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Fumaric acid–*trans*-cinnamamide (1/2)

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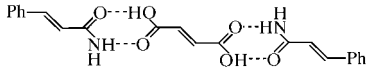
In the title adduct, $C_4H_4O_4{\cdot}2C_9H_9NO$, fumaric acid has a centre of symmetry and is connected to two *trans*-cinnamamide molecules through cyclic hydrogen bonds. A single-crystal photoirradiation promoted the conformational disorder of the fumaric acid.

Comment

The structure of the title adduct, (I), was determined previously based on the X-ray intensity data measured on a Rigaku AFC-5*S* diffractometer (Ito *et al.*, 2000). The structure has been redetermined in the present study in order to compare it directly with that after photoirradiation, measuring the X-ray data on a Rigaku AFC-7*R* diffractometer.



(I)

Conformational disorder of the fumaric acid was detected, which was not taken into account in the previous study (Ito *et al.*, 2000). The population is 7.9 (3)% of the minor conformation, which is suitable for heterogeneous photocycloaddition with a neighbouring cinnamamide molecule. The distance between the centres of the C6*═C6*^{i} [symmetry code: (i) $1-x, 1-y, 1-z$] and C8═C9 bonds is 3.950 (3) Å. In the crystal which had undergone photoirradiation for 3 h, (I′), the population of the minor conformation increased to 14.8 (6)%.

Experimental

Crystals of (I) were grown by slow evaporation from a 2-propanol solution of a 1:2 mixture of fumaric acid and cinnamamide.

Compound (I)

Crystal data

$C_4H_4O_4{\cdot}2C_9H_9NO$
M_r = 410.43
Monoclinic, $P2_1/n$
a = 11.505 (2) Å
b = 5.298 (1) Å
c = 16.886 (2) Å
β = 94.057 (9)°
V = 1026.6 (3) Å^3
Z = 2
D_x = 1.328 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 13.3–14.9°
μ = 0.097 mm^{-1}
T = 298 (1) K
Prism, colourless
0.70 × 0.60 × 0.25 mm

Data collection

Rigaku AFC-7*R* diffractometer
θ–2θ scans
2462 measured reflections
2351 independent reflections
1873 reflections with $I > 2\sigma(I)$
R_{int} = 0.007
θ_{max} = 27.5°
$h = 0 \rightarrow 15$
$k = -7 \rightarrow 0$
$l = -22 \rightarrow 22$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.038
$wR(F^2)$ = 0.107
S = 1.06
2351 reflections
194 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.2732P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.016 (2)

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

O1—C7	1.237 (2)	C6—C6^{i}	1.314 (3)
O2—C5	1.203 (3)	C6*—C6*^{i}	1.29 (4)
O3—C5	1.312 (2)	C7—C8	1.479 (2)
N4—C7	1.322 (2)	C8—C9	1.321 (2)
C5—C6	1.489 (2)		

Symmetry code: (i) $1-x, 1-y, 1-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1^{i}	0.93 (2)	1.65 (2)	2.555 (2)	163 (2)
N4—H4A···O2^{ii}	0.88 (2)	2.44 (2)	3.288 (2)	161 (2)
N4—H4A···O2*^{ii}	0.88 (2)	2.21 (3)	3.08 (2)	171 (2)
N4—H4B···O1^{iii}	0.89 (2)	2.26 (2)	3.105 (2)	160 (2)

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

Compound (I′)

Crystal data

$C_4H_4O_4{\cdot}2C_9H_9NO$
M_r = 410.43
Monoclinic, $P2_1/n$
a = 11.547 (2) Å
b = 5.354 (2) Å
c = 16.820 (2) Å
β = 94.60 (1)°
V = 1036.5 (4) Å^3
Z = 2
D_x = 1.315 Mg m^{-3}
Mo Kα radiation
Cell parameters from 25 reflections
θ = 13.5–15.0°
μ = 0.096 mm^{-1}
T = 298 (1) K
Prism, colourless
0.8 × 0.5 × 0.15 mm

Data collection

Rigaku AFC-7*R* diffractometer	$h = 0 \rightarrow 15$
θ–2θ scans	$k = 0 \rightarrow 7$
2482 measured reflections	$l = -22 \rightarrow 22$
2367 independent reflections	3 standard reflections
1405 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{int} = 0.021$	intensity decay: none
$\theta_{max} = 27.5^\circ$	

Refinement

Refinement on F^2	H atoms: see text
$R(F) = 0.071$	$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 1.00P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.175$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.17$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
2367 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}
181 parameters	

Table 3
Selected geometric parameters (Å) for (I′).

O1—C7	1.234 (4)	C6—C6^{i}	1.322 (8)
O2—C5	1.215 (5)	C6*—C6*^{i}	1.30
O3—C5	1.303 (5)	C7—C8	1.478 (4)
N4—C7	1.321 (5)	C8—C9	1.321 (5)
C5—C6	1.469 (5)		

Symmetry code: (i) $1-x, 1-y, 1-z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (I′).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1^{i}	0.99 (4)	1.56 (3)	2.542 (4)	171 (4)
N4—H4A···O2^{ii}	0.81 (4)	2.50 (4)	3.282 (5)	163 (4)
N4—H4A···O2*^{ii}	0.81 (4)	2.26	3.07	173
N4—H4B···O1^{iii}	0.88 (4)	2.33 (4)	3.154 (5)	155 (3)

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

For (I), the non-H atoms of the major conformation of fumaric acid (O2, O3, C5 and C6) and cinnamamide were refined anisotropically. Those of the minor conformation of fumaric acid (O2*, O3*, C5* and C6*) were refined isotropically, and their U_{iso} parameters were fixed to U_{eq} of the corresponding atom of the major conformation. The bond lengths in the minor conformation were restrained with those of the major one. The H atoms of the minor conformation were omitted. All other H atoms were located from difference syntheses and refined isotropically. The bond distances involving the H atoms are in the range 0.88 (2)–0.97 (2) Å. The R factor decreased from 0.047 to 0.038 by introducing a 7.9 (3)% occupancy of the minor conformation. The UV spectra of a 2-propanol solution of (I) show a π–π^* absorption at 271 nm, and almost no absorption longer than 320 nm. Through a long-pass filter UV34 (T = 10% at 330 nm), a single-crystal of (I) was photoirradiated with a 250-W ultra high pressure Hg lamp for 3 h. The positional parameters of the non-H atoms of the minor conformation of fumaric acid were fixed to those of (I), and their U_{iso} parameters were fixed to U_{eq} of the corresponding atom of the major conformation. The H atoms of the minor conformation were omitted. The population of the minor conformation was refined to be 14.8 (6)%. The bond distances involving the H atoms are in the range 0.75 (3)–0.99 (4) Å.

For (I) and (I′), data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN*.

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