Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hydrogen-bonded networks in *trans*-3-(3-pyridyl)acrylic acid and *rctt*-3,3′-(3,4-dicarboxycyclobutane-1,2-diyl)dipyridinium dichloride

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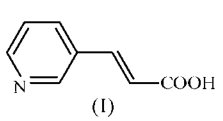
Received 14 April 2007
Accepted 5 June 2007
Online 5 July 2007

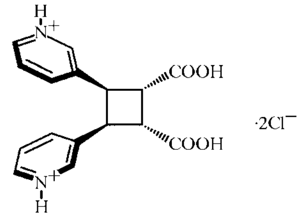
The structure of *trans*-3-(3-pyridyl)acrylic acid, $C_8H_7NO_2$, (I), possesses a two-dimensional hydrogen-bonded array of supramolecular ribbons assembled *via* heterodimeric synthons between the pyridine and carboxyl groups. This compound is photoreactive in the solid state as a result of close contacts between the double bonds of neighbouring molecules [3.821 (1) Å] along the *a* axis. The crystal structure of the photoproduct, *rctt*-3,3′-(3,4-dicarboxycyclobutane-1,2-diyl)dipyridinium dichloride, $C_{16}H_{16}N_2O_4^{2+}\cdot 2Cl^-$, (II), consists of a three-dimensional hydrogen-bonded network built from crosslinking of helical chains integrated by self-assembly of dipyridinium cations and Cl^- anions *via* different O—H···Cl, C—H···Cl and N^+—H···Cl hydrogen-bond interactions.

Comment

Organic reactions performed in the solid state are considered an important green alternative for the preparation of new and conventional compounds (Toda, 2005; MacGillivray *et al.*, 2004; Gao *et al.*, 2004; Tanaka & Toda, 2000; Xiao *et al.*, 2000; Garcia-Garibay, 2003; Ramamurthy & Venkatesan, 1987; Díaz de Delgado *et al.*, 1991). A particular case of solid-state reactions is [2+2]-photocycloaddition, in which the nature and features of the products can be controlled by topochemical parameters (Schmidt, 1971). This alternative offers regio- and stereoselective control combined with quantitative yields. These advantages make the assembly of olefins in the solid state an efficient route for regiocontrolled access to versatile multitopic organic molecules. Such compounds turn out to be very interesting as building blocks for designing novel supramolecular metal assemblies with unusual topologies (Papaefstathiou & MacGillivray, 2002; Papaefstathiou, Milios & MacGillivray, 2004; Papaefstathiou, Hamilton *et al.*, 2004; Papaefstathiou *et al.*, 2005; Lee *et al.*, 2005; Kim & Jung, 2002). As part of our interest in the study of potentially thermally and photoreactive solids (Briceño *et al.*, 2006, 2002, 1999), we have re-investigated the photoreactivity of *trans*-3-(3-pyridyl)acrylic acid, (I), to prepare a tetratopic ligand containing either pyridyl or carboxyl groups. The solid-state reactivity of (I) was previously studied by Lahav & Schmidt (1967). However, neither the crystal structure of the starting material nor that of the dimer have yet been reported in the literature. Here, the crystal structures of (I) and a hydrogen-bonded supramolecular array based on the photoproduct, (II), are reported.



(I)



(II)

The molecule of (I) (Fig. 1) adopts a nearly planar conformation, with a maximum deviation from the mean molecular plane of 0.007 (2) Å. The molecule displays an intramolecular C—H···O hydrogen bond [C···O = 2.765 (2) Å and C3—H3···O1 = 102°], which leads to the formation of a five-membered ring described by the *S*(5) graph-set symbol (Bernstein *et al.*, 1995).

The crystal structure of (I) consists of the self-assembly of molecules *via* a heterodimeric hydrogen-bonded synthon based on the interaction between the pyridyl and carboxyl

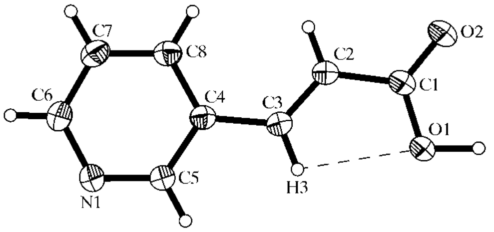


Figure 1
The molecular structure of (I), showing the atom-labelling scheme and the intramolecular hydrogen bond (dashed line). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

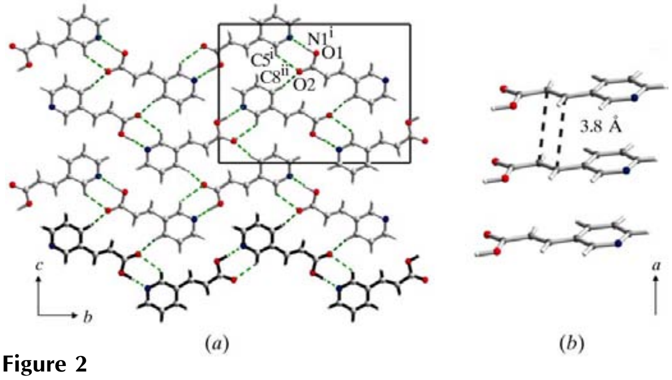


Figure 2
(*a*) A view of the hydrogen-bonded network observed in the crystal structure of (I). (*b*) Close contacts between adjacent molecules along the *a* axis. [Symmetry codes: (i) $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$; (ii) $-x, 1 - y, 1 - z$.]

DOI: 10.1107/S0108270107027497

groups. This supramolecular motif, described as $R_2^2(7)$, is repeated along the *b* direction to generate zigzag supramolecular ribbons with distances $\text{O1}\cdots\text{N1}^{\text{i}} = 2.660\ (2)$ Å and $\text{C5}\cdots\text{O2}^{\text{i}} = 3.263\ (2)$ Å [symmetry code: (i) $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$]. Adjacent ribbons are linked by two complementary C—H⋯O hydrogen bonds [$\text{C8}\cdots\text{O2}^{\text{ii}} = 3.299\ (3)$ Å; symmetry code: (ii) $-x, 1 - y, 1 - z$]. These interactions induce self-assembly of parallel ribbons in an alternating head-to-tail fashion, resulting in a two-dimensional hydrogen-bonded array in the *bc* plane (Fig. 2*a*). The three-dimensional network is achieved by stacking of the sheets through π–π interactions along the *a* axis (interlayer distance *ca* 3.8 Å).

A remarkable feature of the structure of (I) is the presence of close contacts between the double bonds of neighbouring molecules related by translation along the *a* axis [centroid-to-centroid distance = 3.812 (1) Å]. This structural feature is responsible for the photoreactivity that is displayed by (I) in the solid state (Fig. 2*b*).

As expected, UV irradiation of (I) produces the dimer. The ^{1}H NMR spectrum confirms the photocycloaddition (see *Experimental*). The stereochemistry of the product was confirmed by single-crystal structure analysis, which revealed the formation of a typical truxinic acid analogue (head-to-head dimer). This result is in agreement with the expected topochemical control by the crystalline starting material, and with the results previously reported by Lahav & Schmidt (1967) based on the characterization of the compound by ^{1}H NMR spectroscopy and other chemicophysical observations.

The asymmetric unit of (II) consists of the diprotonated β-dimer (Fig. 3) and two Cl$^-$ anions. The cyclobutane ring is slightly puckered; the C4 flap atom deviates by 0.354 (5) Å from the plane of the other three atoms of the four-membered ring. This value is similar to those observed for other substituted cyclobutanes that do not crystallize on a centre of symmetry (Abdelmoty *et al.*, 2005; Kanao *et al.*, 1990; Pani *et al.*, 1995). Both pyridinium rings, as well as the carboxyl groups, are twisted out of the mean plane of the cyclobutane ring: the mean planes of the pyridinium rings based on N1 (C7–C11) and N2 (C12–C16), and carboxyl groups O1/C5/O2 and O4/C6/O3, are rotated by 69.0 (1), 79.1 (1), 35.9 (3) and 86.2 (3)°, respectively (Fig. 3).

An analysis of the bond distances and angles of the pyridyl rings in (I) and (II) only reveals significant differences in the internal C—N—C angle of both protonated N atoms. These values are greater in (II) than in (I) (Tables 1 and 2).

The structure of (II) consists of a three-dimensional hydrogen-bonded network built up by self-assembly of the cations and Cl$^-$ anions *via* different C—H⋯Cl, O—H⋯Cl and N$^+$—H⋯Cl hydrogen-bond interactions. In this structure, the Cl$^-$ anions act as structure-directing agents of this assembly, and each Cl$^-$ anion is an acceptor of multiple hydrogen-bond interactions. Atom Cl1 is an acceptor of four hydrogen bonds from different adjacent dications, whereas atom Cl2 accepts only three hydrogen bonds. Details of the hydrogen-bonding geometry in (II) are given in Table 2. The cations are self-assembled through O—H⋯Cl interactions

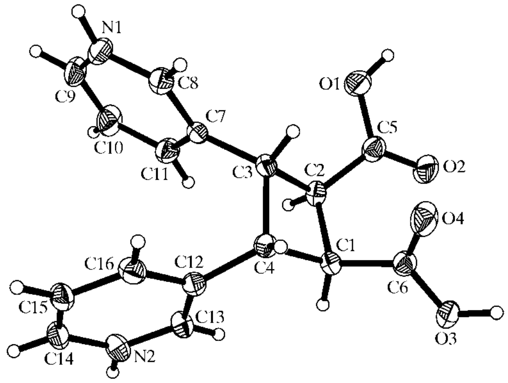


Figure 3
The molecular structure of the dication of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

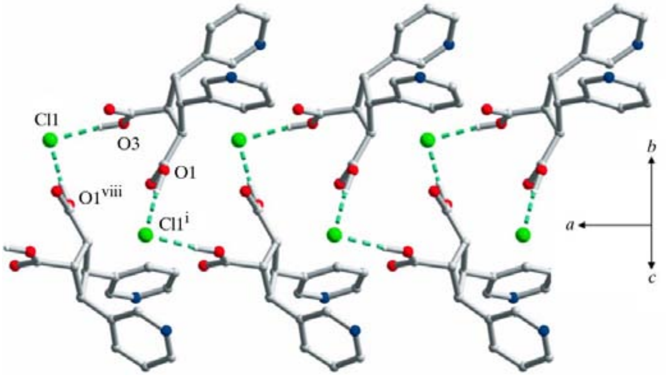


Figure 4
A view along the *a* axis of the one-dimensional helical chains generated by O—H⋯Cl interactions (dashed lines). Most H atoms have been omitted for clarity. [Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$; (viii) $-x - \frac{1}{2}, -y + \frac{1}{2}, -z + 2$.]

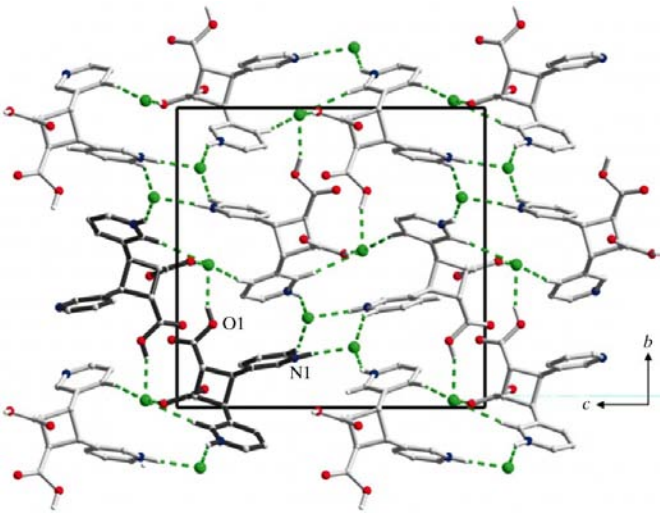


Figure 5
A view of the crystal structure of (II) in the *bc* plane, showing C—H⋯Cl, O—H⋯Cl and N—H⋯Cl interactions (dashed lines). Most H atoms have been omitted for clarity. The darker molecules indicate one of the neighbouring helical arrangements (see *Comment*).

between carboxyl groups and Cl1 atoms, generating one-dimensional helical chains running along the *a* axis (Fig. 4). The central axis about each chain is a twofold screw axis. Neighbouring helical arrangements (shown dark in Fig. 5) are crosslinked by additional $N^+—H\cdots Cl$ hydrogen bonds, involving pyridinium units through the H atom of the protonated ring, and $C—H\cdots Cl$ interactions, to afford a three-dimensional hydrogen-bonded assembly (Fig. 5).

Experimental

trans-3-(3-Pyridyl)acrylic acid, (I), was obtained commercially (Aldrich). Crystals were obtained by slow evaporation of a methanol solution. IR (KBr disc, ν, cm^{-1}): 3500–2300 (O—H), 3052 (=C—H), 1702 (C=O), 1635 (C=C), 1580 and 1418 (C=C and C=N), 1284 (C—O). The photodimer was prepared by topochemical reaction of (I). Crystals and a powdered crystalline material of (I) were irradiated with a 100 W Hg lamp above 302 nm for 3 d. The product was purified as described in the literature (Lahav & Schmidt, 1967) (yield 55–60%). IR (KBr, ν, cm^{-1}): 3500–2300 (O—H), 3057 (=C—H), 2955–2857 (C—H), 1717 (C=O), 1583 and 1422 (C=C and C=N), 1277 (C—O); ^{1}H NMR (d_6-DMSO): δ 8.25 (2H, *s*, J = 1.86 Hz), 8.17 (2H, *d*, J = 3.84 Hz), 7.45 (2H, *d*, J = 6.24 Hz), 7.08 (2H, *dd*, J = 7.83 Hz), 4.25 (2H, *d*), 3.89 (2H, *d*, J = 6.24 Hz). Crystals of (II) were obtained by dissolving the dimer (200 mg) in distilled water (50 ml) and adjusting the pH to 1 with HCl. The resultant solution was allowed to evaporate slowly at room temperature. After 2–3 weeks, pale-yellow crystals suitable for X-ray analysis had formed. Attempts were made to optimize the exposure time, and thus ensure the maximum yield, by monitoring the degree of conversion of the photoreaction by FT–IR spectroscopy. It was found that compound (I) in the presence of KBr is photodegraded by decarboxylation. Interestingly, the CO_2 released is partially trapped in the KBr disc. The CO_2 band is enhanced as a function of the exposure time, and simultaneously a decrease in the relative intensity of the absorption band corresponding to the C=O stretch at 1702 cm^{-1} was observed. After 4 h of irradiation, a loss of resolution in the FT–IR spectrum was observed. This behaviour was not observed during direct UV irradiation of (I); apparently, the KBr matrix induced this process.

Compound (I)

Crystal data

$C_8H_7NO_2$
M_r = 149.15
Monoclinic, $P2_1/c$
a = 3.8205 (6) Å
b = 15.986 (2) Å
c = 11.6080 (12) Å
β = 90.546 (11)°
V = 708.90 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 295 (2) K
0.48 × 0.26 × 0.18 mm

Data collection

Rigaku AFC-7*S* diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.900, $T_{\max}$ = 0.960
1451 measured reflections
1255 independent reflections
876 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.017
3 standard reflections every 150 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.112
S = 1.03
1255 reflections
100 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.13 e Å^{-3}
$\Delta\rho_{\min}$ = −0.16 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C1	1.318 (2)	C2—C3	1.314 (2)
O2—C1	1.213 (2)	C3—C4	1.464 (2)
C1—C2	1.469 (3)		
C6—N1—C5	117.66 (17)	O1—C1—C2	114.55 (16)
O2—C1—O1	123.19 (18)	C3—C2—C1	124.56 (18)
O2—C1—C2	122.25 (18)	C2—C3—C4	127.16 (18)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$N1$^{\rm i}$	1.06	1.61	2.660 (2)	170
C5—H5$\cdots$O2$^{\rm ii}$	0.93	2.58	3.263 (2)	130
C8—H8$\cdots$O2$^{\rm iii}$	0.93	2.44	3.299 (2)	154
C3—H3$\cdots$O1	0.93	2.41	2.765 (2)	102

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x, -y+1, -z+1$.

Compound (II)

Crystal data

$C_{16}H_{16}N_2O_4^{2+}\cdot 2Cl^-$
M_r = 371.21
Orthorhombic, $P2_12_12_1$
a = 7.3938 (13) Å
b = 14.829 (3) Å
c = 15.250 (3) Å
V = 1672.1 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.41 mm^{-1}
T = 295 (2) K
0.48 × 0.23 × 0.16 mm

Data collection

Rigaku AFC-7*S* Mercury diffractometer
Absorption correction: multi-scan (Jacobson, 1998)
$T_{\min}$ = 0.820, $T_{\max}$ = 0.912
19377 measured reflections
3310 independent reflections
2872 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.103
S = 1.15
3310 reflections
220 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.22 e Å^{-3}
$\Delta\rho_{\min}$ = −0.32 e Å^{-3}
Absolute structure: Flack (1983), with 1711 Friedel pairs
Flack parameter: −0.01 (7)

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C5	1.326 (4)	C1—C4	1.556 (3)
O2—C5	1.201 (3)	C1—C2	1.558 (4)
O3—C6	1.316 (3)	C2—C3	1.540 (4)
O4—C6	1.198 (3)	C3—C4	1.579 (4)
C9—N1—C8	122.8 (3)	C2—C3—C4	88.75 (19)
C13—N2—C14	123.3 (3)	C1—C4—C3	88.99 (19)
C4—C1—C2	88.97 (18)	O2—C5—O1	123.7 (3)
C3—C2—C1	90.33 (19)	O4—C6—O3	123.4 (3)

For (I), all H atoms bound to carbon were included in calculated positions. The H atom of the carboxyl group was located in a difference Fourier map. The H atoms were refined using a riding model, with C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,O). For (II), all H

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1OH···Cl1^{i}	0.91	2.17	3.047 (2)	160
O3—H3OH···Cl1	0.93	2.09	3.020 (2)	172
N1—H1N···Cl2	0.92	2.18	3.022 (2)	153
N2—H2N···Cl2^{ii}	0.89	2.31	3.089 (3)	146
C9—H9···Cl2^{iii}	0.93	2.70	3.514 (3)	147
C11—H11···O4^{iv}	0.93	2.43	3.075 (3)	126
C13—H13···Cl1^{iv}	0.93	2.68	3.587 (3)	165
C14—H14···O1^{v}	0.93	2.52	3.221 (3)	133
C15—H15···O2^{vi}	0.93	2.54	3.417 (3)	158
C16—H16···Cl1^{vii}	0.93	2.72	3.641 (3)	169

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+2$; (ii) $-x+\frac{5}{2}, -y, z+\frac{1}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iv) $x+1, y, z$; (v) $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$; (vi) $-x+\frac{3}{2}, -y, z-\frac{1}{2}$; (vii) $-x+\frac{1}{2}, -y, z-\frac{1}{2}$.

atoms bound to carbon were included in calculated positions. H atoms on N and O atoms (carboxyl groups) were located in a difference Fourier map. The H atoms were refined using a riding model, with C—H = 0.93–0.98 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N,O).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993) for (I); *CrystalClear* (Rigaku/MSC, 2000) for (II). Cell refinement: *MSC/AFC Diffractometer Control Software* for (I); *CrystalClear* for (II). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1999) for (I); *CrystalStructure* (Rigaku/MSC, 2004) for (II). For both compounds, program(s) used to solve structure: *SHELXTL-NT* (Bruker, 1998); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT* and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2003).

This work was made possible through funds from FONACIT–MCT (project Nos. LAB-199700821 and G-2005000433).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3092). Services for accessing these data are described at the back of the journal.

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