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*Acta Cryst.* (1993). **C49**, 2137–2139

## Structures of Ethyl 2-Cyano-3-(4-dimethylaminophenyl)propenoate (I) and Ethyl 2-Cyano-3-(4-hydroxy-3-methoxyphenyl)propenoate (II)

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(Received 10 December 1992; accepted 17 May 1993)

### Abstract

The title compounds were prepared as part of a study of ethyl cyanoacetate derivatives which were obtained by condensation of an aldehyde and ethyl cyanoacetate in the presence of a small amount of

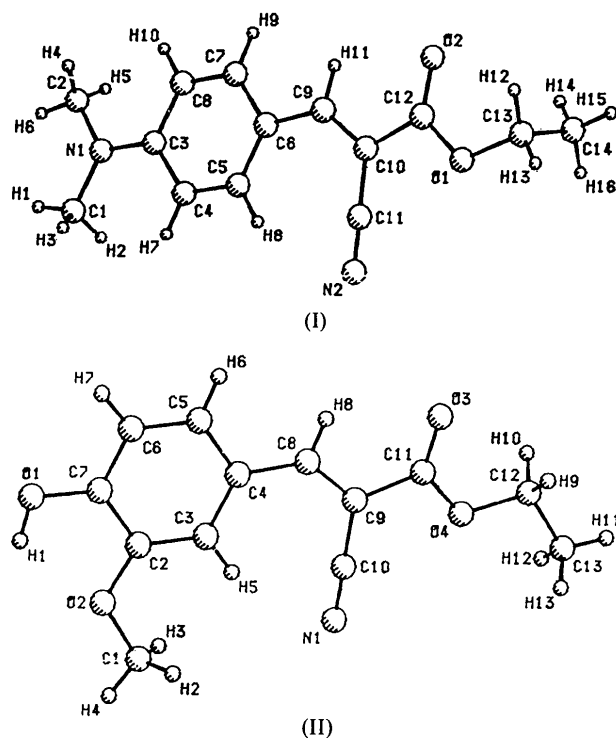


Fig. 1. Structure of compounds (I) and (II).

piperidine. The crystal structures of (I) and (II) have been determined; they belong to space groups  $P\bar{1}$  and  $P2_1/n$ , respectively. The molecules of compound (II) are linked by  $O-H\cdots O^i$  hydrogen bonds [symmetry code: (i)  $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ].

### Comment

Methyl 2-cyano-3-(2-methoxyphenyl)propenoate (Nakatani, Hayashi & Hidaka, 1992) crystallizes in a non-centrosymmetric space group and has large second-harmonic generation (SHG) efficiencies. We have synthesized a series of substituted  $\alpha$ -cyano-cinnamic acid esters, of which the title compounds are two.

This paper reports the results of the crystal structure analyses that allowed determination of the configuration at the substituted  $\alpha$ -cyano-cinnamic acid

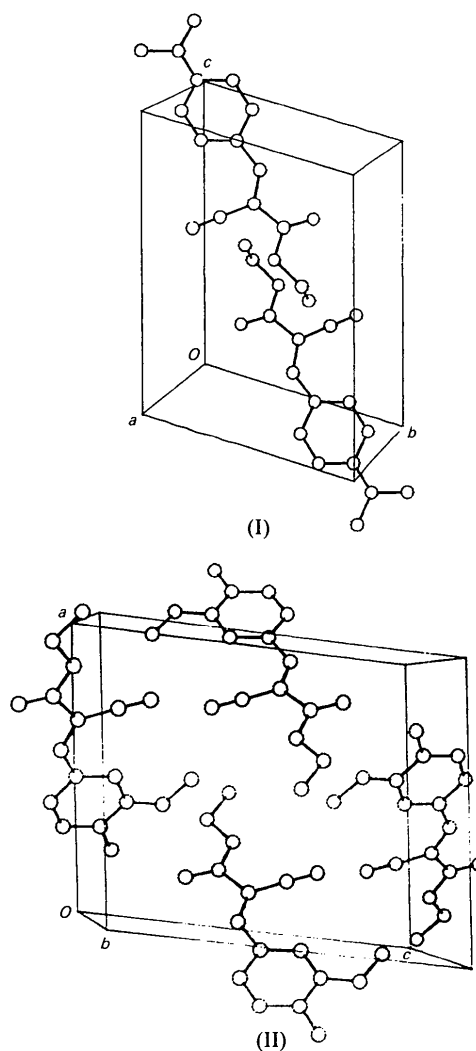


Fig. 2. Packing of molecules in the unit cell for compound (I) and compound (II).

ester in the main reaction product. The *PLUTO* (Motherwell & Clegg, 1978) drawings of the molecules of the two derivatives are shown in Fig. 1.

The orientation of the phenyl ring and the ethyl cyanopropenoate group are defined by the torsion angles in Tables 2 and 3. It is shown that these moieties are nearly coplanar in both compounds. The relevant geometrical parameters of an intermolecular hydrogen bond in compound (II), which is the main influence on molecular packing in the crystal, are O(1)—H(1)⋯O(3<sup>i</sup>) 2.832 (2) Å and O(1)—H(1)⋯O(3<sup>i</sup>) 144.8° [symmetry code: (i)  $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ]. There are no hydrogen bonds in compound (I). The O(1)—C(13)—C(14) angle [111.9 (2)°] in (I) is significantly larger than the O(4)—C(12)—C(13) angle [107.4 (2)°] in (II). This seems to be mainly a result of packing interactions and the existence of the hydrogen bond. Neither crystal has nonlinear optical properties; this has been confirmed by SHG efficiency measurements on a powder sample using the method of Kurtz & Perry (1968).

## Experimental Compound (I)

### Crystal data

C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 244.29  
 Triclinic  
*P* $\bar{1}$   
*a* = 7.605 (2) Å  
*b* = 8.401 (2) Å  
*c* = 11.555 (2) Å  
 $\alpha$  = 106.86 (2)°  
 $\beta$  = 102.57 (2)°  
 $\gamma$  = 102.17 (2)°  
*V* = 659.2 (6) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.23 Mg m<sup>-3</sup>

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71069 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 15–16°  
 $\mu$  = 0.078 mm<sup>-1</sup>  
*T* = 296 K  
 Prismatic  
 1.5 × 0.5 × 0.3 mm  
 Yellow, transparent  
 Crystal source: grown from alcohol solution

### Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: empirical  
 $T_{\min}$  = 0.9247,  $T_{\max}$  = 0.9827  
 2470 measured reflections  
 2296 independent reflections

1883 observed reflections  
 $[I > 3\sigma(I)]$   
 $R_{\text{int}}$  = 1.2%  
 $\theta_{\text{max}}$  = 49.9°  
 $h$  = -6 → 9  
 $k$  = -9 → 10  
 $l$  = -13 → 13  
 3 standard reflections  
 frequency: 60 min  
 intensity variation: 1.0%

### Refinement

Refinement on *F*  
*R* = 0.052  
*wR* = 0.073  
*S* = 2.25

$(\Delta/\sigma)_{\text{max}}$  = 0.0023  
 $\Delta\rho_{\text{max}}$  = 0.15 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -0.24 e Å<sup>-3</sup>  
 Extinction correction: none

1883 reflections  
 163 parameters  
 H-atom parameters not refined  
 $w = 1/\sigma^2(F)$

Atomic scattering factors from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974)

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) for compound (I)

$$B_{\text{eq}} = (8\pi^2/3)(U_{11} + U_{22} + U_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i>
O(1)	0.8415 (2)	0.5825 (2)	-0.3912 (1)	4.67 (5)
O(2)	0.7804 (2)	0.7544 (2)	-0.2254 (1)	5.11 (6)
N(1)	0.7183 (2)	0.0901 (2)	0.1941 (1)	3.75 (5)
N(2)	0.8636 (4)	0.2009 (3)	-0.3634 (2)	6.9 (1)
C(1)	0.7514 (3)	-0.0788 (3)	0.1624 (2)	4.61 (7)
C(2)	0.6492 (3)	0.1453 (3)	0.3027 (2)	4.77 (8)
C(3)	0.7261 (2)	0.1830 (2)	0.1157 (2)	3.10 (5)
C(4)	0.7705 (3)	0.1212 (2)	0.0017 (2)	3.49 (6)
C(5)	0.7819 (2)	0.2167 (2)	-0.0757 (2)	3.37 (6)
C(6)	0.7526 (2)	0.3818 (2)	-0.0453 (2)	3.12 (5)
C(7)	0.7071 (3)	0.4415 (2)	0.0684 (2)	3.53 (6)
C(8)	0.6928 (3)	0.3464 (2)	0.1454 (2)	3.56 (6)
C(9)	0.7650 (2)	0.4933 (2)	-0.1182 (2)	3.32 (6)
C(10)	0.8013 (2)	0.4745 (2)	-0.2312 (2)	3.43 (6)
C(11)	0.8360 (3)	0.3230 (3)	-0.3048 (2)	4.44 (7)
C(12)	0.8058 (2)	0.6186 (3)	-0.2793 (2)	3.75 (6)
C(13)	0.8493 (3)	0.7142 (3)	-0.4494 (2)	5.48 (8)
C(14)	0.6619 (3)	0.6990 (3)	-0.5289 (2)	5.76 (9)

Table 2. Geometric parameters (Å, °) for compound (I)

O(1)—C(12)	1.341 (2)	C(4)—C(5)	1.368 (2)
O(1)—C(13)	1.449 (2)	C(5)—C(6)	1.407 (2)
O(2)—C(12)	1.208 (2)	C(6)—C(7)	1.409 (2)
N(1)—C(3)	1.359 (2)	C(6)—C(9)	1.432 (2)
N(1)—C(1)	1.449 (3)	C(7)—C(8)	1.364 (2)
N(1)—C(2)	1.456 (2)	C(9)—C(10)	1.365 (3)
N(2)—C(11)	1.142 (3)	C(10)—C(11)	1.423 (3)
C(3)—C(8)	1.406 (3)	C(10)—C(12)	1.468 (3)
C(3)—C(4)	1.411 (3)	C(13)—C(14)	1.476 (3)
C(12)—O(1)—C(13)	117.7 (2)	C(8)—C(7)—C(6)	122.5 (2)
C(3)—N(1)—C(1)	121.2 (2)	C(7)—C(8)—C(3)	121.2 (2)
C(3)—N(1)—C(2)	120.6 (2)	C(10)—C(9)—C(6)	132.5 (2)
C(1)—N(1)—C(2)	117.6 (2)	C(9)—C(10)—C(11)	123.5 (2)
N(1)—C(3)—C(8)	121.5 (2)	C(9)—C(10)—C(12)	118.3 (2)
N(1)—C(3)—C(4)	121.6 (2)	C(11)—C(10)—C(12)	118.2 (2)
C(8)—C(3)—C(4)	116.9 (2)	N(2)—C(11)—C(10)	179.7 (4)
C(5)—C(4)—C(3)	121.4 (2)	O(2)—C(12)—O(1)	123.3 (2)
C(4)—C(5)—C(6)	122.0 (2)	O(2)—C(12)—C(10)	124.6 (2)
C(5)—C(6)—C(7)	116.0 (2)	O(1)—C(12)—C(10)	112.1 (2)
C(5)—C(6)—C(9)	126.4 (2)	O(1)—C(13)—C(14)	111.9 (2)
C(7)—C(6)—C(9)	117.6 (2)		
C(8)—C(7)—C(6)—C(9)	-179.6 (7)		
C(4)—C(5)—C(6)—C(9)	178.7 (2)		
C(6)—C(9)—C(10)—C(11)	0.4 (5)		
O(2)—C(12)—C(10)—C(11)	-179.3 (2)		
C(12)—O(1)—C(13)—C(14)	-87.8 (2)		

## Compound (II)

### Crystal data

C<sub>13</sub>H<sub>13</sub>NO<sub>4</sub>  
*M<sub>r</sub>* = 247.25  
 Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 10.644 (2) Å  
*b* = 9.355 (2) Å  
*c* = 12.643 (3) Å  
 $\beta$  = 97.18 (2)°  
*V* = 1249.1 (9) Å<sup>3</sup>

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71069 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 14–15°  
 $\mu$  = 0.092 mm<sup>-1</sup>  
*T* = 296 K  
 Prismatic  
 0.6 × 0.5 × 0.5 mm

Z = 4  
 $D_x = 1.31 \text{ Mg m}^{-3}$

Yellow, transparent  
 Crystal source: grown from  
 alcohol solution

C(3)—C(4)—C(8)	123.5 (2)	O(3)—C(11)—C(9)	123.5 (2)
C(6)—C(5)—C(4)	121.2 (2)	O(4)—C(11)—C(9)	112.0 (1)
C(5)—C(6)—C(7)	120.3 (2)	O(4)—C(12)—C(13)	107.4 (2)
O(1)—C(7)—C(6)	119.4 (2)		

### Data collection

Enraf-Nonius CAD-4  
 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  
 empirical  
 $T_{\min} = 0.774$ ,  $T_{\max} =$   
 1.127  
 2481 measured reflections  
 2362 independent reflections

1857 observed reflections  
 $[I \geq 3\sigma(I)]$   
 $R_{\text{int}} = 0.757862$   
 $\theta_{\max} = 25^\circ$   
 $h = 0 \rightarrow 12$   
 $k = 0 \rightarrow 11$   
 $l = -15 \rightarrow 15$   
 3 standard reflections  
 frequency: 66 min  
 intensity variation: 1.0%

### Refinement

Refinement on F  
 $R = 0.056$   
 $wR = 0.066$   
 $S = 2.08$   
 1857 reflections  
 163 parameters  
 $w = 1/\sigma^2(F)$   
 $(\Delta/\sigma)_{\max} = 0.0004$

$\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (Cromer & Waber, 1974)

C(6)—C(5)—C(4)—C(8)	179.1 (2)
C(2)—C(3)—C(4)—C(8)	-179.7 (2)
C(4)—C(8)—C(9)—C(10)	-0.4 (3)
O(3)—C(11)—C(9)—C(10)	-176.8 (2)
C(11)—O(4)—C(12)—C(13)	174.8 (2)

The title compounds were prepared by condensation of ethyl cyanoacetate with 4-dimethylaminobenzaldehyde for (I) and with 3-methoxy-4-hydroxybenzaldehyde for (II), using piperidine as a catalyst. The crystals were mounted in random orientations on glass fibres. Data were collected with an Enraf-Nonius CAD-4 diffractometer (*CONTROL*; Molecular Structure Corporation, 1989). Scan widths were  $(0.65 + 0.35\tan\theta)^\circ$  for (I) and  $(1.22 + 0.35\tan\theta)^\circ$  for (II). Empirical absorption corrections, based on azimuthal scans of three reflections, were applied [average values of 0.96 and 0.956 were obtained for (I) and (II), respectively]. The data were corrected for Lorentz and polarization factors. The structures were solved by direct methods using *MITHRIL* (Gilmore, 1983) and *DIRDIF* (Beurskens, 1984). The C, O and N atoms were located on an E map. H atoms were placed in geometrically calculated positions with C—H = 0.95 Å, but were not included in the refinement. Anomalous-dispersion corrections were not applied. All calculations were performed on a MicroVAX II computer using the *TEXSAN* (Molecular Structure Corporation, 1987) program package. Views of the molecules and unit cells were produced by the *PLUTO* (Motherwell & Clegg, 1978) program.

Table 3. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for compound (II)

	x	y	z	$B_{\text{eq}}$
O(1)	0.2564 (1)	-0.0466 (1)	0.4353 (1)	4.18 (6)
O(2)	0.0824 (1)	0.0869 (1)	0.2993 (1)	3.85 (6)
O(3)	-0.1782 (1)	0.5478 (1)	0.7250 (1)	3.86 (6)
O(4)	-0.3156 (1)	0.5988 (1)	0.5804 (1)	3.71 (6)
N(1)	-0.2438 (2)	0.4348 (2)	0.3612 (1)	5.9 (1)
C(1)	-0.0097 (2)	0.1551 (2)	0.2242 (1)	4.4 (1)
C(2)	0.0872 (2)	0.1242 (2)	0.4036 (1)	2.84 (7)
C(3)	0.0098 (2)	0.2232 (2)	0.4434 (1)	2.90 (7)
C(4)	0.0237 (2)	0.2541 (2)	0.5532 (1)	2.81 (7)
C(5)	0.1173 (2)	0.1828 (2)	0.6197 (1)	3.32 (7)
C(6)	0.1939 (2)	0.0831 (2)	0.5801 (1)	3.50 (8)
C(7)	0.1801 (2)	0.0527 (2)	0.4728 (1)	3.10 (7)
C(8)	-0.0545 (2)	0.3562 (2)	0.6011 (1)	2.92 (7)
C(9)	-0.1541 (2)	0.4362 (2)	0.5597 (1)	2.90 (7)
C(10)	-0.2054 (2)	0.4351 (2)	0.4496 (2)	3.63 (8)
C(11)	-0.2157 (2)	0.5325 (2)	0.6314 (1)	3.02 (7)
C(12)	-0.3798 (2)	0.7016 (2)	0.6424 (2)	3.89 (8)
C(13)	-0.4801 (2)	0.7721 (3)	0.5679 (2)	5.3 (1)

Table 4. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for compound (II)

O(1)—C(7)	1.357 (2)	C(3)—C(4)	1.407 (2)
O(2)—C(2)	1.359 (2)	C(4)—C(5)	1.391 (2)
O(2)—C(11)	1.427 (2)	C(4)—C(8)	1.448 (2)
O(3)—C(11)	1.209 (2)	C(5)—C(6)	1.373 (3)
O(4)—C(11)	1.326 (2)	C(6)—C(7)	1.377 (2)
O(4)—C(12)	1.463 (2)	C(8)—C(9)	1.349 (3)
N(1)—C(10)	1.142 (2)	C(9)—C(10)	1.430 (2)
C(2)—C(3)	1.376 (2)	C(9)—C(11)	1.486 (2)
C(2)—C(7)	1.405 (2)	C(12)—C(13)	1.487 (3)
C(2)—O(2)—C(1)	118.0 (1)	O(1)—C(7)—C(2)	120.9 (2)
C(11)—O(4)—C(12)	116.5 (1)	C(6)—C(7)—C(2)	119.7 (2)
O(2)—C(2)—C(3)	125.2 (2)	C(9)—C(8)—C(4)	132.0 (2)
O(2)—C(2)—C(7)	114.8 (2)	C(8)—C(9)—C(10)	124.0 (2)
C(3)—C(2)—C(7)	120.0 (1)	C(8)—C(9)—C(11)	119.0 (2)
C(2)—C(3)—C(4)	120.3 (2)	C(10)—C(9)—C(11)	117.0 (2)
C(5)—C(4)—C(3)	118.5 (2)	N(1)—C(10)—C(9)	178.6 (2)
C(5)—C(4)—C(8)	118.0 (1)	O(3)—C(11)—O(4)	124.5 (2)

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71332 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1030]

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