

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

2-[(*E*)-4-(2-Bromophenyl)but-3-en-2-ylidene]malononitrile

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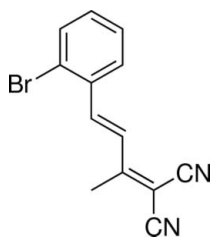
Received 19 November 2010; accepted 26 November 2010

 Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å;
 R factor = 0.039; wR factor = 0.112; data-to-parameter ratio = 14.1.

The title compound, $\text{C}_{13}\text{H}_{19}\text{BrN}_2$, is planar structure except for the methyl H atoms, the maximum atomic deviation for the non-H atoms being 0.100 (1) Å. The bromophenyl and isopropanylidene malononitrile units are located on opposite sides of the $\text{C}=\text{C}$ bond, showing an *E* configuration.

Related literature

For the use of malononitrile-containing compounds as building blocks in syntheses, see: Liu *et al.* (2002); Sepiol & Milart (1985); Zhang *et al.* (2003). For a related structure, see: Chen & Kang (2010).



Experimental

Crystal data

 $\text{C}_{13}\text{H}_{19}\text{BrN}_2$
 $M_r = 273.13$

 Triclinic, $P\bar{1}$
 $a = 7.0353$ (7) Å

 $b = 7.0765$ (5) Å

 $c = 13.3229$ (8) Å

 $\alpha = 82.192$ (6)°

 $\beta = 76.628$ (8)°

 $\gamma = 66.038$ (9)°

 $V = 589.03$ (8) Å³
 $Z = 2$

 Cu $K\alpha$ radiation

 $\mu = 4.52$ mm⁻¹
 $T = 291$ K

 $0.36 \times 0.32 \times 0.24$ mm

Data collection

Oxford Diffraction Xcalibur

Sapphire3 Gemini ultra

diffractometer

Absorption correction: multi-scan

 (*CrysAlis PRO*; Oxford

Diffraction, 2009)

 $T_{\min} = 0.293$, $T_{\max} = 0.410$

4500 measured reflections

2062 independent reflections

 1923 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.112$
 $S = 1.06$

2062 reflections

146 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.59$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.55$ e Å⁻³

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The author thanks the Testing Centre of Sichuan University for the diffraction measurements and is grateful for financial support from China West Normal University (No. 412374).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5097).

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supporting information

Acta Cryst. (2010). E66, o3365 [https://doi.org/10.1107/S1600536810049536]

2-[(*E*)-4-(2-Bromophenyl)but-3-en-2-ylidene]malononitrile**Tai-Ran Kang****S1. Comment**

Malononitrile derivatives have broad application for the preparation of heterocyclic ring compounds. The chemistry of ylidene malononitrile have been studied extensively, From the ring closure reactions, the comounds containing newly formed five or six-membered rings, such as indans (Zhang *et al.*, 2003), naphthalenes (Liu *et al.*, 2002), benzenes (Sepiol *et al.*, 1985) were obtained. Some crystal structures involving ylidene malononitrile groups have been published, including a recent report from our labratory Chen, *et al.*, 2010). As a part of our interest in the synthsis of some complex ring systems, we investigated the title compound (I), which is a diene reagent in Diels-Alder reaction. We report herein the crystal structure of the title compound.

The molecular structure of (I) is shown in Fig. 1. Bond lengths and angles in (I) are normal. The molecule skeleton display an approximately planar structure except for the methyl group.

S2. Experimental

2-(Propan-2-ylidene)malononitrile (0.212 g, 2 mmol) and 2-bromobenzaldehyde (0.366 g, 2 mmol) were dissolved in 2-propanol (2 ml). To the solution was added piperidine (0.017 g, 0.2 mmol), the solution was stirred for 24 h at 343 K. Then the reaction was cooled to room temperature, and the solution was filtered to obtain a yellow solid. Recrystallization from hot ethanol afforded the pure compound. Single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation ethyl acetate solution.

S3. Refinement

H atoms were placed in calculated positions with C—H = 0.93–0.96 Å, and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the others.

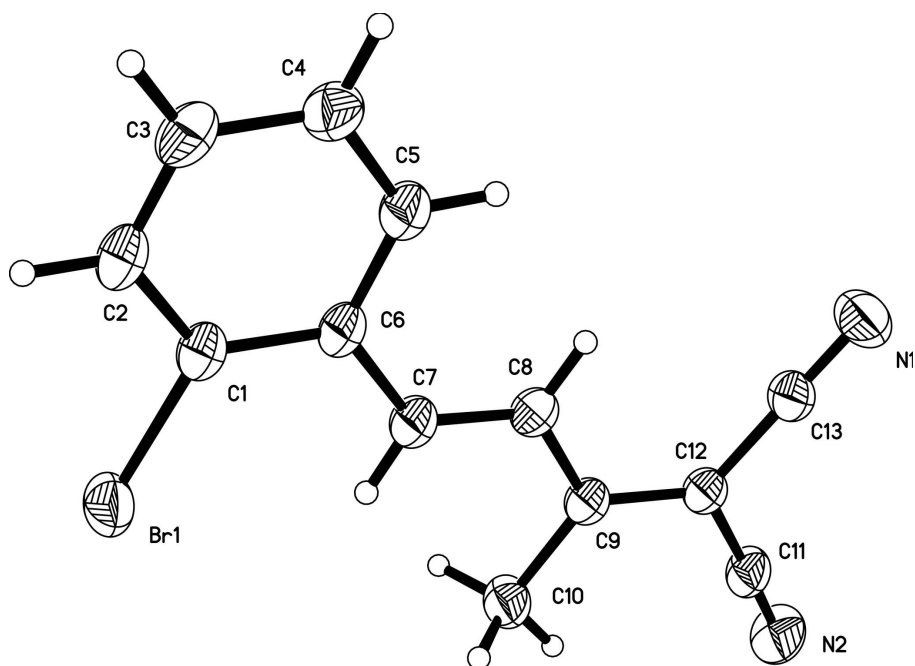


Figure 1

The molecular structure of (I) with 30% probability displacement ellipsoids (arbitrary spheres for H atoms).

2-[(E)-4-(2-Bromophenyl)but-3-en-2-ylidene]propanedinitrile

Crystal data

$C_{13}H_9BrN_2$

$M_r = 273.13$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.0353$ (7) Å

$b = 7.0765$ (5) Å

$c = 13.3229$ (8) Å

$\alpha = 82.192$ (6)°

$\beta = 76.628$ (8)°

$\gamma = 66.038$ (9)°

$V = 589.03$ (8) Å³

$Z = 2$

$F(000) = 272$

$D_x = 1.540$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 3664 reflections

$\theta = 6.8$ – 71.9 °

$\mu = 4.52$ mm⁻¹

$T = 291$ K

Block, yellow

$0.36 \times 0.32 \times 0.24$ mm

Data collection

Oxford Diffraction Xcalibur Sapphire3 Gemini
ultra
diffractometer

Radiation source: Enhance Ultra (Cu) X-ray
Source

Mirror monochromator

Detector resolution: 7.9575 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford Diffraction, 2009)

$T_{\min} = 0.293$, $T_{\max} = 0.410$

4500 measured reflections

2062 independent reflections

1923 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 67.0$ °, $\theta_{\min} = 6.8$ °

$h = -8 \rightarrow 6$

$k = -8 \rightarrow 8$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.112$
 $S = 1.06$
 2062 reflections
 146 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0759P)^2 + 0.0933P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.59 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.55 \text{ e } \text{Å}^{-3}$

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 $F^2 > \sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.67339 (5)	0.15902 (4)	0.54256 (2)	0.06643 (19)
C8	0.8775 (4)	-0.3609 (4)	0.7789 (2)	0.0493 (6)
H8	0.8557	-0.3515	0.8499	0.059*
N2	1.2571 (5)	-1.0939 (4)	0.7188 (2)	0.0735 (8)
C11	1.0519 (4)	-0.7373 (4)	0.7984 (2)	0.0455 (5)
C4	0.5298 (5)	0.2647 (5)	0.8955 (2)	0.0598 (7)
H4	0.4994	0.2887	0.9655	0.072*
C13	1.0087 (4)	-0.7342 (4)	0.9092 (2)	0.0527 (6)
C5	0.6402 (5)	0.0655 (4)	0.8620 (2)	0.0563 (6)
H5	0.6835	-0.0433	0.9103	0.068*
C9	0.9905 (4)	-0.5636 (4)	0.7362 (2)	0.0461 (5)
C7	0.8037 (4)	-0.1879 (4)	0.7217 (2)	0.0516 (6)
H7	0.8277	-0.2024	0.6510	0.062*
C2	0.5107 (4)	0.3937 (4)	0.7208 (3)	0.0563 (7)
H2	0.4684	0.5041	0.6732	0.068*
C10	1.0389 (5)	-0.5797 (5)	0.6211 (2)	0.0584 (7)
H10A	1.1160	-0.7222	0.6044	0.088*
H10B	1.1228	-0.5013	0.5895	0.088*
H10C	0.9087	-0.5260	0.5958	0.088*
C6	0.6889 (4)	0.0226 (4)	0.7573 (2)	0.0478 (6)
N1	0.9737 (5)	-0.7329 (5)	0.9974 (2)	0.0749 (8)
C3	0.4644 (4)	0.4289 (4)	0.8242 (3)	0.0604 (7)
H3	0.3891	0.5629	0.8466	0.072*
C12	1.1667 (4)	-0.9376 (4)	0.7555 (2)	0.0532 (6)
C1	0.6206 (4)	0.1936 (4)	0.6873 (2)	0.0496 (6)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0880 (3)	0.0444 (2)	0.0549 (3)	-0.01383 (17)	-0.01666 (17)	0.00310 (15)
C8	0.0616 (14)	0.0331 (13)	0.0509 (14)	-0.0141 (11)	-0.0134 (11)	-0.0042 (10)
N2	0.0868 (17)	0.0364 (14)	0.0813 (19)	-0.0086 (12)	-0.0094 (14)	-0.0120 (13)
C11	0.0542 (12)	0.0334 (12)	0.0467 (13)	-0.0140 (10)	-0.0109 (10)	-0.0024 (10)
C4	0.0712 (16)	0.0478 (15)	0.0555 (16)	-0.0208 (13)	-0.0032 (13)	-0.0105 (12)
C13	0.0673 (15)	0.0354 (13)	0.0519 (17)	-0.0138 (11)	-0.0196 (12)	0.0028 (11)
C5	0.0706 (16)	0.0384 (14)	0.0559 (16)	-0.0179 (12)	-0.0128 (12)	0.0009 (12)
C9	0.0549 (12)	0.0336 (12)	0.0481 (14)	-0.0145 (10)	-0.0117 (10)	-0.0024 (10)
C7	0.0654 (14)	0.0336 (13)	0.0522 (15)	-0.0145 (11)	-0.0141 (11)	-0.0015 (11)
C2	0.0583 (14)	0.0329 (13)	0.0699 (19)	-0.0105 (11)	-0.0140 (13)	0.0022 (12)
C10	0.0780 (17)	0.0425 (15)	0.0469 (15)	-0.0169 (13)	-0.0093 (13)	-0.0031 (11)
C6	0.0539 (13)	0.0318 (12)	0.0551 (15)	-0.0140 (10)	-0.0119 (11)	0.0003 (10)
N1	0.105 (2)	0.0617 (17)	0.0521 (17)	-0.0232 (15)	-0.0236 (14)	0.0012 (12)
C3	0.0602 (15)	0.0371 (14)	0.076 (2)	-0.0120 (11)	-0.0060 (13)	-0.0109 (13)
C12	0.0629 (15)	0.0354 (14)	0.0566 (16)	-0.0150 (12)	-0.0122 (12)	0.0011 (12)
C1	0.0508 (12)	0.0359 (13)	0.0575 (15)	-0.0125 (10)	-0.0116 (11)	0.0009 (11)

Geometric parameters (\AA , $^\circ$)

Br1—C1	1.908 (3)	C5—H5	0.9300
C8—C7	1.327 (4)	C9—C10	1.502 (4)
C8—C9	1.449 (4)	C7—C6	1.461 (4)
C8—H8	0.9300	C7—H7	0.9300
N2—C12	1.140 (4)	C2—C3	1.373 (5)
C11—C9	1.358 (4)	C2—C1	1.387 (4)
C11—C12	1.437 (4)	C2—H2	0.9300
C11—C13	1.438 (4)	C10—H10A	0.9600
C4—C5	1.383 (4)	C10—H10B	0.9600
C4—C3	1.390 (5)	C10—H10C	0.9600
C4—H4	0.9300	C6—C1	1.412 (4)
C13—N1	1.144 (4)	C3—H3	0.9300
C5—C6	1.401 (4)		
C7—C8—C9	123.3 (3)	C3—C2—C1	120.0 (3)
C7—C8—H8	118.4	C3—C2—H2	120.0
C9—C8—H8	118.4	C1—C2—H2	120.0
C9—C11—C12	120.8 (2)	C9—C10—H10A	109.5
C9—C11—C13	123.1 (2)	C9—C10—H10B	109.5
C12—C11—C13	116.1 (2)	H10A—C10—H10B	109.5
C5—C4—C3	119.7 (3)	C9—C10—H10C	109.5
C5—C4—H4	120.2	H10A—C10—H10C	109.5
C3—C4—H4	120.2	H10B—C10—H10C	109.5
N1—C13—C11	179.5 (3)	C5—C6—C1	116.6 (2)
C4—C5—C6	121.9 (3)	C5—C6—C7	122.1 (2)
C4—C5—H5	119.0	C1—C6—C7	121.3 (3)

C6—C5—H5	119.0	C2—C3—C4	120.2 (3)
C11—C9—C8	121.1 (2)	C2—C3—H3	119.9
C11—C9—C10	120.0 (2)	C4—C3—H3	119.9
C8—C9—C10	119.0 (2)	N2—C12—C11	178.1 (3)
C8—C7—C6	127.4 (3)	C2—C1—C6	121.5 (3)
C8—C7—H7	116.3	C2—C1—Br1	117.1 (2)
C6—C7—H7	116.3	C6—C1—Br1	121.4 (2)
C9—C11—C13—N1	131 (44)	C8—C7—C6—C5	-0.8 (5)
C12—C11—C13—N1	-49 (45)	C8—C7—C6—C1	179.5 (3)
C3—C4—C5—C6	-0.1 (5)	C1—C2—C3—C4	0.9 (4)
C12—C11—C9—C8	-179.0 (2)	C5—C4—C3—C2	-0.5 (5)
C13—C11—C9—C8	0.7 (4)	C9—C11—C12—N2	-6 (10)
C12—C11—C9—C10	1.1 (4)	C13—C11—C12—N2	175 (10)
C13—C11—C9—C10	-179.1 (3)	C3—C2—C1—C6	-0.6 (4)
C7—C8—C9—C11	-176.0 (3)	C3—C2—C1—Br1	178.9 (2)
C7—C8—C9—C10	3.8 (4)	C5—C6—C1—C2	0.0 (4)
C9—C8—C7—C6	-179.9 (3)	C7—C6—C1—C2	179.7 (3)
C4—C5—C6—C1	0.4 (4)	C5—C6—C1—Br1	-179.5 (2)
C4—C5—C6—C7	-179.4 (3)	C7—C6—C1—Br1	0.2 (3)
