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ORIGINAL PAPER

One-Dimensional Hydrogen-Bonded Structures in the 1:1 Proton-Transfer Salts of 4,5-Dichlorophthalic Acid with the Aliphatic Lewis Bases Diisopropylamine and Hexamethylenetetramine

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Abstract The crystal structures of the 1:1 proton-transfer compounds of 4,5-dichlorophthalic acid with the aliphatic Lewis bases diisopropylamine and hexamethylenetetramine, viz. diisopropylaminium 2-carboxy-4,5-dichlorobenzoate (**1**) and hexamethylenetetraminium 2-carboxy-4,5-dichlorobenzoate hemihydrate (**2**), have been determined. Crystals of both **1** and **2** are triclinic, space group $P-1$, with $Z = 2$ in cells with $a = 7.0299(5)$, $b = 9.4712(7)$, $c = 12.790(1)$ Å, $\alpha = 99.476(6)$, $\beta = 100.843(6)$, $\gamma = 97.578(6)°$ (**1**) and $a = 7.5624(8)$, $b = 9.8918(8)$, $c = 11.5881(16)$ Å, $\alpha = 65.660(6)$, $\beta = 86.583(4)$, $\gamma = 86.987(8)°$ (**2**). In each, one-dimensional hydrogen-bonded chain structures are found: in **1** formed through aminium $N^+–H\ldots O_{carboxyl}$ cation–anion interactions. In **2**, the chains are formed through anion carboxyl $O\cdots H–O_{bridging\ water}$ interactions with the cations peripherally bound. In both structures, the hydrogen phthalate anions are essentially planar with short intra-species carboxylic acid $O–H\ldots O_{carboxyl}$ hydrogen bonds [O…O, 2.381(3) Å (**1**) and 2.381(8) Å (**2**)].

Keywords 4,5-Dichlorophthalic acid · Proton-transfer compounds · Aliphatic Lewis bases · Hydrogen bonding

Introduction, Results and Discussion

Introduction

The halo-substituted aromatic dicarboxylic acid 4,5-dichlorophthalic acid (4,5-dichlorobenzene-1,2-dicarboxylic acid: DCPA) has potential for the formation of stable crystalline salts with nitrogen Lewis bases, stabilized by hydrogen-bonding interactions. The p*K*a values, similar to those of phthalic acid (2.95, 5.41) also allow for selective formation of both 1:1 and 1:2 compounds through pH and stoichiometric control, but to date, only a limited number of structures of DCPA compounds have been reported and the large majority of these have been 1:1 acid phthalate salts (Scheme 1).

The first reported examples were the 1:1 ammonium and tetra(*n*-butyl)ammonium salts [1] and more recently the tetramethylammonium salt [2]. Of interest also is the 1:1 salt with the proton sponge compound 1,8-bis(dimethylamino)naphthalene (DMAN) which has steric strain induced by the close proximity of the amine substituent groups [3]. A 1:2 non-transfer adduct compound with *trans*-cinnamamide is also known [4]. Our group therefore began an investigation of the structural chemistry of the 1:1 salts of DCPA with a series of aliphatic and aromatic nitrogen Lewis bases. The overall result, although not outstanding has given a number of crystalline salts for which the crystal structures have been determined [5–11]: (a) with brucine [5]; (b) with the bicyclic bifunctional heteroaromatic bases 8-hydroxyquinoline, 8-aminoquinoline and quinoline-2-carboxylic acid (quinaldic acid) [6], (the last being an unusual 1:1:1:1 salt-quinaldic acid adduct monohydrate compound); (c) with the isomeric monoaminobenzoic acids [7]; with the substituted monocyclic heteroaromatic bases 2-aminopyrimidine, nicotinic acid and isonicotinic acid [8], (the last being a 1:1:1 salt-methyl DCPA monoester which was self-generated in the methanol solvent used); (d) with the drug quinacrine [9]; (e) with 4-chloroaniline [10], and (f) with 1,10-phenanthroline [11].

Among the total set of these 1:1 hydrogen-bonded DCPA compounds, structurally there is generally

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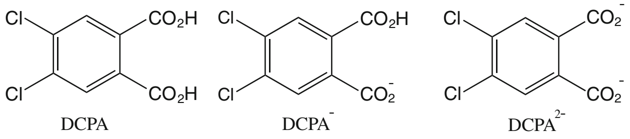
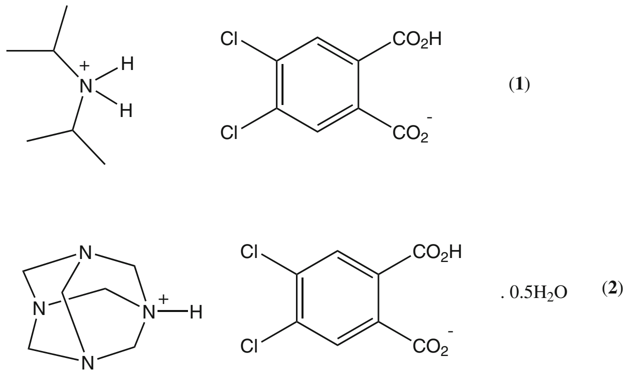


Scheme 1 Schematic of DCPA, DCPA$^-$ and DCPA^{2-} anion species

low-dimensionality with the occurrence of three-dimensional structures in only two examples, the salts with the 3- and 4-aminobenzoic acids [7]. This is due to the structure extensions provided by the secondary carboxylic acid substituent groups in these compounds. The other examples are more commonly one- or two-dimensional but zero-dimensional examples having no secondary hydrogen-bonding extension include the salts with brucine [5], 1, 10-phenanthroline [11] and 2-aminopyrimidine [8] (a discrete cation–anion 'heterotetramer' [12]). In the majority of these examples the hydrogen DCPA anions are essentially planar with the planarity achieved through short intramolecular carboxylic acid O–H…O$_{carboxyl}$ hydrogen bonds, e.g. 2.441(3) Å in the brucinium DCPA compound [5]. In the much less common structures having the non-planar monoanion, e.g. salts with 3- and 4-aminobenzoic acids [7] and with 4-chloroaniline [10], these anions form homomeric hydrogen-bonded chains into which the cationic species are incorporated. Another observation with these structures has been that water molecules of solvation are uncommon despite the fact that the usual solvent systems employed in the syntheses were ethanol–water or methanol–water.

However, apart from the brucinium compound [5] we have had lesser success in obtaining crystalline 1:1 aliphatic Lewis base compounds with DCPA, being limited to those salts reported here, with diisopropylamine (DIPA) and hexamethylenetetramine (HMT), namely anhydrous diisopropylaminium 2-carboxy-4,5-dichlorobenzoate [DIPA$^+$ DCPA$^-$] (**1**) and the hydrated hexamethylenetetraminium 2-carboxy-4,5-dichlorobenzoate hemihydrate [HMT$^+$ DCPA$^-$]·0.5H$_2$O (Scheme 2) (**2**).



Scheme 2 Schematic of [DIPA$^+$ DCPA$^-$] (**1**) and [HMT$^+$ DCPA$^-$]·0.5H2O (**2**)

General Structure Comparison

The structure determinations of compounds [(DIPA)$^+$ (DCPA)$^-$] (**1**) and [(HMT)$^+$ (DCPA)$^-$]·0.5H$_2$O (**2**) show one-dimensional hydrogen-bonded chain structures. As expected in each compound, single proton transfer to the

Table 1 Crystal data for compounds **1** and **2**

Compound	**1**	**2**
CCDC reference	719976	719977
Melting point (°C)	190	168
Molecular formula	$C_{14}H_{19}Cl_2NO_4$	$C_{14}H_7Cl_2N_4O_{4.5}$
M_r	336.20	384.22
Temperature (K)	297(2)	170(2)
Wavelength (λ)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P-1$	$P-1$
a (Å)	7.0299(5)	7.5624(8)
b (Å)	9.4712(7)	9.8918(8)
c (Å)	12.790(1)	11.5881(16)
α (°)	99.476(6)	65.660(6)
β (°)	100.843(6)	86.583(4)
γ (°)	97.578(6)	86.987(8)
V (Å^3)	813.22(11)	788.03(16)
Z	2	2
D_c (g cm^{-3})	1.369	1.619
μ (mm^{-1})	0.413	0.445
F(000)	350	398
Instrument	Oxford diffraction Gemini S CCD Diffractometer	Oxford diffraction Gemini S CCD Diffractometer
Reflections total, θ_{max} (°)	5,320, 25.0	4,107, 25.0
Crystal size (mm)	0.45 × 0.20 × 0.08	0.45 × 0.35 × 0.18
Collection range		
h	−8 to 8	−8 to 8
k	−11 to 11	−11 to 11
l	−14 to 15	−13 to 11
Reflections (independent)	2,823	2,697
Reflections [$F^2 > 2\sigma(F^2)$]	2,263	2,106
R_{int}	0.020	0.024
R_1 [$F^2 > 2\sigma(F^2)$]*	0.043	0.083
$wR2$ (all data)*	0.109	0.230
S*	1.05	1.10
n_p	202	242
Residuals: $\Delta_{max./min}$ (eÅ^{-3})	0.240/−0.250	0.691/−0.544

* $R_1 = (\Sigma|F_o| - |F_c|)/\Sigma\ |F_o|)$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma\ [w(F_o^2)^2]\}^{1/2}$; $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$

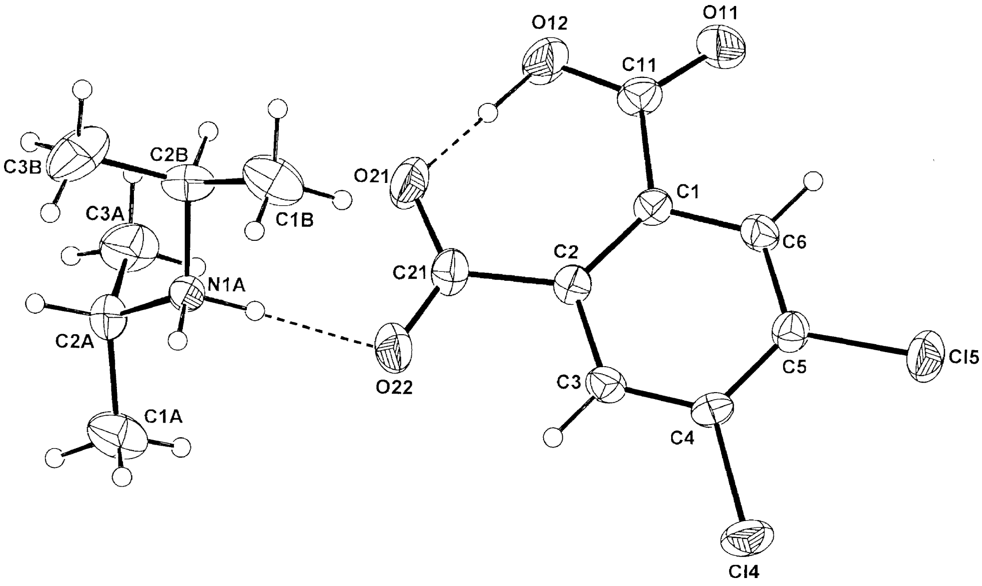


Fig. 1 Molecular configuration and atom numbering scheme for the diisopropylaminium cation and the DCPA monoanion species in **1**. The inter-species hydrogen bond is shown as a *dashed line*. Non-hydrogen atoms are shown as 40% probability displacement ellipsoids [18]

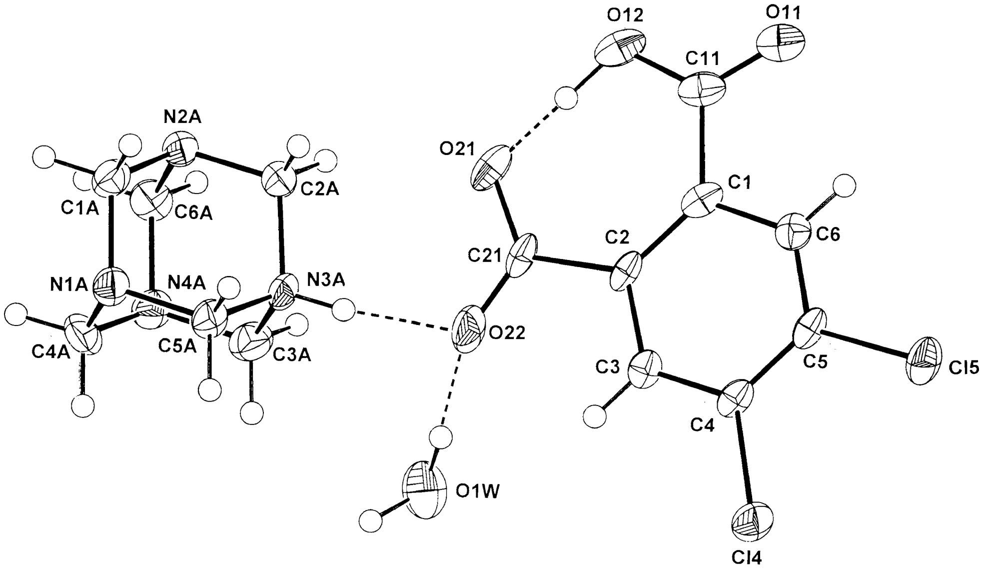


Fig. 2 Molecular configuration and atom numbering scheme for the hexamethylenetetraminium cation, the DCPA monoanion and the hemihydrate water species in **2**. The inter-species hydrogen bonds are shown as *dashed lines*. Non-hydrogen atoms are shown as 40% probability displacement ellipsoids

amino-N of the Lewis base occurs, with a subsequent formation of a primary hydrogen bond between this group and a carboxyl oxygen acceptor of the DCPA anion. Figures 1 and 2 show the molecular configuration and atom naming schemes used for the DCPA anion species and the protonated cation species in **1** and **2**.

The chain structures formed in **1** and **2** are different in their makeup. In **1**, the cation–anion 'heterodimer' is extended along the *b* axial direction of the unit cell through the second aminium proton to a DCPA carboxyl-O acceptor (Table 2; Fig. 3). With **2**, the hydrogen-bonding extension is also along the *b* axial direction in the cell but the primary chain comprises anion carboxyl $O\cdots H\text{-}O_{water}$ associations (Table 1) through both water hydrogen donors (Fig. 4). The HMT cations are peripherally attached to one of the carboxyl oxygen atoms (O22).

The DCPA anions in both **1** and **2** have the essential planarity common among its 1:1 salts, together with the associated short intramolecular $O\text{–}H\ldots O_{carboxyl}$ hydrogen bonds [2.381(3), 2.381(7) Å, respectively]. Torsion angles associated with these groups (C2–C1–C11–O11 and C1–C2–C21–O22) are −170.8(2) and −176.0(2)° for **1** and −173.7(6) and 173.6(5)° for **2**. The planarity also means that there are short intramolecular aromatic ring C–H…O ~ carboxyl ~ interactions, typically for **1**, C3…O22, 2.659(3) Å and C6…O12, 2.657(3) Å (Table 2).

There is an absence in **1** or **2** of short intermolecular Cl···Cl interactions such as has been found in the DCPA

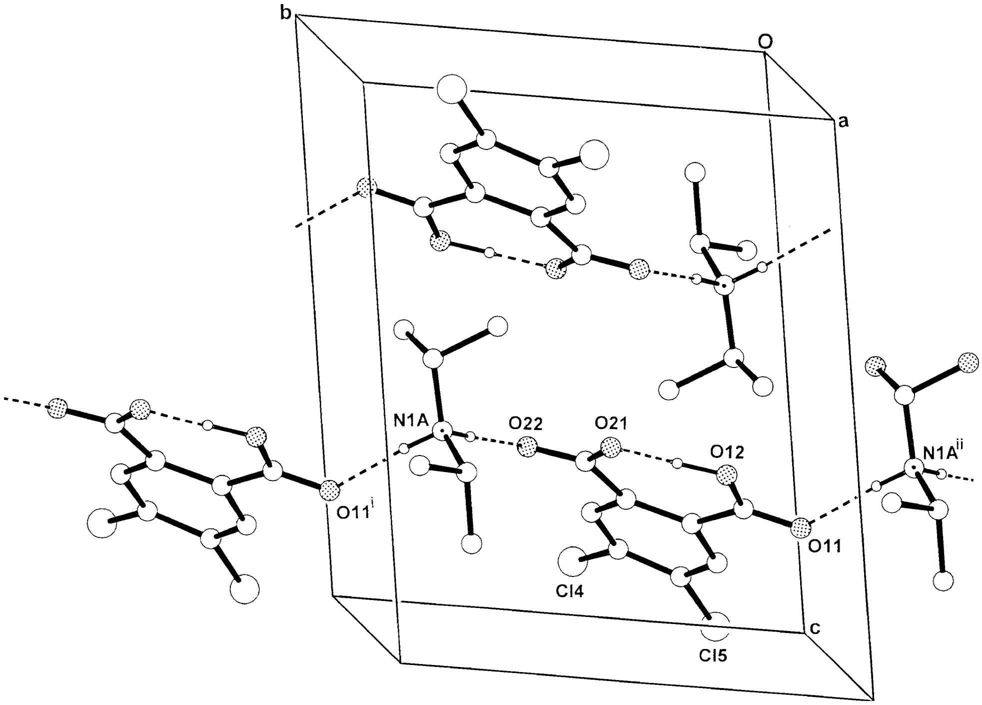


Fig. 3 The one-dimensional hydrogen-bonded chain structures of **1** in a perspective view down the approximate *a* direction of the unit cell. Hydrogen bonds are shown as *dashed lines* [symmetry code ^{ii}: x, $y - 1$, z]. Hydrogen-bonding associations are shown as *dashed lines*

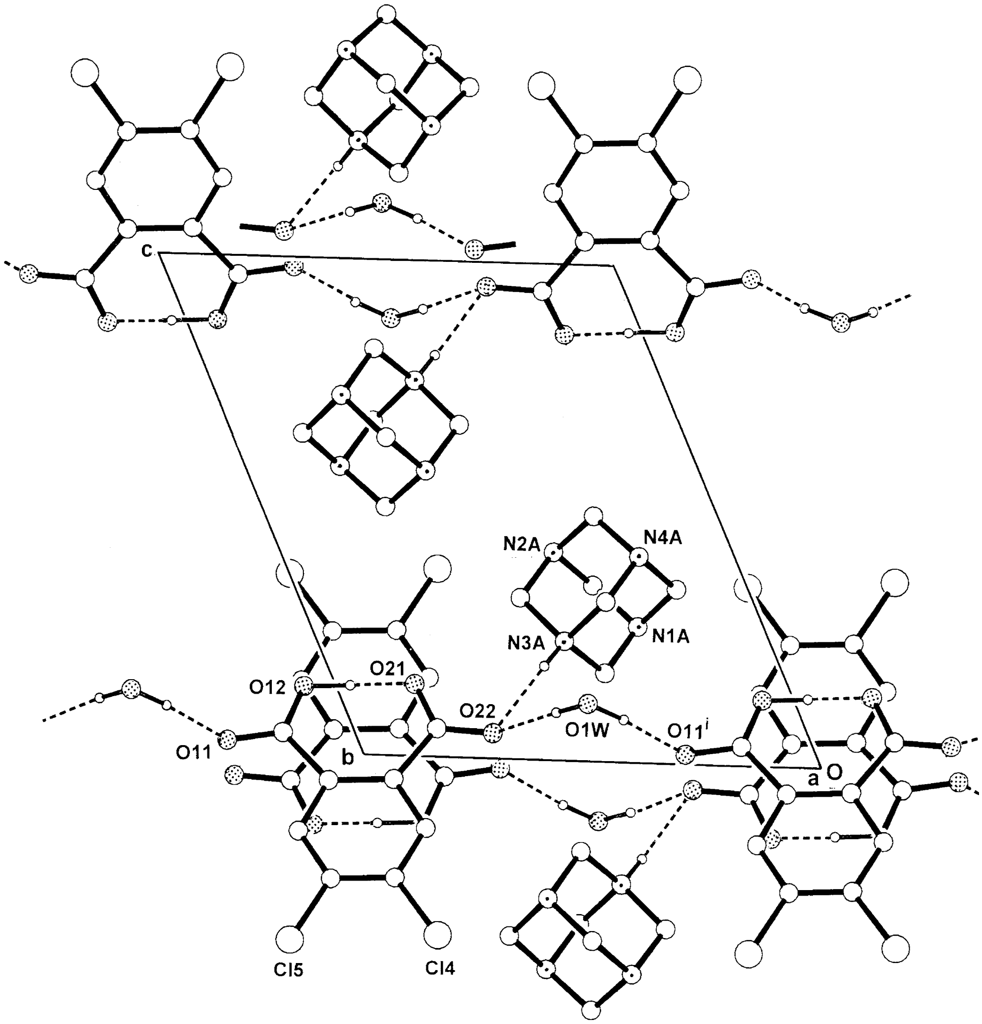


Fig. 4 The one-dimensional hydrogen-bonded chain structures in **2**, viewed down the *a* cell direction of the unit cell [symmetry code ^{ii}: x, $y + 1$, z]

Table 2 Hydrogen-bonding interactions (Å/deg.) for **1** and **2**

D–H…A	D–H	H…A	D…A	∠DH…A
Compound **1**[a]				
O12–H12…O21	1.01(5)	1.37(5)	2.381(3)	180(7)
N1A–H1A…O22	0.91(3)	1.88(3)	2.788(3)	178(3)
N1A–H2A…O11^{i}	0.90(3)	1.90(3)	2.799(3)	174(2)
C3–H3…O22	0.93	2.28	2.659(3)	104
C6–H6…O11	0.93	2.29	2.657(3)	103
Compound **2**[b]				
O12–H12…O21	0.99(6)	1.39(6)	2.381(8)	180(7)
N3A–H3A…O22	0.86(8)	1.90(8)	2.736(7)	162(8)
O1W–H11W…O22	0.94(7)	1.98(7)	2.920(13)	177(7)
O1W–H12W…O11^{i}	0.97(7)	1.84(7)	2.806(14)	174(6)
C3–H3…O22	0.93	2.29	2.666(7)	104
C6–H6…O11	0.93	2.28	2.662(9)	104

[a] Symmetry code: $^{i}x, y + 1, z$

[b] Symmetry code: $^{i}x, y - 1, z$

compounds with the isomeric 3- and 4-aminobenzoic acids [10] [3.2295(6), 3.3243(6) Å and 3.2488(7) Å, respectively]. This phenomenon has previously been described [13] particularly in the structures of the dichloro-substituted aromatic compounds. Absent as well are the short Cl…$O_{carboxyl}$ associations found also in the 3- and 4-aminobenzoates [3.2279(14) Å and 3.2213(15) Å, respectively] [3].

Conclusion

The hydrogen 4,5-dichlorophthalate anions have been shown to promote the formation of one-dimensional structure extension in 1:1 proton-transfer compounds with the secondary and tertiary aliphatic amines considered in this work. These provide further examples demonstrating the preference for the retention of the planar internally hydrogen-bonded DCPA monoanion species in the low-dimensional hydrogen-bonded 1:1 salts with both the aliphatic and aromatic Lewis bases.

Experimental

Preparation

The title compounds **1**and **2** were synthesized by heating together 1 mmol quantities of 4,5-dichlorophthalic acid (4,5-dichlorobenzene-1,2-dicarboxylic acid) and either diisopropylamine (for **1**) or hexamethylenetetramine (1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane or urotropin) (for **2**) in 50 mL of 80% methanol/water under reflux for 10 min. After concentration to ca. 30 mL, total room temperature evaporation of the hot-filtered solutions gave in the case of **1**, a white powder and with **2**, a small quantity of colourless crystal prisms. The powder from **1** was subsequently redissolved in a small quantity of water and on evaporation provided prismatic crystals.

Crystallography

X-ray diffraction data for **1** and **2** were obtained either at ambient temperature [297(2) K] (compound **1**) or at 173(2) K (**2**) on an Oxford Diffraction Gemini S CCD-detector diffractometer by using crystal monochromatized Mo $K\alpha$ radiation. Data were corrected for absorption [14]. The structures were solved by direct methods using either SIR 92 [15] (**1**) or SHELXS 97 [16] (**2**) and refined with anisotropic thermal parameters for all non-hydrogen atoms using SHELXL 97 [16] operating within WinGX [17]. Aminium and water protons were located by difference methods and their positional and isotropic thermal displacement parameters were refined. Others were included in the refinements at calculated positions and treated as riding models with C–H = 0.93 Å (aromatic) or 0.97 – 0.98 Å (aliphatic) and $U_{iso} = 1.2U_{eq}$(attached C). General crystallographic details are given in Table 1.

CCDC 719976 and 719977 contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif by e-mailing datarequest@ccdc.cam.ac.uk, or contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ.

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