

Ammonium 4-methoxycinnamate

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Received 23 March 2004

Accepted 5 April 2004

Online 11 May 2004

In the title compound, $\text{NH}_4^+\cdot\text{C}_{10}\text{H}_9\text{O}_3^-$, bimolecular layers of the anions are formed between layers of the cations. There are $\text{N}\cdots\text{H}\cdots\text{O}$ hydrogen bonds between the ammonium ion and the carboxylate groups of the anions. In the crystal structure, the $\text{C}=\text{C}$ moiety of the cinnamate ion makes an angle of $117.1(2)^\circ$ with that of the nearest neighbour, indicating that a pedal rotation is required before β -type $[2+2]$ -photodimerization can take place, which is the predominant mode of the photochemistry of this compound.

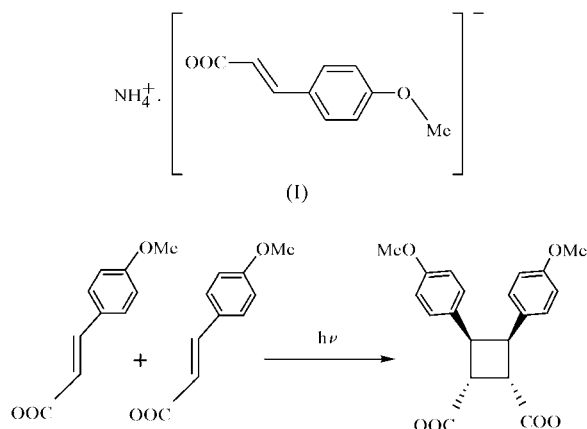
Comment

Organic solid-state reactions have the potential to control the stereoselectivity of chemical reactions. Ammonium salt formation is one way of designing the molecular arrangement of crystals (Ito *et al.*, 1995; Ito & Olovsson, 1997; Ito, 1998). The photoreactivities of the ammonium and isopropylammonium salts of the fumaric acid dianion have been rationalized, based on their crystal structures (Hosomi *et al.*, 1998). It is proposed that a small size or a planar structure of the amine is an important clue for converting photostable crystal packing into photodimerizable packing (Ito *et al.*, 2003). In the present study, the structure of the ammonium salt of 4-methoxycinnamate, (I), has been determined in order to investigate the relationship between the crystal structure and its photoreactivity. The product in the solid-state photolysis of (I) is predominantly the β -type head-to-head dimer (see scheme; Ito *et al.*, 2003).

Compound (I) consists of an ammonium cation and a *p*-methoxycinnamate anion (Fig. 1 and Table 1). The anions form bimolecular layers perpendicular to the *a* axis and the carboxylate groups are oriented on the outside, to form $\text{N}\cdots\text{H}\cdots\text{O}$ hydrogen bonds with the ammonium cations (Fig. 2). This layer structure corresponds to the habit of the plate-like crystals of (I) with a well developed (100) face. All the ammonium H atoms are connected to the carboxylate groups *via* hydrogen bonds (Table 2). Of these, atoms H4A and H4C are involved in bifurcated hydrogen bonds.

The close contact between the $\text{C}_6=\text{C}_7$ moieties in the crystal of (I) is $\text{C}_6\cdots\text{C}_6^i$ or $\text{C}_6\cdots\text{C}_6^{ii}$ of $3.984(1)\text{ \AA}$ [symmetry

codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$]. However, the double bonds are not parallel to each other. Atoms C5 and C6 lie almost on the *c*-glide plane perpendicular to the *b* axis at $y = \frac{1}{4}$, and the $\text{C}_5-\text{C}_6=\text{C}_7-\text{C}_8$ plane makes an angle of $75.9(2)^\circ$



with the glide plane (Fig. 3). Therefore, the $\text{C}_6=\text{C}_7$ bond axis makes an angle of $117.1(2)^\circ$ with the $\text{C}_6^i=\text{C}_7^i$ axis, and the $\text{C}_7\cdots\text{C}_7^i$ distance is $4.667(3)\text{ \AA}$. It seems that a pedal rotation of the cinnamate ion is required to achieve the parallel arrangement of the double bonds which is required before β -type $[2+2]$ -photodimerization can take place. Pedal-like conformational changes and the dimerization of *trans*-cinnamamide in cocrystals with phthalic acid were previously reported by Ito *et al.* (2000) and were unambiguously proved by a partial single-crystal-to-single-crystal transformation (Ohba *et al.*, 2001).

As an extension to the present study, the preliminary crystal structure of ammonium cinnamate, $\text{NH}_4^+\cdot\text{C}_9\text{H}_7\text{O}_2^-$, (II), was also determined. Compound (II) was prepared by a similar method to (I) and colourless thin plate-like crystals were grown from a 2-propanol solution (m.p. 406–408 K). [Crystal data for (II): monoclinic, space group $P2_1/c$, $a = 20.033(4)\text{ \AA}$,

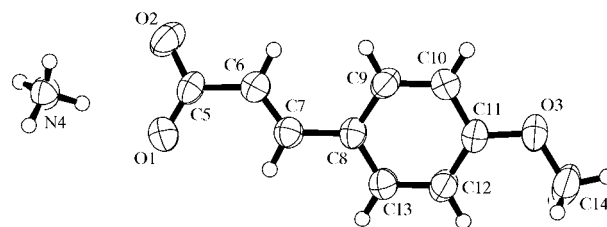


Figure 1

The molecular structure of (I), with displacement ellipsoids plotted at the 50% probability level.

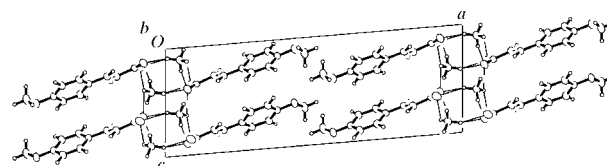
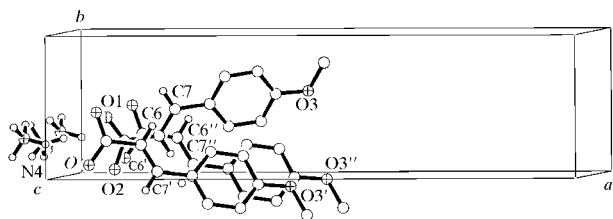


Figure 2

The projection of the crystal structure of (I) along *b*. Thin lines indicate hydrogen bonds.


Figure 3

The arrangement of ions in (I) generated by the c glide at $y = \frac{1}{4}$. Primed atoms are at the symmetry position $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ and double primed atoms are at the symmetry position $(x, \frac{1}{2} - y, z - \frac{1}{2})$.

$b = 5.8741$ (15) Å, $c = 7.8681$ (11) Å, $\beta = 100.572$ (14)°, $V = 910.2$ (3) Å³, $Z = 4$, $D_x = 1.205$ Mg m⁻³, $R(F) = 0.066$ for 560 reflections with $I > 2\sigma(I)$.] Compound (II) consists of an ammonium cation and a cinnamate anion, and the arrangements of the ions and of the N—H...O hydrogen bonds are similar to those in (I). It seems that a pedal rotation is also required in (II) before β -type [2+2]-photodimerization can take place. Bryan *et al.* (1963) reported the crystal structure of ammonium hydrogen dicinnamate, (III), which was prepared by dissolving cinnamic acid and concentrated aqueous ammonia (molar ratio 2:1) in warm ethanol. In (III), the hydrogen dicinnamate anion is centrosymmetric. The two cinnamate moieties are connected by a short O—H...O hydrogen bond around the inversion centre and form N—H...O hydrogen bonds with the ammonium cations. The hydrophobic and hydrophilic layers are stacked alternately, similar to the molecular packing of (I) and (II).

Experimental

The title compound, (I), was prepared by dissolving 4-methoxycinnamic acid and concentrated aqueous ammonia (molar ratio 1:1) in warm aqueous methanol (Ito *et al.*, 2003). Crystals of (I) were grown from a methanol solution (m.p. 448–451 K). The crystal specimen was coated with adhesive to avoid efflorescence.

Crystal data

NH ₄ ⁺ ·C ₁₀ H ₉ O ₃ ⁻	$D_x = 1.248$ Mg m ⁻³
$M_r = 195.22$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 22.077$ (3) Å	$\theta = 10.2$ – 13.6°
$b = 5.9332$ (9) Å	$\mu = 0.09$ mm ⁻¹
$c = 7.9560$ (8) Å	$T = 298$ K
$\beta = 94.76$ (1)°	Plate, colourless
$V = 1038.5$ (2) Å ³	$0.5 \times 0.5 \times 0.1$ mm
$Z = 4$	

Table 1

Selected geometric parameters (Å, °).

O1—C5	1.248 (3)	C6—C7	1.299 (3)
O2—C5	1.255 (3)	C7—C8	1.478 (3)
C5—C6	1.489 (3)		
O1—C5—O2	124.2 (2)	O2—C5—C6	115.3 (2)
O1—C5—C6	120.5 (2)		
O1—C5—C6—C7	11.0 (3)	C6—C7—C8—C9	12.5 (4)
C5—C6—C7—C8	176.6 (2)		

Data collection

Rigaku AFC-7R diffractometer	$h = -28 \rightarrow 28$
ω scans	$k = 0 \rightarrow 7$
2973 measured reflections	$l = -10 \rightarrow 4$
2383 independent reflections	3 standard reflections
1203 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{int} = 0.012$	intensity decay: 0.5%
$\theta_{max} = 27.5^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.0891P]$
$R(F) = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.149$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.01$	$\Delta\rho_{max} = 0.18$ e Å ⁻³
2383 reflections	$\Delta\rho_{min} = -0.19$ e Å ⁻³
127 parameters	
H-atom parameters constrained	

Table 2

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N4—H4A...O1 ⁱ	0.95	2.42	2.956 (3)	115
N4—H4A...O2 ⁱⁱ	0.95	2.09	2.779 (3)	128
N4—H4B...O2 ⁱⁱⁱ	0.95	1.81	2.756 (3)	176
N4—H4C...O1	0.95	2.00	2.913 (2)	160
N4—H4C...O2	0.95	2.49	3.174 (3)	129
N4—H4D...O1 ^{iv}	0.95	1.95	2.887 (3)	168

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

All H atoms were located from difference syntheses, and their positional parameters were recalculated geometrically and fixed, with C—H = N—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(\text{parent atom})$.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1718). Services for accessing these data are described at the back of the journal.

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