

A facile route to poly[1-(2,4,6-trichlorophenyl)-1*H*-1,2,4-triazol-5-yl]alkane derivatives

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The synthesis of the tetrakis{2-[1-(2,4,6-trichlorophenyl)-1*H*-1,2,4-triazol-5-yl]ethoxymethyl}methane derivatives **5a–c**, **6** and **7**, and the nitrotris{2-[1-(2,4,6-trichlorophenyl)-1*H*-1,2,4-triazol-5-yl]ethyl}methane derivatives **9a–c**, **10** and the picrate **11** has been accomplished by reaction of the 1-aza-2-azoniaallene salts **3** with either the aliphatic tetranitrile **1** or trinitrile **8**, in high yields; the X-ray crystal structure of **5b** is also reported.

Introduction

The study of poly(1,2,4-triazole) heterocycles, including poly(1,2,4-triazolyl)borates^{1,2} and poly(1,2,4-triazolyl)alkanes,³ has drawn much attention from various perspectives over the past years, primarily elicited by their successful use as novel scorpionate ligands in coordination chemistry.⁴ In comparison to the popular poly(pyrazol-1-yl)borates⁵ which have been extensively studied since their discovery in 1966–67, poly-(triazolyl)alkanes offer several unique characteristics. For example, the exodentate nitrogen atoms on the 4-position of triazole rings can bridge between metal centers, thereby forming linkage coordination polymers with interesting physical properties and solid-state structures.^{3,4} A 1,2,4-triazole may be reasonably viewed as a unity of pyrazole and imidazole in terms of the coordination geometry. Replacement of the labile B–N bonds in poly(1,2,4-triazolyl)borates by C–N bonds in poly(1,2,4-triazolyl)alkanes may also be advantageous.⁶

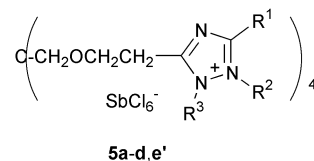
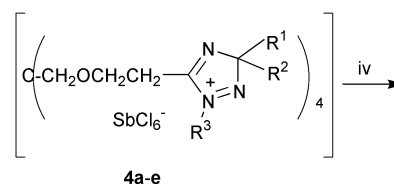
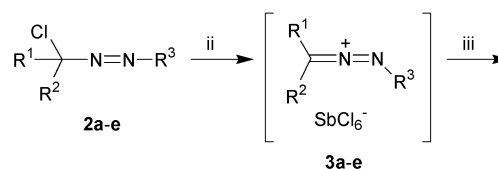
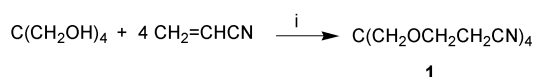
Although the first poly(1,2,4-triazol-1-yl)borates were reported in 1967 by Trofimenko,⁷ methods for synthesis of related poly(1,2,4-triazolyl)alkanes have been scarcely described.⁸ To the best of our knowledge, the only closely related species thus far reported in the literature is restricted to poly(triazol-1-yl)alkanes. It, therefore, appeared worthwhile to design elegant methods for the ready introduction of structurally diverse poly(1,2,4-triazolyl)alkanes. We wish now to report that in our pursuit of the potentiality of polynitriles in reaction with a class of *in situ* generated 1-aza-2-azoniaallene cations, a novel kind of tris- as well as tetrakis(1*H*-1,2,4-triazol-5-yl)alkane compounds can be readily attained by employing pentaerythritol and nitromethane, respectively as the initial scaffold core.

Results and discussion

Synthesis and spectroscopy

According to a literature method,⁹ the tetranitrile **1**, *viz.* 5,5-bis(4-cyano-2-oxabutyl)-1,9-dicyano-3,7-dioxanonane, was prepared by Michael addition of pentaerythritol with four equivalents of acrylonitrile in 90% yield. Also the crystal structure of **1** has been published by Newkome.¹⁰ The author disclosed that this tetranitrile adopts in the crystal structure a four-directional conformation with extended chains, having *gauche*-oriented terminal cyano groups. As a polynitrile, **1** has now become a convenient starting material for the construction of cascade polymers and micellanes.¹¹

The previously described α -chloroazo compound **2a**¹² undergoes efficient chloride-departure by action with one equivalent of SbCl₅ at low temperature (–60 °C), thereby generating the 1-aza-2-azoniaallene salt **3a** as a reactive intermediate. Four-fold reaction of the hetero(cumulene) **3a** with the tetranitrile **1** produced initially the tetrakis(3*H*-1,2,4-triazolium) salt **4a**. On gradually warming to about 30 °C one of the two C(3)-methyl groups in **4a** migrated to N(2) yielding **5a** as the final product in 71% yield (Scheme 1).



R³ = 2,4,6-Cl₃C₆H₂

2-5a: R¹ = R² = Me; **b**: R¹ = Me, R² = Et; **c**: R¹-R² = -(CH₂)₅;

d: R¹ = Pr, R² = H; **e/e'**: R¹ = Me, R² = Bu^t/H.

Scheme 1 Reagents and conditions: i, 40–50 °C, 3 h; ii, SbCl₅, CH₂Cl₂, –60 °C; iii, 0.25 equiv. of **1**, –60 ~ 30 °C; iv, 30 °C, 1 h.

The generality of this sequence was examined using sufficiently different α -chloroazo substrates **2**^{12,13} and the results are summarized in Table 1.

If two different substituents at C(3) of the initially formed adducts **4** compete for the migration, there is no ambiguity regarding the migrating group in all cases studied; the 1,2-shift takes place with the group that accommodates positive charge

Table 1 Synthesis of the tetrakis(1*H*-1,2,4-triazole) derivatives

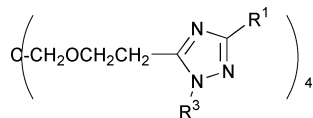
Entry	Substrate	R ¹	R ²	R ³	Product	Yield (%) ^a
1	2a	Me	Me	2,4,6-Cl ₃ C ₆ H ₂	5a	71
2	2b	Me	Et	2,4,6-Cl ₃ C ₆ H ₂	5b	77
3	2c	-(CH ₂) ₅ -		2,4,6-Cl ₃ C ₆ H ₂	5c	81
4	2d	Pr	H	2,4,6-Cl ₃ C ₆ H ₂	6	73
5	2e	Me	Bu'	2,4,6-Cl ₃ C ₆ H ₂	7	76

^a based on isolated product.

more effectively. Thus, along similar lines, the cycloaddition of the hetero(cumulene) cation **3b** across the triple bonds of **1** gave **5b** as the sole product in 77% yield. On the other hand, starting from **3c** derived from cyclohexanone, the cycloaddition proceeded equally well and the rearrangement took place with ensuing ring enlargement and insertion of the nitrogen atom into the carbon skeleton. The tetrakis(1,5-annulated-1*H*-1,2,4-triazolium) salt **5c** was obtained as a pale yellow powder in 81% yield.

Compared to neutral and polyanionic dendrimer molecules, relatively little work has been done on the polycationic analogues.¹⁴ So far the studies of this kind of dendritic molecule seem to be restricted to molecules coated with quaternary ammonium centers on their surface. Our work could be a useful addition to the formation of branched molecules carrying multiple cationic 1,2,4-triazole sites at the periphery.

On the other hand, if a proton competes with an alkyl for the 1,2-shift, the prototropic rearrangement prevails. Thus, from **3d** the N(2)-protonated product **5d** was obtained as an extremely hygroscopic salt. Although **5d** is difficult to crystallize thus precluding its satisfactory characterization, it can be deprotonated with brine at low temperature providing the electrically neutral tetrakis(1*H*-1,2,4-triazole) compound **6** in 73% yield.



6: R¹ = Pr, R³ = 2,4,6-Cl₃C₆H₂;
7: R¹ = Me, R³ = 2,4,6-Cl₃C₆H₂

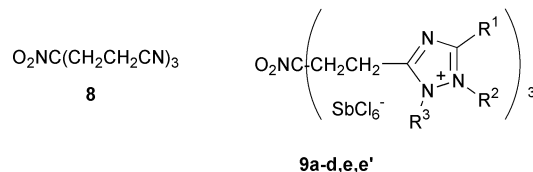
Since α -chloroazo compounds with a germinal H substituent are generally unstable due to smooth rearrangement to the corresponding hydrazonyl chlorides,¹³ an alternative approach to this kind of neutral tetrakis(1,2,4-triazole)s was further envisaged.

The allenium salt **3e** derived from pinacolone was allowed to react with the tetranitrile **1**. As expected, the initially formed heterocycle **4e** underwent a 1,2-*tert*-butyl-shift, however, concurrent elimination of isobutene (2-methylpropene) occurred to provide the protonated tetrakis(1,2,4-triazolium) salt **5e'**. Successive basic work-up of **5e'** afforded the neutral 1,2,4-triazole-tipped compound **7** in an overall yield of 76%.

The synthesis with the tetranitrile **1** is summarized in Table 1.

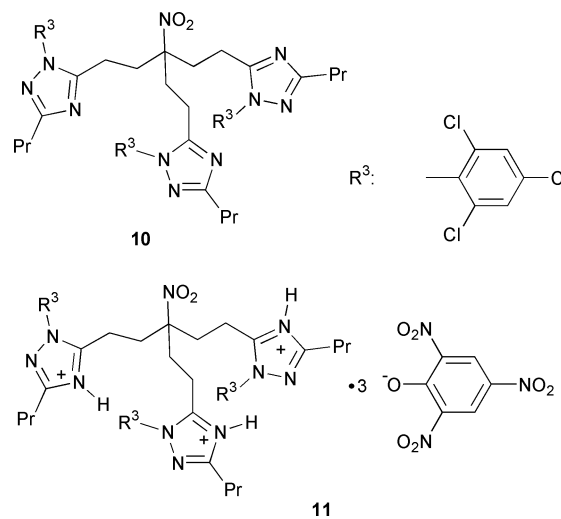
To explore the scope of this reaction, tris(2-cyanoethyl)-nitromethane **8**, prepared by Michael addition reaction of nitromethane with three equivalents of acrylonitrile, was employed as the tripodal framework.¹⁵ Likewise, the same sequence led to the formation of the corresponding tris(1,2,4-triazol-5-yl)alkane compounds **9a-d**. As deduced from both microanalysis and ¹H NMR spectra, compounds **9a-c** were isolated as solvated crystalline materials, with one embedded acetonitrile molecule for **9a** as well as **9b** and approximately two acetonitrile molecules for **9c**. The embedded solvent molecules were not lost during the usual desiccation process.

While other substrates worked equally well, reaction of the α -chloroazo compounds **2e** derived from pinacolone gave only a complex mixture of compounds, from which neither the



8
R³ = 2,4,6-Cl₃C₆H₂
9a: R¹ = R² = Me; **b:** R¹ = Me, R² = Et; **c:** R¹-R² = -(CH₂)₅-;
d: R¹ = Pr, R² = H; **e/e':** R¹ = Me, R² = Bu'/H

expected product **9e** nor **9e'** has been isolated. On the other hand, the free base **10** was achieved by basic work-up of **9d** and characterized as its picrate **11**. The results are gathered in Table 2.



The ¹H NMR and ¹³C NMR spectra of the new compounds are all consistent with the structures as shown. For each compound only two C=N carbon signals are discernible between 161 and 165 ppm, clearly demonstrating the equivalence of all triazole rings on the NMR time-scale. The IR absorption at about 1520 cm⁻¹ is attributable to the triazole rings. In the ¹³C NMR spectra, the signal for the quaternary central carbon in compounds **5** appears at about 46 ppm, whilst in compounds **9** it shifts downfield to about 91 ppm due to the nitro group.

Crystal structure of compound **5b**

Although many polyheterocycles including polyimidazoles¹⁶ and tris(tetrazoles)¹⁷ have been developed and attracted considerable interest for their extensive co-ordination chemistry with metal ions, highly symmetrical tetrakis(1,2,4-triazole)s are, as far as we are aware, hitherto unknown species.

In order to get a detailed knowledge of the spatial structure of the novel poly(1,2,4-triazole)s, an X-ray crystallographic analysis was carried out for **5b**. It was disclosed that the crystal embraced two solvent molecules of CH₂Cl₂. An ORTEP plot for the tetracation of **5b** is shown in Fig. 1.

The study confirms that the molecule retains the intrinsic four-directional conformation in which each of the four appendages attached to the central C atom is extended tetra-

Table 2 Synthesis of the nitrotris(1,2,4-triazol-5-yl)methane derivatives **9**

Entry	Substrate	R ¹	R ²	R ³	Product	Yield (%) ^a
1	2a	Me	Me	2,4,6-Cl ₃ C ₆ H ₂	9a	91
2	2b	Me	Et	2,4,6-Cl ₃ C ₆ H ₂	9b	86
3	2c	-(CH ₂) ₅ -		2,4,6-Cl ₃ C ₆ H ₂	9c	82
4	2d	n-Pr	H	2,4,6-Cl ₃ C ₆ H ₂	9d	87
5	2e	Me	<i>t</i> -Bu	2,4,6-Cl ₃ C ₆ H ₂	—	^b

^a Based on isolated product. ^b No definite products could be isolated.

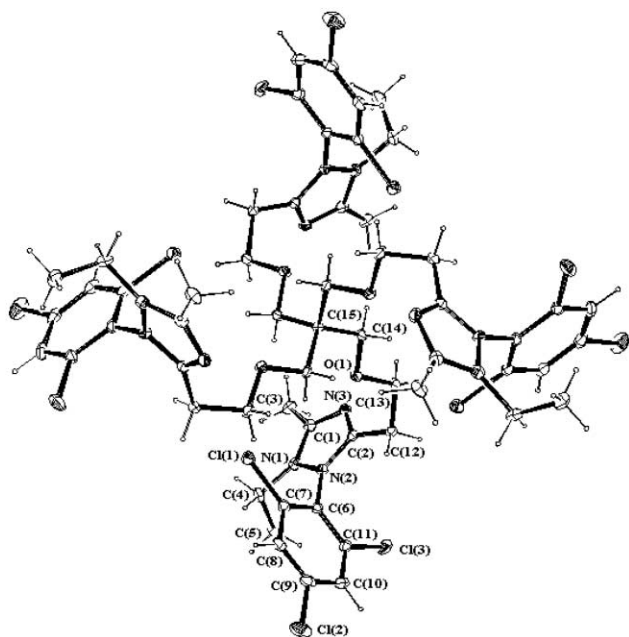


Fig. 1 Molecular structure of cations of **5b**, showing the ideal tetrahedral arrangement of the appendages. Displacement ellipsoids are drawn at the 10% probability level for clarity and H atoms are shown as small spheres of arbitrary radii.

hedrally to a good degree of approximation. The terminal 1,2,4-triazolium rings are peripherally homogeneous and point out ideally to the corners of a tetrahedron. The solvated methylene chloride molecules exhibit disorder with occupancy of 0.5. Molecule **5b** has crystallographic *S*₄ symmetry in the tetragonal crystals and adopts the conformation as shown.

In comparison to the tetranitrile **1**, the bond distances of C15–C14, C14–O, O–C13 and C13–C12 in **5b** haven't significantly varied (Table 3). However, the bond length of C2–C12 [1.501(14) Å] has increased significantly compared with the parent compound [1.379(8) ~ 1.455(5) Å].¹⁰ This is as expected by virtue of the hybridization state change of C(2) from sp to sp².

The triazolium rings in **5b** are nearly planar. However, coplanarity of the triazolium ring and the bulky aryl substituent on N(2) is expected to be prohibited owing to steric hindrance. Actually, each of the aryl ring is virtually perpendicular to the plane of the attached triazole ring, having dihedral angle [C(2)–N(2)–C(6)–C(7)] 97.7(13)°. This, along with the rather long N(2)–C(6) distance of 1.434(13) Å which is indicative of a C(sp²)–N single bond, suggests that there should be no conjugation between the two rings.

The heterocyclic rings contain a rather long N(1)–N(2) distance of 1.366(11) Å characteristic of a single N–N bond. In addition, the other four bond lengths in each of the triazolium rings range between 1.29 and 1.37 Å which coincide with those found in delocalized systems such as 1.34 Å in pyridine.¹⁸

In summary, we report in this paper a practical methodology for synthesis of compounds that are tethered to four or three 1,2,4-triazole rings at the periphery. The NMR data suggest that all the triazole rings are equivalent. The X-ray crystal-

Table 3 Selected bond lengths/Å and bond angles/deg for **5b**

C14–C15	1.504(9)	O1–C14	1.421(10)
O1–C13	1.430(11)	N1–N2	1.366(11)
N1–C1	1.372(13)	N1–C4	1.481(14)
N2–C2	1.360(13)	N2–C6	1.434(13)
N3–C2	1.294(13)	N3–C1	1.336(14)
C1–C3	1.499(15)	C2–C12	1.501(14)
C12–C13	1.490(14)	C14–O1–C13	113.0(7)
N2–N1–C1	105.8(10)	N2–N1–C4	123.8(9)
C2–N2–N1	106.9(9)	N1–N2–C6	122.6(9)
C2–N3–C1	108.4(10)	N3–C1–N1	108.8(11)
N3–C1–C3	128.1(12)	N1–C1–C3	123.1(12)
N3–C2–N2	110.1(10)	N3–C2–C12	127.2(11)
N2–C2–C12	122.6(10)	C13–C12–C2	113.0(9)
O1–C13–C12	108.5(8)	C14–C15–C14*	109.7(4)

lographic analysis of **5b** confirms the structure elucidation. Synthesis of further examples of this kind of poly(1*H*-1,2,4-triazol-5-yl)alkane compounds and the potential application such as use as multidentate ligands in coordination chemistry is underway.

Experimental

General

Melting points are uncorrected. IR spectra were recorded on a Mattson Alpha-centauri FT-IR spectrometer, for solids in potassium bromide discs and for liquids by placing a thin layer of the CCl₄ solution between two potassium bromide discs. ¹H and ¹³C NMR spectra were measured in CD₃CN or CDCl₃ solutions on a Varian 400 or Bruker 300 spectrometer. Chemical shifts (δ) are expressed in ppm using TMS as internal reference. Coupling constant (*J*) values are given in Hz.

Commercially available solvents were dried by standard methods prior to use. All non-aqueous reactions were performed with exclusion of moisture. The α -chloroazo compounds **2** were prepared as reported.^{12,13}

Preparation of tetrakis- and tris(1,2,4-triazolium-5-yl)alkane compounds **5** and **9** as well as the free bases **6**, **7** and **10**. Typical procedures

A solution of SbCl₅ (1.20 g, 4 mmol) in dry CH₂Cl₂ (10 cm³) was added dropwise under a N₂ atmosphere to a stirred and cooled (–60 °C) solution of the tetranitrile **1** (0.35 g, 1 mmol) and **2** (4 mmol) in dry CH₂Cl₂ (10 cm³). If the tripod **8** was employed as the dipolarophile, 0.90 g (3 mmol) of SbCl₅ was used. The resulting mixture was stirred for 1 h then allowed to warm to rt over 5 h. A deep colored solid was precipitated off from the mixture. The solvent was removed under reduced pressure and dry Et₂O (50 cm³) was added to the residues at 0 °C. The upper liquids were carefully decanted and the solid residue was recrystallized from hot MeOH–MeCN (5 : 1) to furnish the respective poly(1,2,4-triazolium) salts **5** or **9**. Basic work-up for the N(2)-protonated counterparts **5d**, **5e'**, and **9d** affords the corresponding N(2)-unsubstituted free bases, which are characterized as their picrates if necessary. Analysis for compounds **9** corresponds to either one or two solvent molecules in the formula.

Tetrakis{2-[2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazol-2-ium-5-yl]ethoxymethyl}methane tetrakis(hexachloroantimonate) 5a

From **2a** and **1**. Product **5a** was provided as a pale-yellow solid. Yield: 71%. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1106, 1555 and 3081; $\delta_{\text{H}}(\text{CD}_3\text{CN})$ 2.84 (12 H, s, 4 × CH₃), 2.97 (8 H, t, *J* 6.0, 4 × CH₂), 3.33 (8 H, s, 4 × OCH₂), 3.78 (8 H, t, *J* 6.0, 4 × OCH₂), 3.85 (12 H, s, 4 × NCH₃), 8.04 (8 H, s, 4 × Cl₃C₆H₂). The product is contaminated by a trace of impurities even though recrystallization was carried out twice from hot MeOH and MeCN. Hence, for this compound no satisfactory microanalytical results have been obtained.

Tetrakis{2-[2-ethyl-3-methyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazol-2-ium-5-yl]ethoxymethyl}methane tetrakis(hexachloroantimonate) 5b

From **2b** and **1**. Precipitation with Et₂O and crystallization from MeOH–MeCN afforded pure **5b** as colorless prisms. Yield: 77%; mp >120 °C (decomp.) (Found: C, 25.0; H, 2.6; N, 6.4. C₅₇H₆₄Cl₃₆N₁₂O₄Sb₄ requires C, 25.0; H, 2.5; N, 6.1%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1086, 1556 and 3076; $\delta_{\text{H}}(\text{CD}_3\text{CN})$ 1.39 (12 H, t, *J* 7.2, 4 × CH₃), 2.88 (12 H, s, 4 × CH₃), 2.94 (8 H, t, *J* 5.7 Hz, 4 × CH₂), 3.22 (8 H, s, 4 × OCH₂), 3.78 (8 H, t, *J* 5.7, 4 × OCH₂), 4.32 (8 H, q, *J* 7.2, 4 × CH₂) and 8.05 (8 H, s, 4 × Cl₃C₆H₂); $\delta_{\text{C}}(\text{CD}_3\text{CN})$ 161.6, 160.7 (C=N), 141.8, 136.0, 131.1, 123.4 (aryl), 69.5, 66.6 (OCH₂), 45.5 (>C<), 44.3, 27.4 (CH₂), 13.5 and 13.3 (CH₃).

Tetrakis{2-[6,7,8,9-tetrahydro-3-(2,4,6-trichlorophenyl)-5H-[1,2,4]triazolo[5,1-*a*]azepin-4-ium-2-yl]ethoxymethyl}methane tetrakis(hexachloroantimonate) 5c

Compound **5c** was obtained as a pale-yellow crystalline solid in the same manner as **5b**. Yield 81%; mp >221 °C (decomp.) (Found: C, 27.4; H, 2.6; N, 5.9. C₆₅H₇₂Cl₃₆N₁₂O₄Sb₄ requires C, 27.4; H, 2.6; N, 5.9%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1120, 1556 and 3075; $\delta_{\text{H}}(\text{CD}_3\text{CN})$ 1.95–2.03 (24 H, m, 12 × CH₂), 2.96 (8 H, t, *J* 5.7, 4 × CH₂), 3.23 (8 H, s, 4 × OCH₂), 3.38 (8 H, t, *J* 5.4, 4 × CH₂), 3.78 (8 H, t, *J* 5.7, 4 × OCH₂), 4.25 (8 H, t, *J* 4.8, 4 × NCH₂) and 8.04 (8 H, s, 4 × Cl₃C₆H₂); $\delta_{\text{C}}(\text{CD}_3\text{CN})$ 165.6, 161.3 (C=N), 141.8, 136.4, 130.9, 123.1 (aryl), 69.5, 66.6 (OCH₂), 45.6 (>C<), 49.8, 28.5, 28.2, 27.2, 25.9 and 23.1 (CH₂).

Tetrakis{2-[3-propyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazol-2-ium-5-yl]ethoxymethyl}methane tetrakis(hexachloroantimonate) 5d and its free base tetrakis{2-[3-propyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazol-5-yl]ethoxymethyl}methane 6

The salt **5d** was obtained as described above from **2d** and **1**. The crude **5d** was dissolved in methylene chloride and stirred with an aqueous solution of NaOH (7.5 equivalents) at rt for 30 min. The resulted mixture was filtrated and the aqueous phase extracted once with methylene chloride. The organic layers were combined and dried over anhydrous magnesium sulfate. Removal of the solvent *in vacuo* afforded the free base **6** as a sticky brownish oil, which solidified upon standing. The crude material was subjected to chromatography over silica gel [acetone–light petroleum (1 : 2) as eluent] to afford **6** as a white solid. Yield 73%; mp 62–63 °C (Found: C, 48.6; H, 4.4; N, 11.9. C₅₇H₆₀Cl₁₂N₁₂O₄ requires C, 48.8; H, 4.3; N, 12.0%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1100, 1518, 1555 and 3060; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.89 (12 H, t, *J* 7.2, 4 × CH₃), 1.40–2.00 (8 H, m, 4 CH₂), 2.43–2.64 (16 H, m, 8 CH₂), 3.20 (s, 8 H, 4 × OCH₂), 3.51 (8 H, t, *J* 5.4, 4 × CH₂) and 7.33 (8 H, s, 4 × Cl₃C₆H₂).

Tetrakis{2-[3-methyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazol-2-ium-5-yl]ethoxymethyl}methane tetrakis(hexachloroantimonate) 5e' and its free base tetrakis{2-[3-methyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazol-5-yl]ethoxymethyl}methane 7

The crude salt **5e'** was prepared from **2e** and **1** in the same

manner as compound **5d**. Basic work-up followed by subsequent chromatography as for **6** afforded the free base **7** as a white microcrystalline solid. As suggested by NMR spectra, the material contains still a trace of unidentified compounds. Yield: 76%. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1084, 1520 and 3059; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.50 (12 H, s, 4 × CH₃), 2.70 (8 H, t, *J* 7.0, 4 × CH₂), 3.28 (8 H, s, 4 × OCH₂), 3.72 (8 H, t, *J* 7.0, 4 × OCH₂) and 7.53 (8 H, s, 4 × Cl₃C₆H₂).

Nitrotris{2-[2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazol-2-ium-5-yl]ethyl}methane tris(hexachloroantimonate) 9a

From **2a** and **8** following the general procedure. Precipitation with Et₂O and crystallization from MeOH–MeCN afforded **9a** as white powders. Yield: 91%; mp >192 °C (decomp.) (Found: C, 23.3; H, 2.1; N, 7.7. C₃₇H₃₆Cl₂₇N₁₀O₂Sb₃·CH₃CN requires C, 23.2; H, 2.0; N, 7.6%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1380, 1545, 2253 and 3076; $\delta_{\text{H}}(\text{CD}_3\text{CN})$ 2.07 (3 H, s, CH₃CN), 2.57 (6 H, t, *J* 6.3, 3 × CH₂), 2.74 (6 H, t, *J* 6.3, 3 × CH₂), 2.82 (9 H, s, 3 × CH₃), 3.82 (9 H, s, 3 × NCH₃) and 8.05 (6 H, s, 3 × Cl₃C₆H₂); $\delta_{\text{C}}(\text{CD}_3\text{CN})$ 161.3, 161.1 (C=N), 141.8, 136.0, 130.9, 123.0 (aryl), 91.4 (NO₂C), 34.6, 13.4 (CH₃), 30.9 and 21.1 (CH₂).

Nitrotris{2-[2-ethyl-3-methyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazol-2-ium-5-yl]ethyl}methane tris(hexachloroantimonate) 9b

From **2b** and **8** as described above. Precipitation with Et₂O and crystallization from MeOH–MeCN afforded **9b** as colorless prisms. Yield: 86%; mp >199 °C (decomp.) (Found: C, 24.4; H, 2.4; N, 7.7. C₄₀H₄₂Cl₂₇N₁₀O₂Sb₃·CH₃CN requires C, 24.5; H, 2.2; N, 7.5%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1390, 1450, 1549, 1569 and 2933; $\delta_{\text{H}}(\text{CD}_3\text{CN})$ 1.37 (9 H, t, *J* 7.2, 3 × CH₃), 2.07 (3 H, s, CH₃CN), 2.57 (6 H, t, *J* 6.3, 3 × CH₂), 2.70 (6 H, t, *J* 6.3, 3 × CH₂), 2.85 (9 H, s, 3 × CH₃), 4.29 (6 H, q, *J* 7.2, 3 × CH₂) and 8.06 (6 H, s, 3 × Cl₃C₆H₂); $\delta_{\text{C}}(\text{CD}_3\text{CN})$ 161.2, 161.0 (C=N), 141.9, 135.9, 131.1, 123.1 (aryl), 91.4 (NO₂C), 44.3, 30.8, 20.9 (CH₂), 13.4 and 13.2 (CH₃).

Nitrotris{2-[6,7,8,9-tetrahydro-3-(2,4,6-trichlorophenyl)-5H-[1,2,4]triazolo[5,1-*a*]azepin-4-ium-2-yl]ethyl}methane tris(hexachloroantimonate) 9c

From **2c** and **8** as described above. Precipitation with Et₂O and crystallization twice from MeOH–MeCN afforded **9c** as a pale-yellow powder. Yield: 82%; mp >125 °C (decomp.) (Found: C, 27.2; H, 2.8; N, 7.7. C₄₆H₄₈Cl₂₇N₁₀O₂Sb₃·2CH₃CN requires C, 27.6; H, 2.5; N, 7.4%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1442, 1557, 2925 and 3081; $\delta_{\text{H}}(\text{CD}_3\text{CN})$ 1.21–2.05 (18 H, m, 9 × CH₂), 2.07 (6 H, s, 2 × CH₃CN), 2.56 (6 H, t, *J* 6.0, 3 × CH₂), 2.72 (6 H, t, *J* 6.0, 3 × CH₂), 3.36 (6 H, t, *J* 5.4, 3 × CH₂), 4.22 (6 H, t, *J* 5.1, 3 × CH₂) and 8.05 (6 H, s, 3 × Cl₃C₆H₂); $\delta_{\text{C}}(\text{CD}_3\text{CN})$ 165.7, 160.8 (C=N), 141.9, 136.3, 130.9, 122.8 (aryl), 91.4 (NO₂C), 49.8, 30.9, 28.4, 28.1, 25.7, 22.8 and 21.2 (CH₂).

Nitrotris{2-[3-propyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazol-2-ium-5-yl]ethyl}methane tris(hexachloroantimonate) 9d and its picrate 11

The salt **9d** was prepared from **2d** and **8** according to the general procedure, resulting in a viscous red oil which solidified on cooling and complete removal of the embedded solvent. This was converted to its picrate **11** by treating with a saturated solution of a slight excess of picric acid in EtOH. Crystallisation twice from absolute EtOH yielded pure picrate **11** as a yellow microcrystalline solid. Yield: 87%; mp >130 °C (decomp.) (Found: C, 40.8; H, 3.0; N, 15.9. C₅₈H₄₈N₁₉O₂₃Cl₉ requires C, 41.0; H, 2.9; N, 15.7%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1345, 1545, 1612 and 3448; $\delta_{\text{H}}(\text{CD}_3\text{CN})$ 0.98 (9 H, t, *J* 7.2, 3 × CH₃), 1.76–1.83 (6 H, m, 3 × CH₂), 2.42 (6 H, t, *J* 5.4, 3 × CH₂), 2.50 (6 H, t, *J* 5.4, 3 × CH₂), 2.74 (6 H, t, *J* 7.2, 3 × CH₂), 7.51 (6 H, s, 3 × Cl₃C₆H₂) and 9.19 (6 H, s, 3 (NO₂)₃C₆H₂O); $\delta_{\text{C}}(\text{CD}_3\text{CN})$ 164.8 (C=N), 155.4,

154.1, 137.8, 137.7, 135.2, 131.1, 129.2, 126.2 (aryl), 91.7 (NO₂C), 32.6, 30.0, 21.2, 20.3 (CH₂) and 13.6 (CH₃).

Retrieval of nitrotris{2-[3-propyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazol-5-yl]ethyl}methane **10**

A solution of the picrate **11** (1.70 g, 1.0 mmol) in CH₂Cl₂ (10 cm³) was shaken with 10% aqueous ammonia (10 cm³) at rt for 30 min. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (10 cm³). The combined organic layers were repeatedly washed with water until neutral and dried over anhydrous magnesium sulfate. The solvent was evaporated off to provide 0.84 g of the free base **10** as an essentially pure solid off-white mass. Yield: 83% based on **9**; mp 58–59 °C. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1376, 1464, 1523, 2962 and 3096; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.91 (9 H, t, J 7.2, 3 × CH₃), 1.62–1.93 (6 H, m, 3 × CH₂), 2.20–2.40 (12 H, m, 6 × CH₂), 2.58 (6 H, t, J 5.4, 3 × CH₂) and 7.36 (6 H, s, 3 × Cl₃C₆H₂).

X-Ray crystallography of compound **5b**

Suitable crystals[†] were grown from CH₂Cl₂–MeOH–CH₃CN as colorless prisms. A crystal of approximate dimensions 0.30 × 0.25 × 0.20 mm was used for data collection. *Crystal data*. Formula: C₅₇H₆₄Cl₁₂N₁₂O₄·4SbCl₆·2CH₂Cl₂, $M = 2914.25$. Crystal system: tetragonal; space group: $P4_2/n$ (# 86); cell constants: $a = b = 20.310(4)$, $c = 13.971(3)$ Å. $U = 5763(2)$ Å³; $Z = 2$; $D_c = 1.680$ g cm⁻³. $\mu(\text{Mo-K}\alpha)$; 1.898 mm⁻¹; $F(000) = 2844$. All measurements were made at 293 K on a Rigaku AFC7R diffractometer by employing graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) and a 12 kW rotating anode generator. The ω - 2θ scan technique to a maximum 2θ -value of 55.0° was used. Scans of $(1.78 + 0.30 \tan\theta)^\circ$ were made at a speed of 16.0° min⁻¹ (in omega). A total of 6977 observed reflections (unique: 6614; $R_{\text{int}} = 0.0289$) were collected and 2486 reflections having $I > 2.00\sigma(I)$ were observed. The structure was solved by direct methods (SHELXS86)¹⁹ and expanded using Fourier techniques.²⁰ The non-hydrogen atoms were refined anisotropically with F^2 , resulting in final agreement factors of $R = 0.0767$, $R_w = 0.2034$.

[†] CCDC reference number 149370. See <http://www.rsc.org/suppdata/p1/b1/b110059a/> for crystallographic files in .cif or other electronic format.

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