C1–C10B–C11B	175.1(15)
C10B–C1–C6B–C7B	−176.1(15)
C6B–C1–C10B–C11B	9.5(11)
C1–C2B–C3B–N1B	175.5(18)
C2B–C3B–N1B–C4B	164.3(18)
C2B–C3B–N1B–C5B	6.1(12)
C1–C6B–C7B–N2B	177.2(19)
C6B–C7B–N2B–C8B	176.8(20)
C6B–C7B–N2B–C9B	10.2(14)
C1–C10B–C11B–N3B	177.4(20)
C10B–C11B–N3B–C12B	−177.3(21)
C10B–C11B–N3B–C13B	4.9(12)

of geminal NCH_3 groups. The same is true for the ^{13}C spectrum, although the NCH_3 signal is broadened. The barrier to rotation about the CN bond has now been determined from 300 MHz ^1H spectra in CD_3CN at lower temperatures, when only the NCH_3 signal splits into two (δ 2.96, 3.18; Δν 65.3 Hz, T_C 3 °C), giving a barrier of $\Delta G^{\neq} = 56.0$ kJ mol^{-1}. This is markedly lower than the CN barrier of ca. 76 kJ mol^{-1} observed for the comparable simple cyanine, the 1,5-bis(dimethylamino)pentamethinium cation,[3] but high enough to be taken as support for structure **1b** rather than structure **1a**. Cooling the sample to −40 °C did not produce further changes in the spectrum, not even incipient broadening of the sharp lines of the ^{13}C spectrum. The unsymmetric conformation (**1c**) must therefore be considered unlikely, although not rigorously excluded if one admits that rotation about the central $C_\beta C_\gamma$ bonds may still be fast at −40 °C. The final piece of information comes from the vicinal ^1H coupling constant across the $C_\alpha C_\beta$ bond,[2] which has a value of 11.9 Hz; very close to the value 11.8 Hz observed[4] for linear cyanines. This shows that the $C_\alpha C_\beta$ bond is *anti* in all three branches, and also that it is not a full double bond, thus again favouring the mesomeric description (**1b**).

Also in the case of dication **2**, both the ^1H and the ^{13}C spectra[2] correspond to a C_3 symmetry or to the C_{3h} symmetry of planar **2a** or **2b**, but with the geminal NCH_3 groups in slow exchange giving rise to two sharp signals at room temperature. The barrier to rotation about the CN bond has now been determined from 300 MHz ^1H spectra in $(CD_3)_2SO$ at higher temperatures when the NCH_3 signals coalesce (δ 3.35, 3.45; Δν 31.6 Hz, T_C 81 °C), giving a barrier of $\Delta G^{\neq} = 74.8$ kJ mol^{-1}. This is somewhat higher than the CN barrier of ca. 65 kJ mol^{-1} observed for the comparable cyanine, the 1,7-bis(dimethylamino)heptamethinium cation,[3] as would be expected for the mesomeric description (**2b**). NMR spectra recorded below 25 °C could not be obtained because of the high viscosity of Me_2SO and the extreme insolubility of this dicationic dye in other solvents at low temperatures. The vicinal ^1H coupling constants across the $C_\alpha C_\beta$ bond has a lower value (10.7 Hz)[2] than in linear cyanines (11.7 Hz),[4] whereas across the $C_\beta C_\gamma$ bond it is higher (14.2 Hz)[2] than in linear cyanines (12.7 Hz).[4] Both values are however large enough to indicate that all three branches have the *anti, anti* conformation. The values also indicate some single-bond double-bond alternation that supports the descriptions **2a** or **2b**, or perhaps an averaged spectrum of conformation **2c**, since this should have full bond alternation in the 'substituent' branch. Such fast-exchange averaging requires, or course, very low rotational barriers in the central $C_\gamma C_\delta$ bonds.

In order to obtain more information on these points it became necessary to know the crystal

Table 3. Final fractional coordinates and equivalent temperature factors with estimated standard deviations for the non-hydrogen atoms of $C_{16}H_{27}N_3^{2+} \cdot 2ClO_4^-$ (**2**).

Atom	*x*	*y*	*z*	U_{eq}[a]/*U*
Cl1	0.20684(17)	0.20684	0.20684	0.0275(9)
O1	0.2725(4)	0.2725	0.2725	0.048(3)
O2	0.2406(5)	0.1026(4)	0.2226(5)	0.051
Cl2	0.61821(17)	0.11821	0.38179	0.0295(9)
O3	0.6826(4)	0.1826	0.3174	0.039(3)
O4	0.6497(5)	0.0104(4)	0.3709(4)	0.041
C1	0.5441(6)	−0.4559	0.5441	0.018(3)
C2	0.5485(6)	−0.3810(6)	0.4629(6)	0.022
C3	0.4883(6)	−0.2970(7)	0.4446(6)	0.021
C4	0.5028(6)	−0.2375(6)	0,3565(6)	0.023
N	0.4524(5)	−0.1562(5)	0.3246(4)	0.022
C5	0.4745(8)	−0.1080(9)	0.2252(8)	0.034
C6	0.3673(9)	−0.1077(9)	0.3812(10)	0.050

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$(atoms on threefold axes of rotation have isotropic temperature factors).

conformations for (**1**) and (**2**) and to compare the NMR spectra of solutions with those of the solids.

Crystal-structure determination

The crystals of $C_{13}H_{24}N_3^+ \cdot ClO_4^-$ (**1**) are monoclinic with cell dimensions a = 7.810(4), b = 14.287(3), c = 15.040(3) Å, β = 97.58(3)°, space group $P2_1/n$, Z = 4, D_x = 1.28 g cm^{-3}, D_m = 1.26 g cm^{-3} (by flotation), V = 1663.5(8) Å^3, μ = 2.53 cm^{-1} (MoK_α), λ(MoK_α) = 0.71069 Å. The crystals of $C_{16}H_{27}N_3^{2+} \cdot 2ClO_4^-$ (**2**) are cubic with cell dimensions a = 12.886(2) Å, space group $P2_13$, Z = 4, D_x= 1.43 g cm^{-3}, D_m = 1.41 g cm^{-3} (by flotation), V = 2140(1) Å^3, μ = 3.30 cm^{-1}. Data were collected on a Nicolet *P*3 automatic four-circle diffractometer at ca. −140 °C (±5 °C) by the ω-scan technique ($2\theta_{max}$ = 50°) with (MoK_α)radiation. The scan rate varied from 2 to 6° min^{-1}, depending on the intensities of the reflections. The intensity of two test reflections, remeasured after every 100 reflections, showed no significant changes during data collection. The intensities were corrected for Lorentz and polarisation effects, but no corrections were made for absorption or secondary extinction (crystal sizes 0.2×0.5×0.5 mm and 0.3×0.3×0.4 mm for **1** and **2**, respectively. The structures were solved by direct methods[5] and refined by the full-matrix least-squares technique.[6] The *E*-map for **1** corresponding to the best figures of merit contained several split peaks indicating a disordered structure. The procedure from this map to the final structure was somewhat lengthy: repeated use of weighted Fourier calculations, intermediate introduction of anisotropic temperature factors (in order to calculate probable positions for partial atoms),[7] careful refinements of multiplicity factors (keeping thermal parameters constant), and calculation of partial hydrogen atom positions (to be used in structure-factor calculations).

Anisotropic temperature factors were introduced for all ordered atoms (C1 and those of the perchlorate anion). Hydrogen atoms, the positions of which were calculated, were included in structure-factor calculations, but not refined. For the cubic structure of (**2**) atoms at threefold axes of rotation (Cl1, O1, Cl2, O3, C1) and hydrogen atoms were refined with isotropic temperature factors. Anisotropic thermal parameters were used for other atoms. Weights in least-squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I) = [C_T + (0.02C_N)^2]^{1/2}$ where C_T is the total number of counts and C_N the net count. The maximum r.m.s. amplitudes of thermal vibration range from 0.23 to 0.37 Å and 0.17 to 0.31 Å for **1** and **2**, respectively. The final *R*-values were 6.9 % (R_w = 6.5 %) for 1586 observed reflections of **1** and 3.9 % (R_w = 3.0 %) for 487 observed reflections for **2**. Standard deviations in bond distances and angles and torsion angles were calculated from the correlation matrices of the final least-squares refinement cycles. Final fractional coordinates with estimated standard deviations for non-hydrogen atoms are given in Tables 1 and 3. Bond distances, bond angles and torsion angles may be found in Tables 2 and 4. Drawings of the molecular structure of the cationic dyes (**1** and **2**), showing the numbering of atoms, are presented in Figs. 2 and 4, respectively. Stereoscopic views of the unit-cell contents are shown in Figs. 3 and 5. Lists of hydrogen-atom parameters, thermal parameters and observed and calculated struc-

Table 4. Bond distances (Å) and angles (°) and torsion angles (°) with estimated standard deviations for $C_{16}H_{27}N_3^{2+} \cdot 2ClO_4^-$ (**2**). The primes correspond to various three-fold axial symmetry operators.

Distance		Distance	
Cl1–O1	1.466(4)	Cl1–O2	1.426(6)
Cl2–O3	1.438(4)	Cl2–O4	1.455(6)
C1–C2	1.425(8)	C2–C3	1.353(8)
C3–C4	1.382(9)	C4–N	1.299(7)
N–C5	1.452(9)	N–C6	1.457(9)
Angle		**Angle**	
O1–Cl1–O2	106.6(3)	O2–Cl1–O2′	112.2(4)
O3–Cl2–O4	109.5(3)	O4–Cl2–O4′	109.4(4)
C2–C1–C2′	120.0(5)	C1–C2–C3	130.3(8)
C2–C3–C4	120.6(8)	C3–C4–N	129.7(8)
C4–N–C5	121.7(8)	C4–N–C6	124.3(8)
C5–N–C6	113.9(8)		
Torsion angle			
C2′–C1–C2–C3	3.7(8)		
C2″–C1–C2–C3	−178.2(8)		
C1–C2–C3–C4	−176.1(9)		
C2–C3–C4–N	178.6(9)		
C3–C4–N–C5	−175.5(9)		
C3–C4–N–C6	1.9(9)		

ture factors are obtainable from Per Groth on request.

Discussion of the crystal structures

There are two independent but closely similar monocationic molecules **A** and **B** in the unit cell of the monoperchlorate **1** forming the disordered structure shown in Fig. 2. The molecules have approximate C_3 symmetry, each branch being rotated about the central $C_\beta C_\gamma$ bond in a propeller-like fashion by an average of 24° in molecule **A** and by 15° in molecule **B**. Otherwise, the branches are very nearly planar. All three branches within each molecule are strictly independent crystallographically, but the molecular parameters (Table 2) are nevertheless so close that the differences can be considered as being insignificant. Only values averaged over all six branches are therefore presented for discussion in Table 5 together with data for other linear and branched cyanines. The molecular packing (Fig. 3) shows however that two branches of each planar cation molecule are engaged in a stacking arrangement with neighbouring molecules, reminiscent of the masonry-type pattern observed in the crystal structures of linear cyanines,[8] while the third branch has no such close interactions with neighbouring cations. The branches are all extended in the *anti* conformation, in agreement with the cyanine-like ^{1}H NMR coupling constants already discussed. The bond lengths however show clear differences from those of cyanines (Table 5) and display an alternation in double bond character along each branch. This is about as expected for the mesomeric description (**1b**), and perhaps not as strong as expected for structure **1a** alone. At any rate, this bond alternation seems to be less dramatic than the alternation in π-electron density inherent in cyanine systems and reflected in the ^{13}C chemical shifts[2,4] (Table 6). The values of the skeletal valency angles in linear cyanines are known[9] to depend on this charge alternation, being larger for carbons with positive charge (sp^2 hybridization) and smaller for carbons with negative charge (sp^3 hybridization), although the presence of one hydrogen substituent makes the angles generally larger than 120° and 109.5°, respectively. In the pentamethinium cyanine (Table 5) the valency-angle alternation is clear, but in our branched cyanine (**1**) the effect is not noticeable. The reason for this is obviously steric: the valency angle at the positive central γ-carbon becomes fixed at ca. 120° for symmetry reasons, while the valency angle at the negative β-carbon is further increased

Table 5. Essential molecular parameters of branched cyanine perchlorates and comparable linear cyanine perchlorates.

Cation	Averaged bond lengths/Å				Averaged skeletal valency angles/°			
	NC_α	$C_\alpha C_\beta$	$C_\beta C_\gamma$	$C_\gamma C_\delta$	C_α	C_β	C_γ	C_δ
Tris(dimethylimoniomethyl)methide dication[a]	1.30	1.42	–	–	128	(119)	–	–
Tris(2-dimethylaminoethenyl)methylium cation (**1**)[b]	1.35	1.36	1.43	–	126	124	(119)	–
Tris(3-dimethylimonio-1-propenyl)methide dication (**2**)[b]	1.30	1.38	1.35	1.43	130	121	130	(120)
1,3-Bis(dimethylamino)trimethinium cation[c]	1.32	1.39	–	–	124	116	–	–
1,5-Bis(dimethylamino)pentamethinium cation[c]	1.33	1.39	1.38	–	126	118	123	–
1,7-Bis(dimethylamino)heptamethinium cation[d]	1.32	1.38	1.39	1.37	129	120	127	122

[a]Non-planar.[1] [b]This work. [c]Based on several reported structures surveyed earlier.[1] [d]As chloride tetrahydrate.[10]

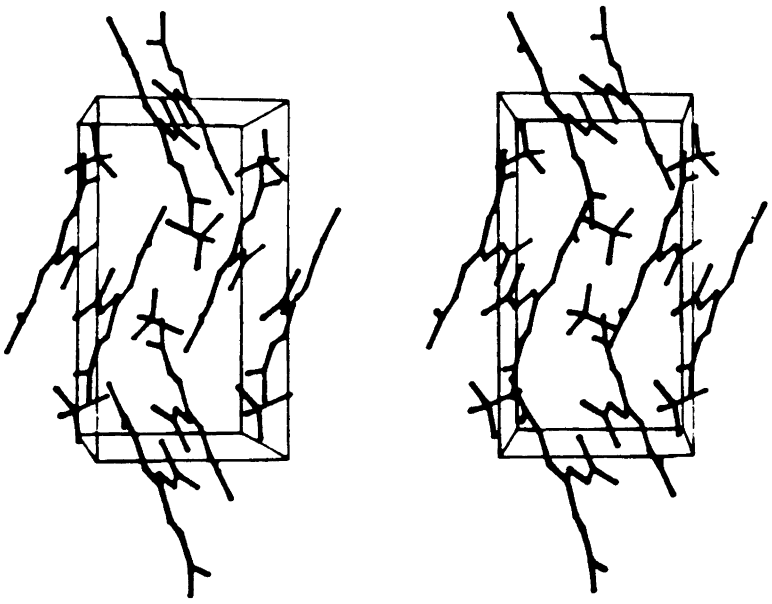

Fig. 3. Stereo view of the unit-cell contents for cyanine perchlorate (**1**).

by repulsion between its vicinal α-carbon and the β-carbon of the next branch. Thus, summing up, we conclude that the observed differences in bond lengths and valency angles can be attributed to electronic and steric perturbations of an essentially cyanine-like structure caused by the branching.

The crystal structure of the diperchlorate of the dicationic molecule (**2**) shown in Fig. 4 is very unusual, being cubic with full utilization of the trigonal symmetry of the cations and the tetrahedral symmetry of the anions. All three cyanine branches are therefore equivalent, and the significant molecular parameters of Table 3 can be directly transferred to Table 5 for comparison. The molecular packing (Fig. 5) reveals no tendency to parallel stacking of planar cations, which would also be incompatible with the observed symmetry. The deviation from planar C_{3h} symmetry for the cations is very slight; rotations by

Table 6. ^{13}C NMR chemical shifts (δ) for branched cyanines in solid (MAS) and in solution.

Branched cyanine	C_α	C_β	C_γ	C_δ	NCH_3	NCH_3
Perchlorate (**1**)						
Solid[a]	150.7 (broad)	92.5 94.5	165.2	–	45.0 46.3 (broad)	36.2 37.6 (broad)
CD_3CN soln,[b] −40 °C	153.2	94.6	167.1	–	45.8	37.8
Diperchlorate (**2**)						
Solid[a]	168.1 168.9	105.2	154.3	113.0	47.3 48.2	38.4 39.3
Me_2SO soln,[b] 25 °C	165.8	106.6	155.1	114.6	47.1	34.1

[a]At 50 MHz on a Bruker MSL 200 instrument. [b]At 75 MHz on a Varian XL 300 instrument.

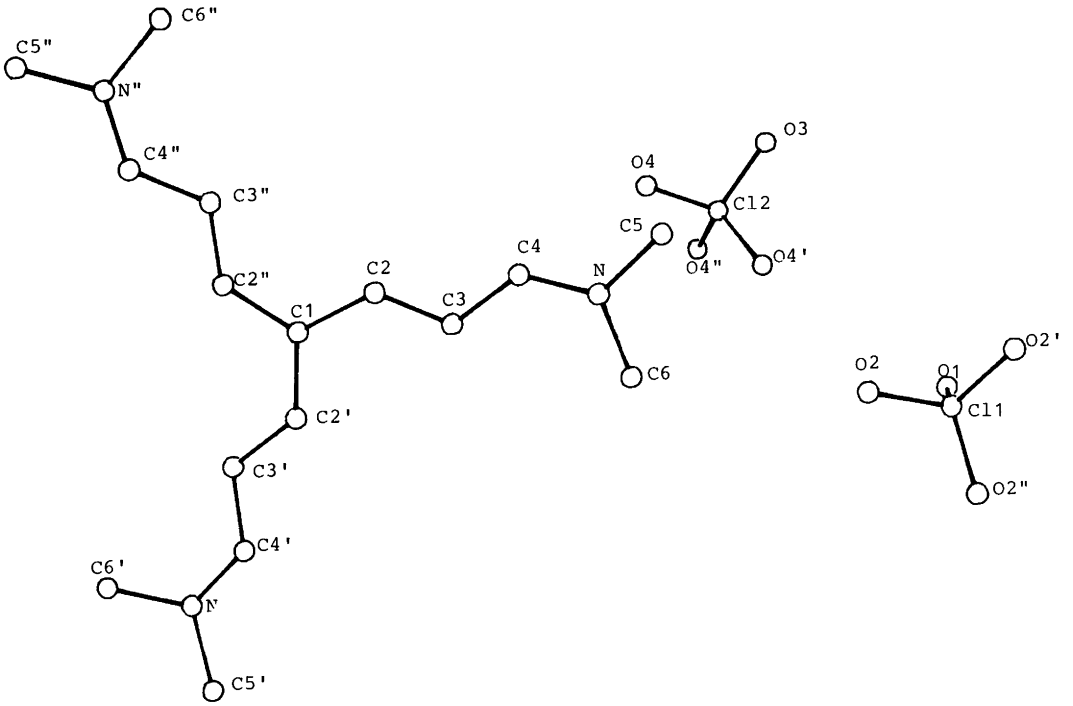

Fig. 4. Perspective drawing of cyanine diperchlorate (**2**) in the asymmetric unit showing the numbering of atoms.

only 4° about the central $C_\gamma C_\delta$ bonds produce a low-pitched propeller. The branches are otherwise very closely planar and in the extended *anti, anti* conformation, as is also inferred from the cyanine-like ^1H coupling constants discussed before. These are somewhat smaller across the $C_\alpha C_\beta$ bond than the $C_\beta C_\gamma$ bond, and reflect nicely the longer, respectively shorter, bond lengths (Table 5). The alternation of bond character extends further to the long central $C_\gamma C_\delta$ bond and to the short terminal NC_α bond, contrasting strongly with the comparable heptamethinium cyanine[10] (Table 5). This is about as expected for the mesomeric description (**2b**), and less than expected for

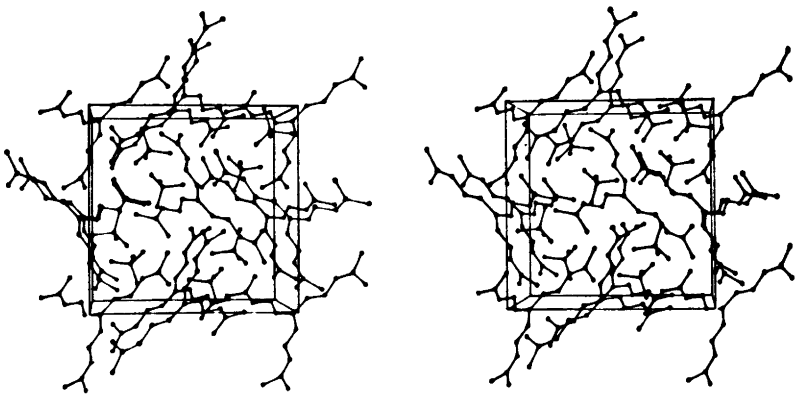

Fig. 5. Stereo view of the unit-cell contents for cyanine diperchlorate (**2**).

2a alone. On the other hand, the valency angles are close to those for the heptamethinium cyanine (Table 5) and support the cyanine-like structure with π-electron density alternation on atoms. Thus, also in this case, the branched cation is essentially cyanine-like, but is perturbed electronically and sterically by the branching.

NMR spectroscopy of the solid state

Considering the low double-bond character of the central CC bonds, as indicated by the observed lengths for these bonds in the crystal structures of **1** and **2**, and the difficulty in obtaining low-temperature NMR spectra in solution, it became of interest to compare the ^{13}C chemical shifts for the solid-state conformer with those of the still unknown solution conformer (or any averaged mixtures). High-resolution magic-angle-spinning (MAS) ^{13}C spectra were obtained for both solids at 50 MHz, and the results are shown in Table 6 and compared with solution data. The MAS spectra were complicated by residual splittings of all NCH and NCH_3 carbons due to incomplete removal of dipolar coupling to the ^{14}N nucleus.[11] In the case of **1** such carbon signals are too broad and too incompletely resolved to be discussed, but the sharp C_γ line shows that only one conformation is present, and the two sharp C_β lines (ratio 1:2) reflect correctly the difference between the two branches which participate in stacking and the one branch which does not. Comparing the ^{13}C shifts of the solid with those of the solution, the differences are too marginal to allow conclusions to be drawn. In the case of **2** the sharp solid-phase carbon lines (Table 6) are in perfect agreement with the highly symmetric structure found by X-ray analysis, with only the NCH and NCH_3 carbons showing a narrow splitting due to residual dipolar coupling to ^{14}N (intensity ca. 2:1). Comparing the ^{13}C shifts of the solid with those of the solution, differences are again small, except for one NCH_3, but some shift now upfield, others downfield. For this reason we hesitate to conclude that the solution must also, in this case, contain exclusively the C_3 conformer. There are two additional reasons for our hesitation. The first is that the corresponding dichloride, which is more soluble, gives a temperature-variable NMR spectrum, which we cannot, however, yet interpret. The second reason is that another pair of branched cyanines, related to **1** and **2**, respectively, but containing complex aromatic end groups, adopt different conformations in the solid state. One is monocationic,[12] like **1**, and has a C_3 conformation of type **1b**, whereas the other is dicationic,[13] like **2**, and has an unsymmetric conformation of type **2c**.

Further studies of this problem are in progress.

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