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Structure of 4,7-Bis(4-mercaptobenzoyl)-1-tosyl-1,4,7-triazacyclononane

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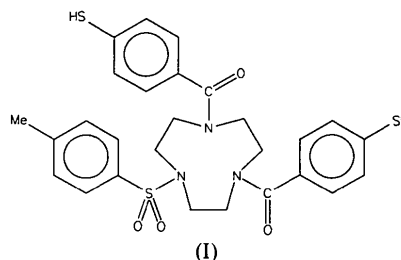
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Abstract. 4,7-Bis(4-mercaptobenzoyl)-1-tosyl-1,4,7-triazacyclononane-*n*-hexane (2/1), $C_{27}H_{29}N_3O_4S_3 \cdot 0.5C_6H_{14}$, $M_r = 598.8$, monoclinic, $P2_1/3$, $a = 24.113$ (5), $b = 11.020$ (5), $c = 12.065$ (4) Å, $\beta = 100.07$ (2)°, $V = 3156.7$ Å³, $Z = 4$, $D_x = 1.260$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.6$ cm⁻¹, $F(000) = 1268$, $T = 293$ K, $R = 0.085$ for 2493 observed reflections. The triazacyclononane ring has a 'twist-chair-chair' conformation, with a pseudotwofold symmetry axis in the ring. Two of the substituent groups are directed to opposite sides of the ring, the third is more equatorially orientated; all are at approximately sp^2 -hybridized N atoms. The two thiol groups form S—H···O hydrogen bonds connecting molecules in chains.

Introduction. Recently we synthesized the novel tridentate trithiol, 1,4,7-tris(4-mercaptobenzoyl)-1,4,7-triazacyclononane, which acts as a tripodal ligand to Fe₄S₄ metal clusters generating a site-differentiated Fe site (Evans, Leigh & Santana, 1991; Evans, Garcia, Leigh, Newton & Santana, 1992). As a minor product in the preparation of this molecule, we obtained crystals of the title compound (I). Presumably a small amount of 1-tosyl-1,4,7-triazacyclononane had been present in the 1,4,7-tri-

azacyclononane starting material used in the synthesis. We describe below a two-step synthesis to the title compound; the spectroscopic properties of this material are identical to those of the crystals used in the structural determination.



Experimental. The title molecule was prepared in two steps, but the protected-thiol intermediate was also isolated and characterized.

4,7-Bis[4-(acetylthio)benzoyl]-1-tosyl-1,4,7-triazacyclononane. To a slurry of 1,4,7-triazacyclononane trihydrochloride (157 mg, 0.66 mmol) and triethylamine (0.40 g, 0.55 cm³, 3.94 mmol) in dichloromethane (25 cm³), was added solid 4-toluenesulfonyl chloride (125 mg, 0.66 mmol). After stirring for 2 min, 4-(acetylthio)benzoyl chloride (283 mg,

1.32 mmol) was added to the solution. The mixture was stirred at room temperature for 3 h, the solution then washed with saturated aqueous NaHCO₃ (2 × 100 cm³), 5% HCl (aq.) and brine. After drying over anhydrous MgSO₄ the solution was concentrated to ca 5 cm³ and hexane (20 cm³) added. The precipitate was collected, washed with hexane, and dried. Recrystallization from dichloromethane/hexane gave a white product (60%). Analysis found: C 57.3, H 5.0, N 6.4, S 14.8%; C₃₁H₃₃N₃O₆S₃ requires: C 58.20, H 5.20, N 6.57, S 15.03%. ¹H NMR (CD₂Cl₂, reference SiMe₄): 7.6 (4H, *m*, —C₆H₄SO₂—), 7.36 (8H, *m*, —C₆H₄CO—), 3.80 (8H, *m*, —CH₂NCO—), 3.40 (4H, *m*, —CH₂NSO₂—), 2.42 (9H, *s*, CH₃, OCH₃).

4,7-Bis(4-mercaptobenzoyl)-1-tosyl-1,4,7-triazacyclononane. The acyl-protected dithiol prepared above (86.9 mg, 0.136 mmol) was heated for 3 h under reflux in methanol (60 cm³) under dinitrogen, with trimethylsilyl chloride (5.56 g, 6.50 cm³, 51 mmol). Solvent was removed by evaporation and the residue dissolved in dichloromethane (25 cm³), filtered through anhydrous MgSO₄, concentrated to ca 5 cm³, and diethyl ether (20 cm³) added. The white precipitate was collected, washed with diethyl ether, and dried (50%). Analysis of the precipitate found: C 57.8, H 5.0, N 7.55, S 16.7%; analysis of the crystals found: C 58.5, H 5.8, N 7.2, S 17.6%; C₂₇H₂₉N₃O₄S₃ requires: C 58.36, H 5.26, N 7.56, S 17.31%. ¹H NMR (CD₂Cl₂): 7.60 (4H, *m*, —C₆H₄SO₂—), 7.30 (8H, *m*, —C₆H₄CO—), 3.65 (8H, *m*, —CH₂NCO—), 3.62 (3H, *s*, SH), 3.40 (4H, *m*, —CH₂NSO₂—), 2.42 (3H, *s*, CH₃).

X-ray analysis of the title compound. Crystals were colourless prisms with a thin diamond-shaped cross-section. A crystal of ca 0.20 × 0.30 × 0.85 mm, mounted on glass fibre, was examined photographically before being transferred to an Enraf-Nonius CAD-4 diffractometer for determination of accurate cell parameters (from the goniometer settings of 25 reflections, each centred in four orientations, having θ ca 10.5°) and measurement of diffraction intensities (by the θ - ω scan method) to $\theta_{\max} = 22.5^\circ$ (ranges of *h*, *k* and *l* indices: -26/26, 0/12 and 0/14).

The intensities were corrected for Lorentz-polarization effects and for slight deterioration of the crystal (ca 3% deterioration over the period of data collection was shown by the intensities of two monitor reflections, 841 and 643); a small absorption correction (minimum/maximum transmission factors 0.930/0.953) was also applied from measurement of the crystal and indexing of its faces.

Of the 4588 measured intensities, 265 were systematically absent (confirming the space group) and 219 were duplicate-equivalent reflections (merged with $R = 0.060$). 4104 independent reflections were input to the SHELX76 program (Sheldrick, 1976) for determination of the structure

Table 1. Final fractional atomic coordinates ($\times 10^4$) and isotropic or equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

The H atoms and solvent atoms were treated isotropically; for the remaining atoms $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$. The site occupancy factor (s.o.f.) is 1.0 unless otherwise given.

| | x | y | z | $U_{\text{iso}}/U_{\text{eq}}$ | s.o.f. |
|--------------------------|------------|------------|------------|--------------------------------|--------|
| N(1) | 2194 (3) | 4918 (5) | 3538 (5) | 46 (2) | |
| C(2) | 2130 (3) | 5348 (6) | 2380 (7) | 54 (3) | |
| C(3) | 2680 (3) | 5437 (6) | 1910 (7) | 56 (3) | |
| N(4) | 3010 (3) | 6569 (5) | 2209 (5) | 52 (2) | |
| C(5) | 3580 (3) | 6439 (7) | 2792 (7) | 58 (3) | |
| C(6) | 3653 (3) | 6323 (6) | 4062 (7) | 55 (3) | |
| N(7) | 3402 (3) | 5213 (5) | 4435 (5) | 48 (2) | |
| C(8) | 2956 (3) | 5339 (7) | 5117 (7) | 57 (3) | |
| C(9) | 2412 (3) | 5748 (6) | 4452 (7) | 52 (3) | |
| C(1) | 2000 (3) | 3836 (7) | 3794 (7) | 52 (3) | |
| O(1) | 1978 (3) | 3569 (5) | 4785 (5) | 68 (2) | |
| C(11) | 1845 (3) | 2918 (6) | 2879 (6) | 47 (3) | |
| C(12) | 1316 (4) | 2498 (7) | 2614 (7) | 60 (3) | |
| C(13) | 1171 (4) | 1582 (8) | 1820 (7) | 64 (3) | |
| C(14) | 1581 (4) | 1086 (7) | 1293 (6) | 55 (3) | |
| C(15) | 2119 (3) | 1507 (7) | 1549 (6) | 55 (3) | |
| C(16) | 2245 (4) | 2401 (7) | 2343 (7) | 58 (3) | |
| S(1) | 1383 (1) | -43 (2) | 245 (2) | 85 (1) | |
| H(1) | 1846 (38) | -846 (77) | 390 (72) | 97 (28) | |
| C(4) | 2797 (4) | 7545 (7) | 1590 (8) | 63 (3) | |
| O(4) | 2346 (3) | 7518 (5) | 965 (6) | 84 (3) | |
| C(41) | 3139 (3) | 8698 (6) | 1679 (7) | 57 (3) | |
| C(42) | 3248 (4) | 9382 (7) | 2630 (7) | 61 (3) | |
| C(43) | 3513 (4) | 10507 (7) | 2634 (7) | 65 (3) | |
| C(44) | 3661 (4) | 10908 (7) | 1642 (8) | 75 (4) | |
| C(45) | 3568 (5) | 10221 (8) | 696 (8) | 96 (5) | |
| C(46) | 3296 (4) | 9107 (8) | 722 (7) | 77 (4) | |
| S(4) | 3981 (2) | 12354 (3) | 1562 (3) | 130 (2) | |
| H(4) | 4101 (29) | 12730 (63) | 2518 (62) | 64 (21) | |
| S(7) | 3773.8 (9) | 3979 (2) | 4581 (2) | 53.2 (7) | |
| O(71) | 3391 (2) | 2980 (4) | 4373 (5) | 66 (2) | |
| O(72) | 4208 (2) | 4135 (4) | 3905 (5) | 65 (2) | |
| C(71) | 4103 (3) | 3855 (7) | 5973 (7) | 57 (3) | |
| C(72) | 4606 (3) | 4454 (8) | 6366 (7) | 62 (3) | |
| C(73) | 4880 (4) | 4282 (9) | 7438 (8) | 74 (4) | |
| C(74) | 4685 (4) | 3511 (11) | 8163 (8) | 89 (4) | |
| C(75) | 4161 (5) | 2983 (11) | 7811 (10) | 109 (5) | |
| C(76) | 3890 (4) | 3110 (9) | 6726 (9) | 86 (4) | |
| C(77) | 5005 (5) | 3292 (14) | 9349 (9) | 136 (6) | |
| Solvent <i>n</i> -hexane | | | | | |
| C(81) | 77 (28) | 3925 (67) | 5160 (101) | 258 (27) | 0.5 |
| C(82) | 0 | 5000 | 5000 | 207 (25) | 0.5 |
| C(83) | 171 (41) | 5043 (114) | 3743 (77) | 262 (40) | 0.5 |
| C(84) | 162 (28) | 5153 (58) | 2493 (58) | 178 (23) | 0.3 |
| C(85) | 48 (44) | 4170 (111) | 6037 (133) | 264 (40) | 0.3 |
| C(86) | 566 (36) | 4807 (74) | 4484 (76) | 241 (29) | 0.3 |
| C(87) | 140 (45) | 3809 (107) | 4402 (120) | 236 (57) | 0.3 |

by direct methods (using the EEES routine). Refinement was by full-matrix least-squares methods and was terminated with $R = 0.085$ and $wR = 0.091$ [$w = (\sigma_F^2 + 0.00515F^2)^{-1}$] for the 2493 reflections with $I > 2\sigma_I$.

In the triazacyclononane moiety all the non-H atoms were refined anisotropically with H atoms included in idealized positions, their parameters riding on the parent C atoms; the H atoms of the methyl group were refined with geometrical constraints. The two thiol H atoms were located in difference maps and refined independently.

A solvent molecule, hexane, was found, disordered about a centre of symmetry. This molecule was not satisfactorily resolved and seven atom sites of various occupancies were included in the structure-factor calculations. There were no peaks of significance remaining in the final difference map.

Scattering-factor curves for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149). Computer programs used in this analysis have been noted above and listed by Anderson, Richards & Hughes (1986); they were run on a MicroVAX II computer in the Nitrogen Fixation Laboratory. Atomic parameters are listed in Table 1.*

Discussion. In the crystal, the molecule (Fig. 1) does not take a conformation which might readily suggest the tripod shape that was hoped for, even allowing for the replacement of the tosyl group by a third mercaptobenzoyl group.

Distances and angles in the molecule are listed in Table 2. The triazacyclononane ring has a 'twist-chair-chair' conformation, showing a pseudo-two-fold symmetry axis through C(8) and the midpoint of the C(3)—N(4) bond. The torsion angles in the ring follow a pattern similar to those estimated for conformation XIII described by Hendrickson (1964) for cyclononanes. The N(4)—C(4) and N(7)—S(7) bonds are directed to opposite sides of the ring plane and N(1)—C(1) is a more equatorially oriented bond.

Hendrickson (1964) showed that there are several distinct conformations for cyclononane rings, many of them readily interconverted by pseudo-rotation or by symmetrical flipping between chair- and boat-type forms. It would seem quite feasible that the ring of the title molecule should be able to change its shape without difficulty to one in which the three substituent groups are all directed to the same side of the ring.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55821 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1031]

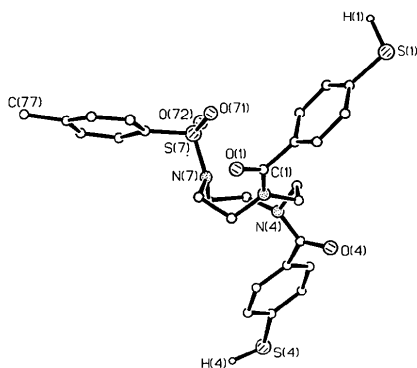


Fig. 1. View of a molecule of 4,7-bis(4-mercaptobenzoyl)-1-tosyl-1,4,7-triazacyclononane.

Table 2. Bond lengths (Å), bond angles (°), torsion angles of the macrocycle (°) and hydrogen-bond geometry (Å, °)

| | | | |
|---------------------|------------|---------------------|------------|
| N(1)—C(2) | 1.457 (9) | C(15)—C(16) | 1.371 (10) |
| N(1)—C(9) | 1.458 (9) | C(4)—O(4) | 1.211 (10) |
| N(1)—C(1) | 1.337 (9) | C(4)—C(41) | 1.507 (11) |
| C(2)—C(3) | 1.534 (11) | C(41)—C(42) | 1.359 (11) |
| C(3)—N(4) | 1.489 (9) | C(41)—C(46) | 1.355 (11) |
| N(4)—C(5) | 1.439 (9) | C(42)—C(43) | 1.394 (11) |
| N(4)—C(4) | 1.358 (10) | C(43)—C(44) | 1.380 (11) |
| C(5)—C(6) | 1.516 (11) | C(44)—C(45) | 1.355 (12) |
| C(6)—N(7) | 1.471 (8) | C(44)—S(4) | 1.781 (8) |
| N(7)—C(8) | 1.471 (9) | C(45)—C(46) | 1.396 (12) |
| N(7)—S(7) | 1.622 (6) | S(7)—O(71) | 1.430 (5) |
| C(8)—C(9) | 1.482 (10) | S(7)—O(72) | 1.446 (5) |
| C(1)—O(1) | 1.242 (9) | S(7)—C(71) | 1.732 (9) |
| C(1)—C(11) | 1.496 (10) | C(71)—C(72) | 1.389 (11) |
| C(11)—C(12) | 1.343 (10) | C(71)—C(76) | 1.388 (11) |
| C(11)—C(16) | 1.375 (10) | C(72)—C(73) | 1.360 (11) |
| C(12)—C(13) | 1.394 (11) | C(73)—C(74) | 1.360 (13) |
| C(13)—C(14) | 1.378 (11) | C(74)—C(75) | 1.388 (14) |
| C(14)—C(15) | 1.363 (11) | C(74)—C(77) | 1.522 (13) |
| C(14)—S(1) | 1.779 (8) | C(75)—C(76) | 1.364 (13) |
| S(1)—H(1) | 1.41 (9) | S(4)—H(4) | 1.21 (7) |
| C(2)—N(1)—C(9) | 119.1 (6) | N(4)—C(4)—C(41) | 118.6 (8) |
| C(2)—N(1)—C(1) | 121.9 (6) | O(4)—C(4)—C(41) | 119.0 (8) |
| C(9)—N(1)—C(1) | 118.6 (6) | C(4)—C(41)—C(42) | 123.4 (7) |
| N(1)—C(2)—C(3) | 114.9 (6) | C(4)—C(41)—C(46) | 116.8 (8) |
| C(2)—C(3)—N(4) | 115.0 (6) | C(42)—C(41)—C(46) | 119.5 (7) |
| C(3)—N(4)—C(5) | 117.3 (6) | C(41)—C(42)—C(43) | 121.2 (7) |
| C(3)—N(4)—C(4) | 113.4 (7) | C(42)—C(43)—C(44) | 118.0 (8) |
| C(5)—N(4)—C(4) | 125.8 (6) | C(43)—C(44)—C(45) | 121.5 (8) |
| N(4)—C(5)—C(6) | 115.8 (6) | C(43)—C(44)—S(4) | 120.9 (7) |
| C(5)—C(6)—N(7) | 113.4 (6) | C(45)—C(44)—S(4) | 117.6 (7) |
| C(6)—N(7)—C(8) | 118.3 (6) | C(44)—C(45)—C(46) | 118.8 (9) |
| C(6)—N(7)—S(7) | 118.7 (5) | C(41)—C(46)—C(45) | 121.0 (8) |
| C(8)—N(7)—S(7) | 117.6 (5) | N(7)—S(7)—O(71) | 107.3 (3) |
| N(7)—C(8)—C(9) | 113.0 (6) | N(7)—S(7)—O(72) | 106.3 (3) |
| N(1)—C(9)—C(8) | 112.7 (6) | O(71)—S(7)—O(72) | 120.1 (3) |
| N(1)—C(1)—O(1) | 120.7 (7) | N(7)—S(7)—C(71) | 108.8 (3) |
| N(1)—C(1)—C(11) | 119.0 (7) | O(71)—S(7)—C(71) | 106.4 (3) |
| O(1)—C(1)—C(11) | 120.2 (7) | O(72)—S(7)—C(71) | 107.6 (4) |
| C(1)—C(11)—C(12) | 120.9 (7) | S(7)—C(71)—C(72) | 121.2 (6) |
| C(1)—C(11)—C(16) | 121.5 (7) | S(7)—C(71)—C(76) | 121.5 (7) |
| C(12)—C(11)—C(16) | 117.5 (7) | C(72)—C(71)—C(76) | 117.3 (8) |
| C(11)—C(12)—C(13) | 121.8 (8) | C(71)—C(72)—C(73) | 120.6 (8) |
| C(12)—C(13)—C(14) | 119.4 (8) | C(72)—C(73)—C(74) | 122.2 (9) |
| C(13)—C(14)—C(15) | 119.5 (7) | C(73)—C(74)—C(75) | 117.6 (9) |
| C(13)—C(14)—S(1) | 118.7 (6) | C(73)—C(74)—C(77) | 121.9 (10) |
| C(15)—C(14)—S(1) | 121.8 (6) | C(75)—C(74)—C(77) | 120.4 (10) |
| C(14)—C(15)—C(16) | 119.3 (7) | C(74)—C(75)—C(76) | 120.6 (10) |
| C(11)—C(16)—C(15) | 122.6 (7) | C(71)—C(76)—C(75) | 121.2 (9) |
| N(4)—C(4)—O(4) | 122.3 (8) | | |
| C(14)—S(1)—H(1) | 104.0 (35) | C(44)—S(4)—H(4) | 106.7 (33) |
| C(9)—N(1)—C(2)—C(3) | 76.5 (8) | C(5)—C(6)—N(7)—C(8) | -119.8 (7) |
| N(1)—C(2)—C(3)—N(4) | -82.9 (8) | C(6)—N(7)—C(8)—C(9) | 73.5 (8) |
| C(2)—C(3)—N(4)—C(5) | 122.6 (7) | N(7)—C(8)—C(9)—N(1) | 59.5 (8) |
| C(3)—N(4)—C(5)—C(6) | -85.6 (8) | C(8)—C(9)—N(1)—C(2) | -116.9 (7) |
| N(4)—C(5)—C(6)—N(7) | 64.9 (8) | | |
| S(1)—O(4') | 3.559 (7) | S(4)—O(72'') | 3.406 (6) |
| H(1)···O(4') | 2.21 (9) | H(4)···O(72'') | 2.26 (7) |
| S(1)—H(1)···O(4') | 158 (6) | S(4)—H(4)···O(72'') | 156 (5) |

Symmetry code: (') $x, y - 1, z$; (') $x, y + 1, z$.

Structures for two other tri-substituted triazacyclononanes have been reported: the cation $[\text{Me}_3\text{H}(\text{N}_3\text{C}_6\text{H}_{12})]^+$ (Wieghardt, Brodka, Peters, Peters & Simon, 1987) and a molecule with rather bulkier substituent groups, $L_3(\text{N}_3\text{C}_6\text{H}_{12})$ where $L = 2\text{-hydroxy-3,5-dimethylbenzyl}$ (Moore, Fanwick & Welch, 1989). The shapes in the triazacyclononane rings in these show two more of Hendrickson's patterns: the cationic ring has a 'boat-chair' confor-

mation with approximately 3*m* (C_{3v}) symmetry (type XVII), and the tribenzyl derivative adopts a 'twist-chair-boat' shape with an approximate twofold symmetry axis, C₂ (type XV). The ring shapes in both these molecules are probably influenced by intramolecular hydrogen bonding connecting the N—H group (of the cation) and the O—H groups (of the tribenzyl moiety) with the ring N atoms. In both of these, the three alkyl substituent groups are equatorially arranged at N atoms with sp³ hybridizations; the N atoms are between 0.37 and 0.49 Å displaced from the planes of the three adjacent C atoms. In the title molecule, the N atoms show more nearly sp²-type arrangements, with displacements of 0.055 (6) and 0.156 (6) Å for the mercaptobenzoyl groups and 0.205 (6) Å for the tosyl group.

Peaks corresponding to likely H atoms of the two thiol groups, at S(1) and S(4), were identified in difference maps, and these H atoms were included in the later cycles of refinement. Both are involved in S—H···O hydrogen bonds, linking the molecules in

chains parallel to the *b* axis (Table 2). This is not the elongated direction of the crystal, which is parallel to the *c* axis. Other intermolecular contacts, between neighbouring triazacyclononane molecules and involving the disordered hexane molecules, are at normal van der Waals distances.

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Structure of *trans*-1-{2-[(2-Butoxy)phenylcarbamoyloxy]cycloheptylmethyl}-piperidinium Chloride

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Abstract. C₂₄H₃₉N₂O₃⁺.Cl[−], *M_r* = 439.0, monoclinic, *P*2₁/*n*, *a* = 9.114 (7), *b* = 18.747 (11), *c* = 14.185 (9) Å, β = 104.57 (6)°, *V* = 2346 (1) Å³, *Z* = 4, *D_m* = 1.25 (1), *D_x* = 1.243 Mg m^{−3}, λ(Mo *K*α) = 0.71069 Å, μ = 0.187 mm^{−1}, *F*(000) = 952, *T* = 293 K, final *R* = 0.057 for 1451 unique observed reflections. The title compound, which is a potent local anesthetic of the phenylcarbamate type, was designed to explore the stereostructural requirements of the anesthetic receptor by locking the phenylcarbamate–amine link into a semirigid system. The mean planes through the piperidine (chair conformation) and the cycloheptane (twist-chair form) rings are approximately normal to each other, with a dihedral angle of 108.7 (5)°. As usually observed in

2-alkoxyphenylcarbamates, the butoxy group is conjugated and the carbamate function deconjugated with the aromatic ring. There is one hydrogen-bond interaction between the protonated amine and the Cl anion, with an N···Cl[−] distance of 3.106 (3) Å.

Introduction. The title compound belongs to the phenylcarbamate class of local anesthetics which are esters of 2-alkoxyphenylcarbamoyl acid with primary or secondary amines. Common structural features of these compounds are a (protonated) amine N atom, a phenylcarbamate moiety, a two- or three-C-atom spacer separating this pair of anesthesiophoric groups, and a hydrophobic moiety, typically in the *ortho* position on the phenyl ring. Previous studies,