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(*R*,*E*)-[4-(Benzyloxy)-2-(cinnamoyloxy)-4-oxobutyl]trimethylammonium chloride hydrochloride

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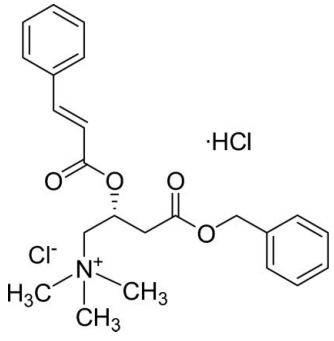
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.049; wR factor = 0.206; data-to-parameter ratio = 20.2.

The title compound, $C_{23}H_{28}NO_4^+\cdot Cl^-\cdot HCl$, is a quaternary ammonium salt with a scaffold similar to that of acetyl-L-carnitine hydrochloride. The two Cl atoms in the structure are tightly bonded by a strong Cl—H···Cl hydrogen bond with a Cl···Cl separation of 3.068 (2) Å. The cations are held together partly by a range of C—H···O and C—H···π interactions.

Related literature

Adams & Ulich (1920) report the synthesis of cinnamoyl chloride. Pharmaceutical applications of L-carnitine and cinnamic acid are described by Christov *et al.* (2006), Crill & Helms (2007) and Kim *et al.* (2006). Acetyl-L-carnitine hydrochloride is described by Destro & Heyda (1977) and Weber *et al.* (1995). Background information related to Cl—H···Cl hydrogen bonds is given by Stoyanov *et al.* (2006), Atwood *et al.* (1990) and Luo *et al.* (2002).



Experimental

Crystal data

$C_{23}H_{28}NO_4^+\cdot Cl^-\cdot HCl$
M_r = 454.37
Orthorhombic, $P2_12_12_1$
a = 10.1670 (4) Å
b = 10.4488 (4) Å
c = 22.9795 (11) Å
V = 2441.18 (18) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.29 mm^{-1}
T = 293 (2) K
0.41 × 0.26 × 0.23 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2005)
T_{min} = 0.889, T_{max} = 0.935
19537 measured reflections
5648 independent reflections
3350 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.206
S = 0.81
5648 reflections
279 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Absolute structure: Flack (1983), 2454 Friedel pairs
Flack parameter: −0.01 (11)

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 and *Cg*2 are the centroids of the C1–C6 and C18–C23 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9*A*···O4^{i}	0.97	2.42	3.299 (4)	150
C11—H11*A*···O4^{i}	0.97	2.49	3.336 (4)	146
C12—H12*A*···O2^{i}	0.96	2.49	3.103 (6)	121
C13—H13*C*···Cl1^{ii}	0.96	2.72	3.587 (6)	151
C12—H12*B*···*Cg*2^{iii}	0.96	2.62	3.551 (5)	164
C20—H20···*Cg*1^{iv}	0.93	2.95	3.776 (4)	148
Cl1—H1*A*···Cl2	1.37	1.70	3.068 (2)	176
C10—H10···O4	0.98	2.28	2.712 (4)	105
C13—H13*B*···O4	0.96	2.40	3.324 (6)	161
C14—H14*B*···O3	0.96	2.45	3.069 (5)	122
C17—H17···O4	0.93	2.49	2.828 (4)	102

Symmetry codes: (i) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x+1, y, z$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x-1, y-1, z$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2065).

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supplementary materials

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(*R*,*E*)-[4-(Benzyloxy)-2-(cinnamoyloxy)-4-oxobutyl]trimethylammonium chloride hydrochloride

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Comment

L-carnitine and cinnamic acid are reported to have some pharmaceutical applications (Crill & Helms, 2007; Christov *et al.*, 2006; Kim *et al.*, 2006). In order to study the biological activities of novel synthetic *L*-carnitine derivatives, a cinnamoyl *L*-carnitine benzoate was prepared and its crystal structure (Fig. 1) is reported here.

The title compound is a quaternary ammonium salt with a scaffold similar to that of acetyl-*L*-carnitine hydrochloride (Destro & Heyda, 1977; Weber *et al.*, 1995). C16—C17 (1.332 Å) and C15—C16 and C17—C18 (1.467 and 1.466 Å) have bond lengths typical for partially delocalized C—C single and C=C double bonds, thus pointing towards the existence of a conjugated system along the chain O3—C15—C16—C17—C18. All other bond distances and angles are well within the expected ranges.

The compound is a hydrochloride solvate and the two chlorine atoms in the structure are tightly bonded by a strong Cl—H···Cl hydrogen bond as is evident from the small separation of the two chlorine atoms (3.068 (2) Å), which is very close to the standard value of 3.11Å in hydrogen dichloride ions (Atwood *et al.*, 1990). Cl···Cl nonbonding contacts other than Cl—H···Cl hydrogen bonds exhibit values usually larger than 3.36Å (Stoyanov *et al.*, 2006). The hydrogen atom was tentatively localized in a difference density map, and the values are in agreement with previously reported data when taking the accuracy of the X-ray experiment for the determination of hydrogen atoms into account. The refined H—Cl distance of 1.37Å is slightly longer than that reported for the covalent HCl molecule in the gaseous state without a Cl—H···Cl bond (1.28 Å, Luo *et al.*, 2002), and the H···Cl separation of 1.70Å is slightly longer than the previously reported values (1.65 Å, Atwood *et al.*, 1990).

The molecules are held together partly by a range of two C—H···O and, owing to the existence of two benzene rings, two C—H···π interactions. (see the Hydrogen-bond geometry table), which contribute to the stabilization of the molecular geometry and the crystal strucuture.

Experimental

1. Preparation of cinnamoyl chloride: Cinnamoyl chloride was prepared according to the reported method (Adams & Ulich, 1920).

2. Preparation of (*R*,*E*)-3-carboxy-2-(cinnamoyloxy) -*N*,*N*,*N*-trimethylpropan-1-ammonium chloride:

L-carnitine hydrochloride (30.06 g, 0.125 mol) was dissolved in anhydrous trifluoroacetic acid (100 ml), followed by the addition of excess cinnamoyl chloride in an ice bath. The resulting mixture was stirred at 318–323 K until the starting material disappeared as evidenced by TLC (about 20 h). After the reaction was completed, the solvent was removed *in vacuo* and 400 ml acetone were added. The mixture was stirred for another 2 h, the white precipitate was removed, and then 800 ml diethyl ether were added to the filtrate. The resultant mixture was cooled to room temperature and filtered, the

white precipitate obtained was then collected and recrystallized from ethanol-diethyl ether (V:V=1:4) to afford the target compound as colourless needles (36.30 g, 76.0% yield).

3. Preparation of (*R*,*E*)-4-chloro-2-(cinnamoyloxy)- *N*,*N*,*N*-trimethyl-4-oxobutan-1-ammonium chloride:

(*R*,*E*)-3-carboxy-2-(cinnamoyloxy)-*N*,*N*,*N*-trimethylpropan −1-ammonium chloride (26.4 g, 0.09 mol) was dissolved in 100 ml of dichlormethane at 273 K, to which freshly distilled oxalyl chloride (15 ml, 0.12 mol) was added dropwise. The resulting mixture was reacted at 318–323 K for 4 h. The solvent was removed *in vacuo* and the white residue obtained was directly used in the following reaction without further purification.

4. Synthesis of the title compound

The above intermediate was dissolved in 100 ml of anhydrous dimethyl sulfoxide (DMSO) followed by the addition of phenylmethanol (20 ml, 0.18 mol) at room temperature. The resulting mixture was reacted at 323 K for 5 h. After adding 80 ml of diethyl ether and stirring for another 2 h, a white precipitate was collected and dried *in vacuo* at 313 K. The crude product was recrystallized from a mixture of acetic ether/diethyl ether (V:V=1:2, 75 ml) to give the title compound as colourless crystals (21.80 g, 58.0% yield).

m.p. 363–365 K; IR (KBr, ν cm^{-1}): 3067, 3027(CH), 1729, 1695(C=O), 1669, 1628(C=C), 1504, 1588(Ar—C), 1486, 1431(CH_2, CH_3), 1208(C—N) 681, 695, 723, 758, 917(Ar); ^{1}H NMR (MeOD, p.p.m.): 2.71–2.76(m, 2H, –CH_2), 2.98(s, 9H, –CH_3), 3.58, 3.60 (d, 2H, N—CH_2), 3.71–3.76 (dd, 1H, J=5.7; 13.2 Hz, N—CH_2), 4.79(d, 2H, O—CH_2), 5.60–5.64(m, 1H, –CH—O), 6.05, 6.10 (1*H*, d, J=4.8 Hz, CH=), 6.34, 6.40 (1*H*, d, J=4.8 Hz, =CH), 6.84–7.00 (m, 5H, $CH_2C_6H_5$), 7.10–7.40 (m, 5H, CH—C_6H_5); ^{13}C NMR (MeOD, p.p.m.): 26.45(C7), 129.0(C1), 127.7(C2,C4,C6), 129.0(C3), 141.2(C5), 68.4(C7), 167.1(C8), 37.2(C9), 63.6(C10), 70.2(C11), 54.7(C12,C13,C14), 158.5(C15), 128.2(C16), 136.2(C17), 135.2(C18), 126.4(C19, C23), 128.7(C20, C21, C22); ESI-MS (m/*z*): 436.2 $[M+H]^+$; Analysis found: C 61.28, H 6.83, N 3.01%; calculated for $C_{23}H_{29}O_4Cl_2N$: C 60.74, H 6.38, N 3.08%.

20 mg of the title compound were dissolved in 5 ml of 95% methanol, then a mixture of acetic acid and diethyl ether (V:V=1:2, 15 ml) was added slowly, the resulting slightly cloudy solution was kept at 263 K for 24 h. Slow evaporation gave colourless single crystals, which were suitable for X-Ray analysis.

Refinement

All H atoms except H1A bound to the Cl atoms were placed in geometrically calculated positions and refined using a riding model with C—H = 0.97 Å (for CH_2 groups) and 0.96 Å (for CH_3 groups). Their isotropic displacement parameters U_{iso} were set to 1.2 times (1.5 times for CH_3 groups) the equivalent displacement parameter U_{eq} of their parent atoms.

In the refinement, the H atom attached to Cl atom was obtained from a difference density map as the highest peak after assignement of all other hydrogen atoms. The peak (0.32 e $Å^{-3}$ at 0.2314 0.4121 0.2017) was localized 0.68 Å from Cl(2) and 1.32 Å from Cl(1), respectively. Considering the charge equilibrium, the H atom attached to the Cl atom could be suitable for the peak. Upon refinement the *R* factor dropped from 0.0511 to 0.0489, and the equivalent dispalcement parameter of the H atom refined to 0.091. In the final model the U_{iso} value was set to be 1.5 times U_{eq} of that of the closest Cl atom.

Figures

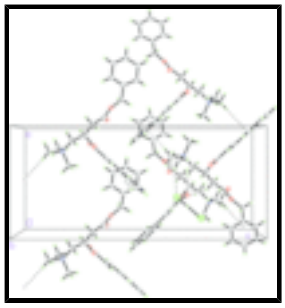

Fig. 1. View of the molecule showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

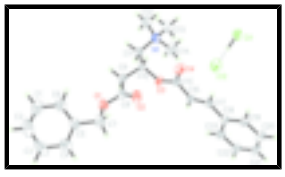

Fig. 2. Molecular packing diagram viewed along the *b* axis. H atoms bonded to C atoms have been omitted for clarity.

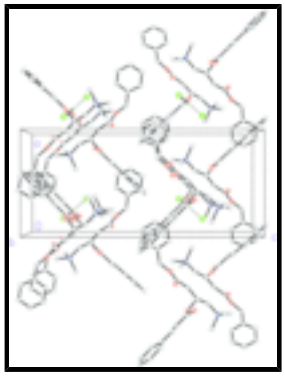

Fig. 3. Stereoview of part of the crystal structure of the title compound, showing the formation of hydrogen bonds. Dashed lines indicate the hydrogen bonding interactions.

(*R*,*E*)-[4-(Benzyloxy)-2-(cinnamoyloxy)- 4-oxobutyl]trimethylammonium chloride hydrochloride

Crystal data

$C_{23}H_{28}NO_4^+ \cdot Cl^- \cdot H_1Cl_1$	$D_x = 1.236$ Mg m^{-3}
$M_r = 454.37$	Melting point: 363-365K K
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 10.1670$ (4) Å	Cell parameters from 3797 reflections
$b = 10.4488$ (4) Å	$\theta = 2.6$–21.0º
$c = 22.9795$ (11) Å	$\mu = 0.29$ mm^{-1}
$V = 2441.18$ (18) Å^3	$T = 293$ (2) K
$Z = 4$	Prism, colourless
$F_{000} = 960$	0.41 × 0.26 × 0.23 mm

Data collection

Bruker APEXII CCD area-detector diffractometer	5648 independent reflections
Radiation source: fine-focus sealed tube	3350 reflections with $I > 2\sigma(I)$

Monochromator: graphite	R_{int} = 0.040
T = 293(2) K	θ_{max} = 27.6º
φ and ω scans	θ_{min} = 2.1º
Absorption correction: multi-scan (APEX2; Bruker, 2005)	h = −13→10
T_{min} = 0.889, T_{max} = 0.935	k = −13→13
19537 measured reflections	l = −29→29

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1668P)^2 + 0.001P]$ where $P = (F_o^2 + 2F_c^2)/3$
Least-squares matrix: full	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)]$ = 0.049	$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$wR(F^2)$ = 0.206	$\Delta\rho_{min}$ = −0.25 e Å^{-3}
S = 0.81	Extinction correction: none
5648 reflections	Absolute structure: Flack (1983), 2454 Friedel pairs
279 parameters	Flack parameter: −0.01 (11)
H-atom parameters constrained	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	1.5794 (5)	0.6771 (5)	0.3970 (3)	0.0975 (15)
H1	1.6264	0.7037	0.3645	0.117*
C2	1.6308 (5)	0.6890 (5)	0.4490 (3)	0.108 (2)
H2	1.7145	0.7239	0.4527	0.130*
C3	1.5644 (7)	0.6513 (5)	0.4982 (3)	0.109 (2)
H3	1.6028	0.6603	0.5347	0.131*
C4	1.4367 (5)	0.5985 (4)	0.49251 (19)	0.0781 (11)
H4	1.3891	0.5742	0.5252	0.094*
C5	1.3849 (3)	0.5841 (4)	0.43810 (15)	0.0598 (8)
C6	1.4565 (5)	0.6255 (4)	0.39051 (19)	0.0771 (11)
H6	1.4205	0.6182	0.3535	0.093*
C7	1.2561 (5)	0.5165 (5)	0.4303 (2)	0.0883 (14)
H7A	1.2715	0.4291	0.4179	0.106*

H7B	1.2092	0.5142	0.4671	0.106*
C8	1.0922 (3)	0.5120 (3)	0.35739 (15)	0.0540 (7)
C9	1.0245 (3)	0.5897 (3)	0.31191 (15)	0.0551 (7)
H9A	1.0902	0.6249	0.2859	0.066*
H9B	0.9803	0.6609	0.3306	0.066*
C10	0.9248 (3)	0.5160 (3)	0.27626 (13)	0.0484 (7)
H10	0.9662	0.4409	0.2585	0.058*
C11	0.8743 (3)	0.6043 (3)	0.23001 (14)	0.0594 (8)
H11A	0.9495	0.6339	0.2078	0.071*
H11B	0.8372	0.6785	0.2493	0.071*
C12	0.7716 (6)	0.6435 (6)	0.1363 (2)	0.113 (2)
H12A	0.7571	0.7297	0.1494	0.170*
H12B	0.7022	0.6189	0.1103	0.170*
H12C	0.8544	0.6387	0.1164	0.170*
C13	0.8013 (5)	0.4216 (5)	0.1668 (2)	0.0918 (13)
H13A	0.7359	0.3963	0.1390	0.138*
H13B	0.7994	0.3642	0.1994	0.138*
H13C	0.8866	0.4189	0.1489	0.138*
C14	0.6389 (4)	0.5535 (6)	0.2142 (2)	0.0973 (15)
H14A	0.6177	0.6371	0.2287	0.146*
H14B	0.6376	0.4931	0.2457	0.146*
H14C	0.5754	0.5288	0.1854	0.146*
C15	0.7964 (3)	0.3504 (3)	0.32137 (13)	0.0478 (7)
C16	0.6979 (3)	0.3258 (3)	0.36670 (13)	0.0460 (6)
H16	0.6558	0.3936	0.3852	0.055*
C17	0.6692 (3)	0.2054 (3)	0.38118 (13)	0.0472 (7)
H17	0.7132	0.1416	0.3608	0.057*
C18	0.5758 (3)	0.1630 (3)	0.42578 (13)	0.0482 (7)
C19	0.5485 (3)	0.0341 (3)	0.43073 (15)	0.0553 (8)
H19	0.5914	−0.0241	0.4067	0.066*
C20	0.4571 (4)	−0.0096 (4)	0.47148 (17)	0.0682 (10)
H20	0.4374	−0.0964	0.4737	0.082*
C21	0.3967 (4)	0.0752 (4)	0.50804 (17)	0.0734 (11)
H21	0.3367	0.0459	0.5355	0.088*
C22	0.4246 (4)	0.2045 (4)	0.50423 (18)	0.0758 (11)
H22	0.3829	0.2619	0.5291	0.091*
C23	0.5146 (4)	0.2490 (4)	0.46349 (15)	0.0634 (9)
H23	0.5340	0.3359	0.4614	0.076*
Cl2	0.34728 (19)	0.4253 (2)	0.25740 (8)	0.1340 (6)
N1	0.7733 (3)	0.5557 (3)	0.18732 (12)	0.0619 (7)
O1	1.1776 (3)	0.5832 (2)	0.38699 (11)	0.0688 (7)
O2	1.0754 (3)	0.4004 (2)	0.36643 (13)	0.0726 (7)
O3	0.81958 (19)	0.47657 (18)	0.31532 (9)	0.0479 (5)
O4	0.8494 (3)	0.2695 (2)	0.29206 (11)	0.0683 (7)
Cl1	0.15256 (13)	0.39911 (12)	0.15612 (6)	0.0978 (4)
H1A	0.2369	0.4149	0.2018	0.147*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.070 (3)	0.079 (3)	0.144 (5)	−0.001 (2)	0.023 (3)	−0.009 (3)
C2	0.071 (3)	0.066 (3)	0.187 (7)	0.001 (2)	−0.032 (4)	0.007 (4)
C3	0.124 (4)	0.074 (3)	0.130 (5)	0.010 (3)	−0.081 (4)	−0.003 (3)
C4	0.095 (3)	0.065 (2)	0.075 (2)	0.016 (2)	−0.020 (2)	0.0058 (19)
C5	0.0508 (18)	0.064 (2)	0.064 (2)	0.0027 (16)	−0.0048 (15)	−0.0002 (16)
C6	0.077 (3)	0.074 (2)	0.081 (3)	−0.006 (2)	0.006 (2)	−0.017 (2)
C7	0.066 (2)	0.111 (3)	0.088 (3)	−0.018 (2)	−0.023 (2)	0.038 (3)
C8	0.0402 (15)	0.0566 (18)	0.0652 (19)	−0.0015 (13)	0.0066 (14)	0.0054 (15)
C9	0.0482 (16)	0.0491 (15)	0.0681 (19)	−0.0052 (14)	−0.0019 (15)	0.0114 (15)
C10	0.0399 (14)	0.0460 (15)	0.0593 (17)	−0.0063 (13)	0.0092 (13)	0.0046 (13)
C11	0.0593 (19)	0.0567 (18)	0.0623 (19)	−0.0174 (16)	−0.0050 (15)	0.0104 (16)
C12	0.129 (4)	0.124 (4)	0.086 (3)	−0.052 (4)	−0.041 (3)	0.049 (3)
C13	0.097 (3)	0.088 (3)	0.091 (3)	−0.004 (3)	−0.017 (3)	−0.018 (2)
C14	0.053 (2)	0.140 (5)	0.100 (3)	0.003 (3)	−0.006 (2)	0.014 (3)
C15	0.0490 (17)	0.0421 (14)	0.0524 (16)	−0.0023 (13)	0.0060 (13)	−0.0033 (13)
C16	0.0440 (15)	0.0473 (15)	0.0466 (14)	−0.0017 (12)	0.0046 (12)	0.0005 (12)
C17	0.0445 (15)	0.0454 (15)	0.0517 (15)	−0.0005 (13)	0.0039 (13)	−0.0024 (12)
C18	0.0408 (14)	0.0533 (16)	0.0505 (15)	0.0009 (13)	−0.0002 (13)	0.0099 (13)
C19	0.0486 (17)	0.0518 (16)	0.0654 (19)	0.0045 (15)	0.0097 (15)	0.0088 (15)
C20	0.063 (2)	0.059 (2)	0.082 (2)	−0.0047 (18)	0.0094 (19)	0.0221 (18)
C21	0.066 (2)	0.085 (3)	0.069 (2)	−0.010 (2)	0.0172 (19)	0.019 (2)
C22	0.076 (2)	0.084 (3)	0.068 (2)	−0.004 (2)	0.028 (2)	−0.0030 (19)
C23	0.068 (2)	0.057 (2)	0.065 (2)	−0.0015 (17)	0.0157 (18)	−0.0021 (16)
Cl2	0.1186 (12)	0.1575 (15)	0.1259 (11)	−0.0422 (12)	0.0160 (10)	−0.0017 (11)
N1	0.0561 (16)	0.0646 (17)	0.0651 (17)	−0.0086 (13)	−0.0024 (13)	0.0080 (14)
O1	0.0624 (14)	0.0648 (14)	0.0792 (16)	−0.0067 (12)	−0.0189 (12)	0.0145 (12)
O2	0.0708 (16)	0.0542 (14)	0.0927 (17)	−0.0047 (13)	−0.0099 (14)	0.0186 (13)
O3	0.0420 (11)	0.0416 (10)	0.0601 (11)	−0.0014 (8)	0.0139 (9)	0.0014 (9)
O4	0.0802 (16)	0.0450 (11)	0.0795 (15)	−0.0014 (12)	0.0327 (14)	−0.0070 (11)
Cl1	0.0803 (7)	0.0913 (8)	0.1218 (9)	−0.0201 (6)	0.0286 (7)	−0.0118 (7)

Geometric parameters (Å, °)

C1—C2	1.310 (8)	C12—H12C	0.9600
C1—C6	1.368 (7)	C13—N1	1.506 (6)
C1—H1	0.9300	C13—H13A	0.9600
C2—C3	1.374 (9)	C13—H13B	0.9600
C2—H2	0.9300	C13—H13C	0.9600
C3—C4	1.416 (9)	C14—N1	1.499 (6)
C3—H3	0.9300	C14—H14A	0.9600
C4—C5	1.365 (5)	C14—H14B	0.9600
C4—H4	0.9300	C14—H14C	0.9600
C5—C6	1.383 (6)	C15—O4	1.208 (4)
C5—C7	1.499 (6)	C15—O3	1.347 (3)
C6—H6	0.9300	C15—C16	1.468 (4)

C7—O1	1.454 (5)	C16—C17	1.333 (4)
C7—H7A	0.9700	C16—H16	0.9300
C7—H7B	0.9700	C17—C18	1.466 (4)
C8—O2	1.197 (4)	C17—H17	0.9300
C8—O1	1.330 (4)	C18—C19	1.379 (5)
C8—C9	1.492 (5)	C18—C23	1.395 (5)
C9—C10	1.514 (4)	C19—C20	1.396 (5)
C9—H9A	0.9700	C19—H19	0.9300
C9—H9B	0.9700	C20—C21	1.367 (6)
C10—O3	1.456 (3)	C20—H20	0.9300
C10—C11	1.497 (4)	C21—C22	1.383 (7)
C10—H10	0.9800	C21—H21	0.9300
C11—N1	1.508 (4)	C22—C23	1.390 (5)
C11—H11A	0.9700	C22—H22	0.9300
C11—H11B	0.9700	C23—H23	0.9300
C12—N1	1.488 (5)	Cl2—H1A	1.7033
C12—H12A	0.9600	Cl1—H1A	1.3661
C12—H12B	0.9600		
?···?	?		
C2—C1—C6	120.1 (6)	H12A—C12—H12C	109.5
C2—C1—H1	119.9	H12B—C12—H12C	109.5
C6—C1—H1	119.9	N1—C13—H13A	109.5
C1—C2—C3	121.8 (5)	N1—C13—H13B	109.5
C1—C2—H2	119.1	H13A—C13—H13B	109.5
C3—C2—H2	119.1	N1—C13—H13C	109.5
C2—C3—C4	119.0 (5)	H13A—C13—H13C	109.5
C2—C3—H3	120.5	H13B—C13—H13C	109.5
C4—C3—H3	120.5	N1—C14—H14A	109.5
C5—C4—C3	118.8 (5)	N1—C14—H14B	109.5
C5—C4—H4	120.6	H14A—C14—H14B	109.5
C3—C4—H4	120.6	N1—C14—H14C	109.5
C4—C5—C6	119.1 (4)	H14A—C14—H14C	109.5
C4—C5—C7	119.9 (4)	H14B—C14—H14C	109.5
C6—C5—C7	120.9 (4)	O4—C15—O3	123.3 (3)
C1—C6—C5	121.1 (5)	O4—C15—C16	125.3 (3)
C1—C6—H6	119.4	O3—C15—C16	111.4 (2)
C5—C6—H6	119.4	C17—C16—C15	119.4 (3)
O1—C7—C5	109.6 (3)	C17—C16—H16	120.3
O1—C7—H7A	109.8	C15—C16—H16	120.3
C5—C7—H7A	109.8	C16—C17—C18	127.0 (3)
O1—C7—H7B	109.8	C16—C17—H17	116.5
C5—C7—H7B	109.8	C18—C17—H17	116.5
H7A—C7—H7B	108.2	C19—C18—C23	119.2 (3)
O2—C8—O1	123.3 (3)	C19—C18—C17	118.9 (3)
O2—C8—C9	125.9 (3)	C23—C18—C17	121.9 (3)
O1—C8—C9	110.8 (3)	C18—C19—C20	120.6 (3)
C8—C9—C10	114.3 (3)	C18—C19—H19	119.7
C8—C9—H9A	108.7	C20—C19—H19	119.7

C10—C9—H9A	108.7	C21—C20—C19	120.0 (3)
C8—C9—H9B	108.7	C21—C20—H20	120.0
C10—C9—H9B	108.7	C19—C20—H20	120.0
H9A—C9—H9B	107.6	C20—C21—C22	120.1 (3)
O3—C10—C11	111.1 (3)	C20—C21—H21	119.9
O3—C10—C9	107.6 (2)	C22—C21—H21	119.9
C11—C10—C9	107.5 (2)	C21—C22—C23	120.3 (4)
O3—C10—H10	110.2	C21—C22—H22	119.8
C11—C10—H10	110.2	C23—C22—H22	119.8
C9—C10—H10	110.2	C22—C23—C18	119.8 (3)
C10—C11—N1	119.2 (3)	C22—C23—H23	120.1
C10—C11—H11A	107.5	C18—C23—H23	120.1
N1—C11—H11A	107.5	C12—N1—C14	108.9 (4)
C10—C11—H11B	107.5	C12—N1—C13	109.2 (4)
N1—C11—H11B	107.5	C14—N1—C13	106.7 (4)
H11A—C11—H11B	107.0	C12—N1—C11	108.2 (3)
N1—C12—H12A	109.5	C14—N1—C11	111.0 (3)
N1—C12—H12B	109.5	C13—N1—C11	112.8 (3)
H12A—C12—H12B	109.5	C8—O1—C7	116.1 (3)
N1—C12—H12C	109.5	C15—O3—C10	118.0 (2)
C6—C1—C2—C3	−0.2 (8)	C16—C17—C18—C23	−7.1 (5)
C1—C2—C3—C4	−0.2 (8)	C23—C18—C19—C20	2.4 (5)
C2—C3—C4—C5	1.5 (7)	C17—C18—C19—C20	−178.0 (3)
C3—C4—C5—C6	−2.3 (6)	C18—C19—C20—C21	−1.9 (6)
C3—C4—C5—C7	173.8 (4)	C19—C20—C21—C22	0.9 (6)
C2—C1—C6—C5	−0.6 (7)	C20—C21—C22—C23	−0.3 (7)
C4—C5—C6—C1	1.9 (6)	C21—C22—C23—C18	0.8 (6)
C7—C5—C6—C1	−174.1 (4)	C19—C18—C23—C22	−1.8 (5)
C4—C5—C7—O1	139.3 (4)	C17—C18—C23—C22	178.6 (3)
C6—C5—C7—O1	−44.7 (6)	C10—C11—N1—C12	−162.3 (4)
O2—C8—C9—C10	1.3 (5)	C10—C11—N1—C14	78.3 (4)
O1—C8—C9—C10	−179.7 (3)	C10—C11—N1—C13	−41.3 (4)
C8—C9—C10—O3	64.7 (3)	O2—C8—O1—C7	2.7 (5)
C8—C9—C10—C11	−175.5 (3)	C9—C8—O1—C7	−176.3 (3)
O3—C10—C11—N1	−62.9 (4)	C5—C7—O1—C8	152.0 (3)
C9—C10—C11—N1	179.6 (3)	O4—C15—O3—C10	−7.4 (5)
O4—C15—C16—C17	5.6 (5)	C16—C15—O3—C10	173.8 (2)
O3—C15—C16—C17	−175.6 (3)	C11—C10—O3—C15	122.9 (3)
C15—C16—C17—C18	178.9 (3)	C9—C10—O3—C15	−119.7 (3)
C16—C17—C18—C19	173.3 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9A···O4^{i}	0.97	2.42	3.299 (4)	150
C11—H11A···O4^{i}	0.97	2.49	3.336 (4)	146
C12—H12A···O2^{i}	0.96	2.49	3.103 (6)	121
C13—H13C···Cl1^{ii}	0.96	2.72	3.587 (6)	151

C12—H12B···Cg2^{iii}	0.96	2.62	3.551 (5)	164
C20—H20···Cg1^{iv}	0.93	2.95	3.776 (4)	148
Cl1—H1A···Cl2	1.37	1.70	3.068 (2)	176
C10—H10···O4	0.98	2.28	2.712 (4)	105
C13—H13B···O4	0.96	2.40	3.324 (6)	161
C14—H14B···O3	0.96	2.45	3.069 (5)	122
C17—H17···O4	0.93	2.49	2.828 (4)	102

Symmetry codes: (i) −*x*+2, *y*+1/2, −*z*+1/2; (ii) *x*+1, *y*, *z*; (iii) −*x*+1, *y*+1/2, −*z*+1/2; (iv) *x*−1, *y*−1, *z*.

Fig. 1

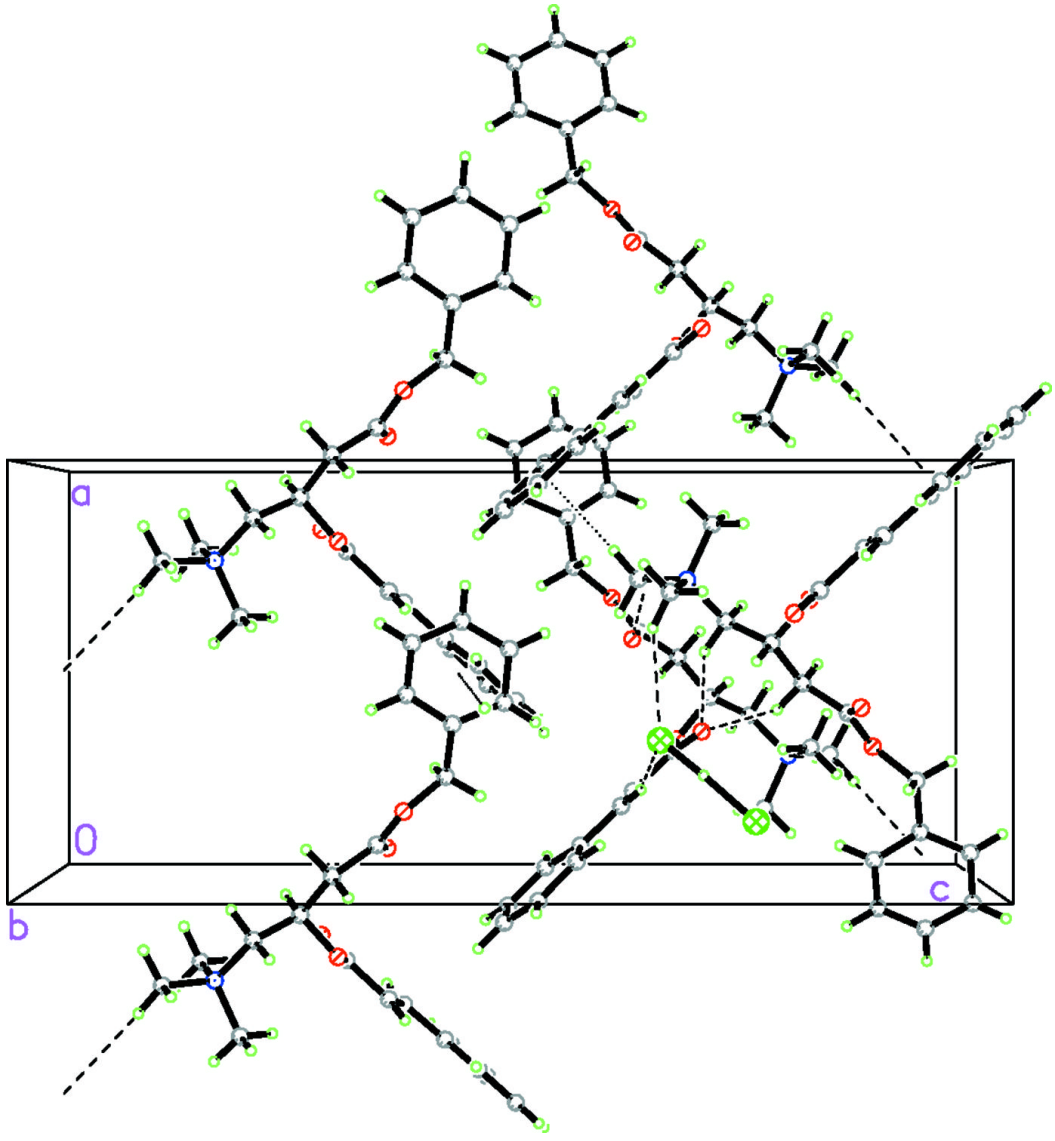

Fig. 2

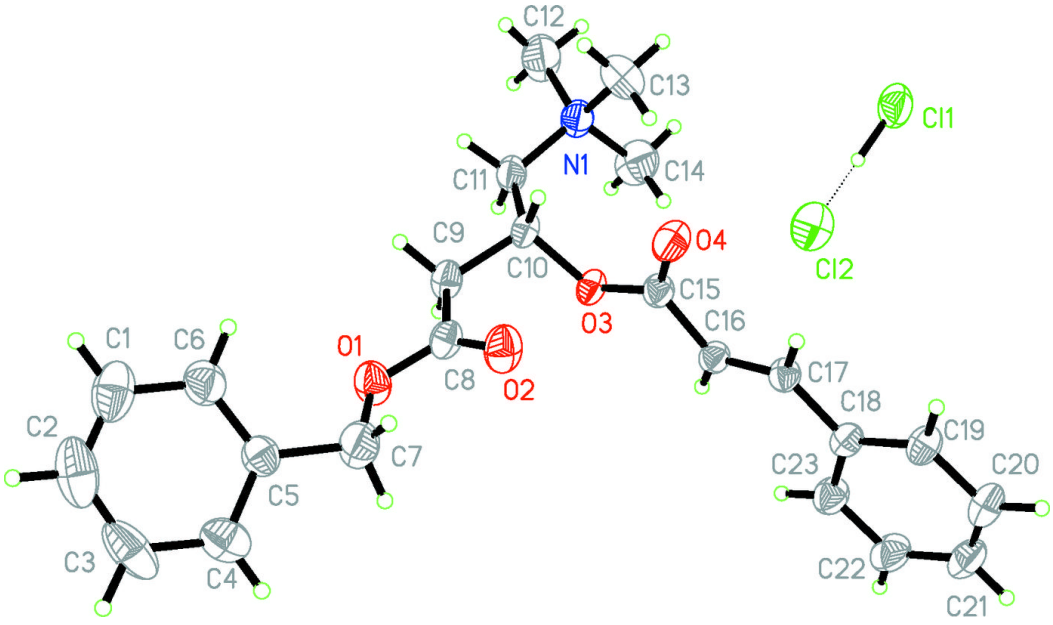
C12
C13
Cl1
N1
C11
C14
C9
O4
C10
Cl2
C15
O3
C16
C1
C6
O1
C8
O2
C17
C18
C2
C7
C19
C23
C20
C5
C3
C4
C22
C21

Fig. 3