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Conformational polymorphs of 22-cyano-*N*-methyl-5-phenyl-pent-2-en-4-ynamide

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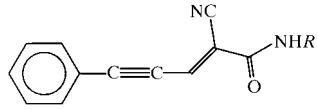
Although the two polymorphic modifications, (I) and (II), of the title compound, $C_{13}H_{10}N_2O$, crystallize in the same space group ($P2_1/c$), their asymmetric units have Z' values of 1 and 2, respectively. These are conformational polymorphs, since the molecules in phases (I) and (II) adopt different rotations of the phenyl ring with respect the central 2-cyanocarboxy-aminoprop-2-enyl fragment. Calculations of crystal packing using *Cerius*[2] [Molecular Simulations (1999). 9685 Scranton Road, San Diego, CA 92121, USA] have shown that (I) is more stable than (II), by 1.3 kcal mol^{-1} for the crystallographically determined structures and by 1.56 kcal mol^{-1} for the optimized structures (1 kcal mol^{-1} = 4.184 kJ mol^{-1}). This difference is mainly attributed to the different strengths of the hydrogen bonding in the two forms.

Comment

Derivatives of 2-cyanoacrylic acid with unsaturated substituents in the 3-position are of great interest because of their potential bioactivity and versatility in the synthesis of polymeric and heterocyclic compounds. For example, such compounds can undergo polymerization under very mild conditions (Gololobov & Gruber, 1997; Denchev & Kabaivanov, 1993). In addition, our previous structural studies show that topochemical reactions can occur in some of these derivatives, namely in 2-cyano-(2*E*)-penta-2,4-dienoic acid and its ethyl ester (Borbulevych *et al.*, 1998). As part of our further structural investigation of this class of compounds (Borbulevych *et al.*, 1998, 1999; Golding *et al.*, 1999; Khrustalev *et al.*, 1996), we present here our results on two polymorphic modifications, (I) and (II), of the title compound, (1).

Although the two polymorphic modifications crystallize in the same space group, *viz.* $P2_1/c$, there are two independent molecules, *A* and *B*, in the asymmetric unit of form (II), whereas there is only one for form (I). Most bond lengths in (I) and (II) are equal to within three standard uncertainties (Tables 1 and 4). It should be mentioned that in (II*A*), the N2—C13 bond is somewhat elongated [1.466 (3) Å], and the O1═C1 bond length of 1.213 (3) Å is shortened, compared



(1) R = Mc
(2) R = Ph

with those in (I) and (II*B*). On the other hand, the C═O bond is equal to that found in the analogous phenyl-substituted compound, (2) (Borbulevych *et al.*, 1999). The variation in this bond length is attributed to the difference of the hydrogen bonds in compounds (1) and (2) (see below).

The 2-cyanocarboxyaminoprop-2-enyl fragment (N2/C1/O1/C2/C3/C6/N1) in (I) and (II) is rather flattened, despite the presence of shortened intramolecular contacts (see Tables 2 and 5). The maximum deviations from the least-squares mean plane passing through all non-H atoms of this fragment are observed for O1 in each case, and are 0.1430 (8), 0.066 (2) and −0.131 (2) Å for (I), (II*A*) and (II*B*), respectively.

The main differences between the geometry of the molecules in (I) and (II) are attributed to the degree of rotation of the phenyl ring with the respect to the 2-cyanocarboxy-aminoprop-2-enyl fragment. In (I) and (II*B*), the C7–C12 ring is considerably twisted, with interplanar angles between these fragments of 34.94 (4) and 43.0 (1)°, respectively. However, in (II*A*), the phenyl ring is almost coplanar with the above-mentioned fragment, as shown by the corresponding dihedral angle of 8.9 (1)°. Moreover, where only one IR band (at 1581 cm^{-1}), corresponding to the vibrations of the conjugated PhC≡CCH═C fragment, appears in the IR spectra of (I), two such bands (at 1566 and 1583 cm^{-1}) are seen for (II). We attribute this observation to the presence of two molecules having different rotations of the phenyl ring.

In (I), the molecules are linked into infinite chains through intermolecular hydrogen bonds (Table 3), and similar chains are seen for (II) (Table 6). However, in (II), each chain

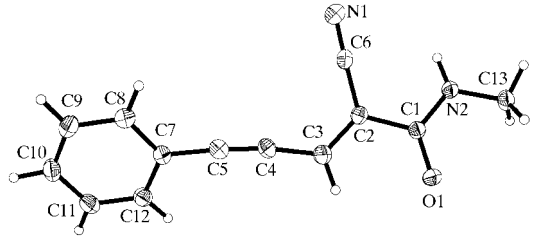


Figure 1
A molecular view of (1) in polymorphic form (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

consists exclusively of molecules of type *A* or type *B*. Therefore, molecules of (I) and (II) are not linked into centrosymmetric dimers by intermolecular hydrogen bonding, in contrast with derivatives of 2-cyanopenta-2,4-dienoic acid (Borbulevych *et al.*, 1998; Golding *et al.*, 1999). A similar hydrogen-bonding network was observed in (2) (Borbulevych *et al.*, 1999).

In order to allow comparison between the polymorphic forms (I) and (II), calculations of the crystal lattice energies for their crystallographic and optimized structures were carried out using the Dreiding 2.21 force field (Mayo *et al.*, 1990). According to these calculations (see *Experimental*) the X-ray structure of (I) is more stable than that of (II) by 1.3 kcal mol^{-1}. We attribute this difference mainly to differences in the contribution made by the hydrogen bonding (Table 7). Optimization of the structures of (I) and (II) gives

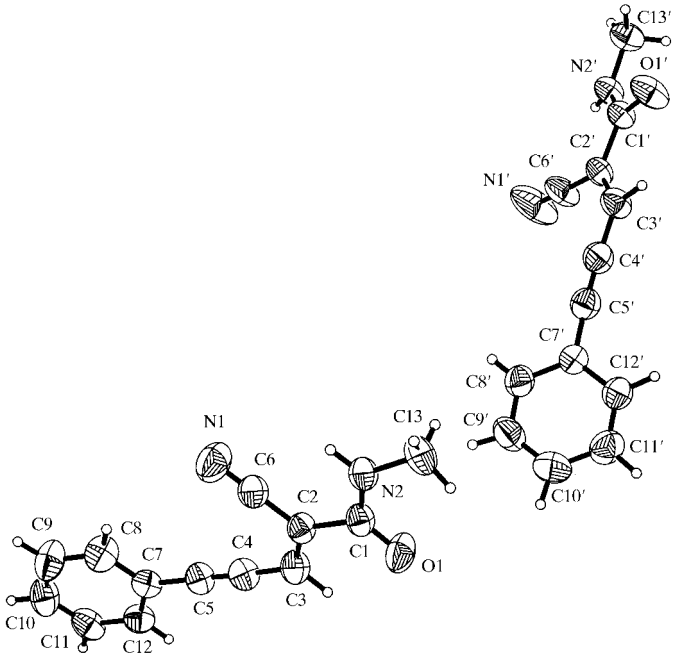


Figure 2
A molecular view of (1) in polymorphic form (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

rise to similar results, *i.e.* (I) being more stable than (II) by 1.56 kcal mol^{-1}. In this case, the van der Waals energy contributions are equal, but for (I), the hydrogen-bonding and Coulombic contributions are lower by 1.03 and 0.53 kcal mol^{-1}, respectively. Thus, we conclude that the difference in the lattice energies arises from differences in the energies associated with hydrogen bonding, which appear to be somewhat stronger in (I).

Experimental

Compound (1) was synthesized by the Knoevenagel condensation method. A clear solution of *N*-methyl cyanoacetamide (0.98 g, 0.01 mol) and phenylpropiolic aldehyde (1.44 g, 0.01 mol) in *N*-methylpyrrolidone (NMP, 3 ml) was stirred with aluminium oxide (5 g) as catalyst until the exothermic reaction had ceased and the reaction mixture had solidified. After being left to stand overnight at room temperature, further NMP (5 ml) was added. The precipitate was filtered off and washed with NMP (5 ml). The filtrate was poured into water and the precipitate was separated and crystallized from toluene (yield 67%). Spectroscopic analysis: ^{1}H NMR (400.26 MHz, acetone, δ, p.p.m): 2.90 (d, J = 4.8 Hz, 3H, CH_3), 7.47–7.62 (m, 7H, CH + NH + 5H$_{arom}$). Crystals of the polymorphic forms (I) and (II) were obtained by isothermal evaporation from CCl_4 and n-C_6H_{14} solutions, respectively. The melting point of (I) is 381 K and that of (II) is 384 K. IR spectra were recorded on a Perkin–Elmer 1725 FT–IR spectrometer with a modified sample holder (Shchegolikhin & Lazareva, 1997).

Compound (1), form (I)

Crystal data

$C_{13}H_{10}N_2O$
M_r = 210.23
Monoclinic, $P2_1/c$
a = 11.9794 (18) Å
b = 8.9951 (13) Å
c = 10.0786 (16) Å
β = 101.557 (3)°
V = 1064.0 (3) Å^3
Z = 4
D_x = 1.312 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 540 reflections
θ = 2–24°
μ = 0.09 mm^{-1}
T = 110 (2) K
Square prism, yellow
0.5 × 0.4 × 0.3 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.958, T_{max} = 0.975
8003 measured reflections
2991 independent reflections
2195 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 30.1°
$h = -16 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.116
S = 0.97
2991 reflections
185 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.077P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

O1—C1	1.2315 (13)	C2—C3	1.3462 (15)
N1—C6	1.1480 (16)	C2—C6	1.4329 (15)
N2—C1	1.3338 (14)	C3—C4	1.4096 (15)
N2—C13	1.4513 (14)	C4—C5	1.2035 (15)
C1—C2	1.5050 (15)	C5—C7	1.4274 (15)

Table 2
Short contacts (Å) for (1), form (I).

O1···H3	2.44 (2)	C6···H2	2.46 (2)

Table 3
Hydrogen-bonding geometry (Å, °) for (1), form (I).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1^{i}	0.91 (2)	2.02 (2)	2.860 (1)	153 (1)

Symmetry code: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

Compound (1), form (II)

Crystal data

$C_{13}H_{10}N_2O$	D_x = 1.244 Mg m^{-3}
M_r = 210.23	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 24 reflections
a = 22.652 (12) Å	θ = 10–11°
b = 9.728 (7) Å	μ = 0.08 mm^{-1}
c = 10.269 (5) Å	T = 293 (2) K
β = 97.29 (4)°	Needle, yellow
V = 2245 (2) Å^3	0.5 × 0.2 × 0.2 mm
Z = 8	

Data collection

Enraf–Nonius CAD-4 diffractometer	θ_{max} = 27°
$\theta/2\theta$ scans	$h = -28 \rightarrow 0$
4929 measured reflections	$k = 0 \rightarrow 12$
4810 independent reflections	$l = -12 \rightarrow 13$
2134 reflections with $I > 2\sigma(I)$	2 standard reflections
R_{int} = 0.079	every 90 reflections
	intensity decay: 3.4%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.052	$w = 1/[\sigma^2(F_o^2) + (0.091P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.169	$(\Delta/\sigma)_{max}$ = 0.001
S = 0.96	$\Delta\rho_{max}$ = 0.16 e Å^{-3}
4810 reflections	$\Delta\rho_{min}$ = −0.22 e Å^{-3}
291 parameters	

Table 4
Selected geometric parameters (Å, °) for (1), form (II).

O1—C1	1.213 (3)	O1′—C1′	1.228 (3)
N1—C6	1.138 (4)	N1′—C6′	1.131 (3)
N2—C1	1.332 (3)	N2′—C1′	1.329 (3)
N2—C13	1.466 (3)	N2′—C13′	1.450 (3)
C1—C2	1.513 (3)	C1′—C2′	1.495 (3)
C2—C3	1.346 (4)	C2′—C3′	1.335 (3)
C2—C6	1.423 (4)	C2′—C6′	1.420 (3)
C3—C4	1.414 (4)	C3′—C4′	1.411 (4)
C4—C5	1.199 (3)	C4′—C5′	1.191 (4)
C5—C7	1.424 (4)	C5′—C7′	1.432 (4)

Table 5
Short contacts (Å) for (1), form (II).

C6···H2	2.38	C6′···H2′	2.41
O1′···H3′	2.45		

Table 6
Hydrogen-bonding geometry (Å, °) for (1), form (II).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1^{ii}	0.86	2.46	3.163 (4)	139.3
N2′—H2′···O1′^{iii}	0.86	2.19	2.939 (3)	145.1

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

Optimization of the crystal structures of (I) and (II) and calculation of the lattice energies were carried out using *Cerius*^{2} (Molecular Simulations, 1999), taking into account their monoclinic cell setting (*i.e.* the angles α and γ were constrained) using the 'Smart Minimizer' option of the *Cerius*^{2} package. Using this option, optimization begins with a steepest descent method, followed by a quasi-Newton method and finishing with a truncated Newton method.

Table 7
Total and component energies (kcal mol^{-1}) for the crystallographic and optimized structures of the two polymorphs of (1).

Energy	(1), (I)^a	(1), (I)^b	(1), (II)^a	(1), (II)^b
Total	−28.15	−29.21	−26.85	−27.65
van der Waals	−21.57	−22.34	−21.83	−22.34
Coulombic	−4.22	−4.42	−3.70	−3.89
Hydro gen-bonding	−2.36	−2.45	−1.32	−1.42

Notes: (*a*) crystallographic structure; (*b*) optimized structure.

Atom–atom potentials were estimated using the Dreiding 2.21 force field (Mayo *et al.*, 1990) and atomic charges were estimated using the charge equilibration method (Rappé & Goddard, 1991). All molecules in the crystal were treated as rigid entities. In this case, the total lattice energy is the sum of three contributions, namely van der Waals, Coulombic and hydrogen bonding. For polymorph (I), all H atoms were refined isotropically. For polymorph (II), H atoms were treated as riding, with C—H = 0.93–0.96 Å, N—H = 0.86 Å and $U_{iso}(H) = nU_{eq}$ of the parent atom, where n = 1.5 for methyl H atoms and n = 1.2 for other H atoms.

For compound (1), form (I), data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998). For compound (1), form (II), data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*. For both polymorphs, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1452). Services for accessing these data are described at the back of the journal.

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