organic compounds

Methyl 3-amino-2-cyanoacrylate

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In the title compound, $C_5H_6N_2O_2$, which is an example of a push–pull olefin, a network of N—H$\cdots$O and N—H$\cdots$N interactions helps to establish the crystal packing. The length of the nominal olefinic C=C bond is 1.385 (2) Å.

Related literature

For related structures, see: Szulzewsky *et al.* (1984). For background, see: Cook (1969); Dyke (1973); Nalwa *et al.* (1997); Chemla & Zyss (1987).
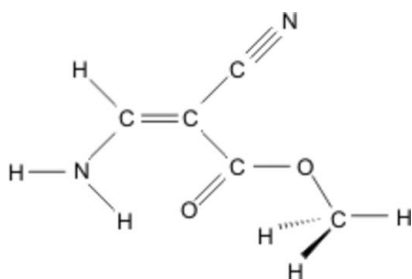
Experimental

Crystal data

$C_5H_6N_2O_2$
$M_r = 126.12$
Monoclinic, $P2_1/n$
$a = 3.785$ (1) Å
$b = 10.787$ (2) Å
$c = 14.784$ (3) Å
$\beta = 95.98$ (3)°

$V = 600.3$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 100$ K
$0.53 \times 0.21 \times 0.04$ mm

Data collection

Oxford Diffraction GEMINI R diffractometer
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{min} = 0.946$, $T_{max} = 0.998$

6877 measured reflections
1095 independent reflections
856 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.106$
$S = 1.11$
1095 reflections
83 parameters

17 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots$A	D—H	H$\cdots$A	$D\cdots$A	D—H$\cdots$A
N2—H2B$\cdots$O1	0.86	2.16	2.764 (2)	127
N2—H2B$\cdots$O1^i	0.86	2.20	2.906 (3)	139
N2—H2A$\cdots$N1^{ii}	0.86	2.20	2.928 (2)	143

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2451).

References

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supplementary materials

Methyl 3-amino-2-cyanoacrylate

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Comment

The title compound, (I), belongs to the family of so-called push–pull ethylenes. Push–pull alkenes are highly reactive organic compounds with the general formula depicted in Fig. 3, where for X = NH or NR^1 and X = O the R^1 and R^2 can be hydrogen, alkyl or hetero(aryl) group (*e.g.* electron donor groups) and R^3, R^4 are electron acceptor groups such as –CN, –COR, –COOR, SO_2CH_3 and NO_2. They are useful as starting reactants or intermediates for many pharmaceutical, polymer, dye and other syntheses (Cook, 1969, Dyke, 1973).

Due to the opposite character of the substituents, the olefinic C=C double bond order is reduced and accompanied by the increased bond orders of the bonds between the olefinic carbon atoms and their electron donor and electron acceptor groups, respectively. This leads to the substantial decrease of the rotational barrier about the C=C double bond and to the increase of an analogous barrier about the adjacent bonds. These changes are connected with the separation of the positive and negative charges and electron delocalization within the π-electron system. The polar character of push-pull ethylenes, electronic interactions between substituents as well as the double bond are responsible for their non-linear optical properties and their use as new electro-optics materials (Nalwa *et al.*, 1997, Chemla & Zyss, 1987).

The study of a similar compound, ethyl 3-amino-2-cyanocrotonate, revealed the *Z* orientation of the ester group (*cis* position with respect to the amino group, *i.e. Z*-isomer) and the *Z* orientation of the carbonyl oxygen (towards the C=C double bond position, *Z*-conformer) (Szulzewsky *et al.*, 1984). Such a geometry was observed also in the case of methyl-2-cyano-3-aminoacrylate. The C=C bond length of 1.385 (2)Å in (I) is somewhat shorter than in the case of ethyl 3-amino-2-cyanocrotonate (1.404 Å). The =C—N and =C—C(*trans*) bond lengths of values 1.308 (2)/1.420 (2) Å, respectively are in a good agreement with those for ethyl 3-amino-2-cyanocrotonate which are 1.309/1.420 Å, respectively. The =C—C(*cis*) bond length of the value 1.449 (2)Å is somewhat longer as in the case of 3-amino-2-cyanocrotonate (1.431 Å).

Experimental

To methyl methoxymethylenecyanoacetate (1.41 g, 10 mmol) in methanol (10 ml), an aqueous solution of ammonia (12 mmol) was added dropwise (amount according to concentration and density) over a period of 30 min with stirring. The slightly warmed mixture was stirred overnight at room temperature. The reaction mixture was then briefly heated to reflux (*ca* 20 min). After ensuring that no starting derivative remained (thin-layer chromatography; Silufol 254, Kavalier Czechoslovakia; eluent chloroform-methanol 10:1 *v/v*, detection UV light 254 nm), the reaction mixture was evaporated on a vacuum evaporator and chromatographed on silica gel (eluent dichloromethane-methanol 10:1 *v/v*). The obtained product was recrystallized from a minimal amount of chloroform and n-hexane mixture in refrigerator to yield colourless blocks of (I).

supplementary materials

Refinement

The olefinic (C—H = 0.93 Å) and amino (N—H = 0.86 Å) hydrogen atoms were positioned geometrically and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C,N)$. The methyl H atoms were located in a difference Fourier map and included in the model as a rigid rotating group, with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$.
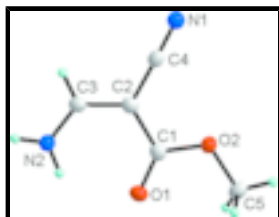
Figures

Fig. 1. The molecular structure of (I) with displacement ellipsoids drawn at the 60% probability level (arbitrary spheres for the H atoms).
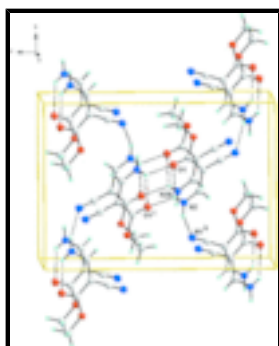

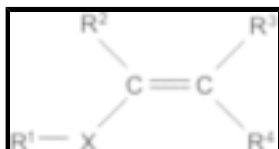Fig. 2. Packing diagram for (I) with the hydrogen-bond interactions are indicated by dashed lines.

Fig. 3. The general formula for push–pull alkenes, where for $X = NH$ or NR^1 and $X = O$ the R^1 and R^2 can be hydrogen, alkyl or hetero(aryl) group (*e.g.* electron-donor groups) and R^3, R^4 are electron-acceptor groups such as –CN, –COR, –COOR, –SO$_2$CH$_3$ and –NO$_2$.

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Crystal data

$C_5H_6N_2O_2$	$F_{000} = 264$
$M_r = 126.12$	$D_x = 1.395$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 4197 reflections
$a = 3.785$ (1) Å	$\theta = 3.8–30.4°$
$b = 10.787$ (2) Å	$\mu = 0.11$ mm^{-1}
$c = 14.784$ (3) Å	$T = 100$ K
$\beta = 95.98$ (3)°	Slab, colourless
$V = 600.3$ (2) Å^3	$0.53 \times 0.21 \times 0.04$ mm
$Z = 4$	

Data collection

Oxford Diffraction GEMINI R diffractometer	1095 independent reflections
Radiation source: fine-focus sealed tube	856 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.025$
$T = 100$ K	$\theta_{max} = 25.4°$
Rotation method data acquisition using ω and φ scans	$\theta_{min} = 4.6°$
Absorption correction: analytical (CrysAlis RED; Oxford Diffraction, 2006)	$h = -4 \rightarrow 4$
$T_{min} = 0.946$, $T_{max} = 0.998$	$k = -12 \rightarrow 12$
6877 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.106$	$w = 1/[\sigma^2(F_o^2) + (0.0584P)^2 + 0.1974P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.002$
1095 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
83 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
17 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
O1	0.1333 (3)	0.38235 (11)	0.56002 (8)	0.0238 (3)
O2	0.3605 (3)	0.23064 (10)	0.65388 (7)	0.0211 (3)
N1	0.8157 (4)	0.35812 (13)	0.84585 (10)	0.0246 (4)
N2	0.3268 (4)	0.62174 (13)	0.61008 (9)	0.0234 (4)

H2B	0.2041	0.5812	0.5677	0.028*
H2A	0.3452	0.7010	0.6063	0.028*
C4	0.6658 (4)	0.39141 (14)	0.77822 (11)	0.0186 (3)
C2	0.4814 (4)	0.43641 (15)	0.69625 (10)	0.0185 (3)
C1	0.3076 (4)	0.35106 (15)	0.63025 (11)	0.0179 (3)
C3	0.4853 (4)	0.56287 (15)	0.68030 (11)	0.0194 (4)
H3A	0.6145	0.6111	0.7242	0.023*
C5	0.1961 (4)	0.14209 (15)	0.58854 (12)	0.0236 (4)
H5C	0.2630	0.0595	0.6076	0.028*
H5B	0.2742	0.1579	0.5299	0.028*
H5A	−0.0575	0.1503	0.5849	0.028*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0283 (6)	0.0225 (6)	0.0195 (6)	0.0013 (5)	−0.0032 (4)	−0.0002 (4)
O2	0.0253 (6)	0.0171 (5)	0.0203 (6)	−0.0004 (4)	−0.0003 (5)	−0.0008 (4)
N1	0.0288 (8)	0.0206 (8)	0.0233 (7)	0.0006 (6)	−0.0026 (5)	−0.0009 (6)
N2	0.0302 (8)	0.0176 (7)	0.0214 (7)	−0.0019 (5)	−0.0027 (6)	0.0005 (5)
C4	0.0192 (8)	0.0165 (8)	0.0205 (7)	0.0000 (6)	0.0035 (5)	−0.0019 (6)
C2	0.0179 (7)	0.0192 (6)	0.0184 (7)	0.0011 (6)	0.0024 (5)	−0.0001 (5)
C1	0.0168 (7)	0.0186 (6)	0.0187 (7)	0.0007 (6)	0.0038 (5)	0.0009 (5)
C3	0.0192 (7)	0.0204 (7)	0.0186 (7)	0.0001 (6)	0.0021 (6)	−0.0013 (6)
C5	0.0238 (8)	0.0217 (8)	0.0250 (9)	−0.0023 (6)	0.0010 (7)	−0.0047 (6)

Geometric parameters (Å, °)

O1—C1	1.2185 (19)	C4—C2	1.420 (2)
O2—C1	1.3545 (19)	C2—C3	1.385 (2)
O2—C5	1.452 (2)	C2—C1	1.449 (2)
N1—C4	1.154 (2)	C3—H3A	0.9300
N2—C3	1.308 (2)	C5—H5C	0.9600
N2—H2B	0.8600	C5—H5B	0.9600
N2—H2A	0.8600	C5—H5A	0.9600
C1—O2—C5	114.70 (12)	O2—C1—C2	113.03 (13)
C3—N2—H2B	120.0	N2—C3—C2	126.96 (15)
C3—N2—H2A	120.0	N2—C3—H3A	116.5
H2B—N2—H2A	120.0	C2—C3—H3A	116.5
N1—C4—C2	178.10 (17)	O2—C5—H5C	109.5
C3—C2—C4	117.98 (14)	O2—C5—H5B	109.5
C3—C2—C1	121.57 (14)	H5C—C5—H5B	109.5
C4—C2—C1	120.40 (15)	O2—C5—H5A	109.5
O1—C1—O2	122.53 (14)	H5C—C5—H5A	109.5
O1—C1—C2	124.44 (15)	H5B—C5—H5A	109.5
C5—O2—C1—O1	0.6 (2)	C3—C2—C1—O2	174.06 (13)
C5—O2—C1—C2	−178.86 (12)	C4—C2—C1—O2	−3.4 (2)
C3—C2—C1—O1	−5.3 (2)	C4—C2—C3—N2	−178.63 (15)
C4—C2—C1—O1	177.15 (14)	C1—C2—C3—N2	3.8 (2)

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2B⋯O1	0.86	2.16	2.764 (2)	127
N2—H2B⋯O1[i]	0.86	2.20	2.906 (3)	139
N2—H2A⋯N1[ii]	0.86	2.20	2.928 (2)	143

Symmetry codes: (i) $-x$, $-y+1$, $-z+1$; (ii) $-x+3/2$, $y+1/2$, $-z+3/2$.

Fig. 1

Fig. 2

Fig. 3