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ISSN 2414-3146

1,3-Bis(2-cyanopropan-2-yl)-5-methylbenzene

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Received 15 January 2019
Accepted 19 March 2019

Edited by S. Parkin, University of Kentucky, USA

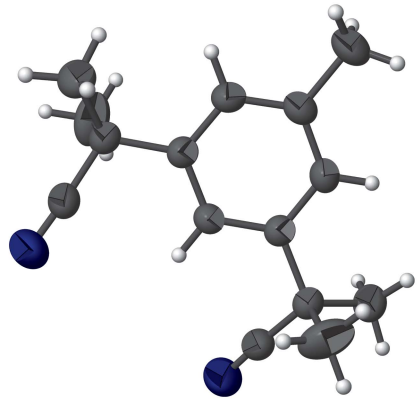
Keywords: 1,3-di(dimethylcyanomethyl)-5-methylbenzene; spectroscopic studies; crystal structure; non-covalent interaction.

CCDC reference: 1904010

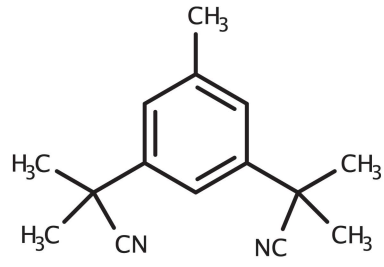
Structural data: full structural data are available from iucrdata.iucr.org

The complete molecule of the title compound [systematic name: 2,2′-(5-methyl-1,3-phenylene)bis(2-methylpropanenitrile)] is generated by a crystallographic twofold axis, which leads to disorder of the H atoms on the methyl group attached to the benzene ring. The dihedral angle between the benzene ring and the nitrile group is 26.2 (2)°. In the crystal, pairs of weak C—H···π interactions link molecules into dimers. The molecule absorbs at 212 nm as a result of a π–π* transition.

3D view



Chemical scheme



Structure description

Anastrazole (1,3-di-(dimethylcyanomethyl)-5-([1,2,4]triazolylmethyl) benzene) is an active pharmaceutical ingredient that is used as a drug in the treatment of post-menopausal endocrine-responsive breast cancer (Varelas *et al.*, 2007; Geisler *et al.*, 1996; Dowsett *et al.*, 2001) and it has cytotoxic impact against breast, liver hepatocellular and glandular cancer cells. The title compound, 1,3-di(dimethylcyanomethyl)-5-methyl-benzene (MCMB) is used as a starting material (Hsieh *et al.*, 2008) for the synthesis of anastrazole we now describe its crystal structure.

The asymmetric unit of the title compound consists of half a molecule of MCMB, with the other half being generated by a crystallographic twofold rotation axis (symmetry operation $-x, y, \frac{3}{2} - z$) (Fig. 1). Individual bond lengths and angles are unremarkable. The dihedral angle between the benzene ring and the carbonitrile moiety is 24.81 (16)°.

Within the crystal, molecules are linked by C—H···π interactions, with a C—H···Cg^{i} [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 2 - z$] distance d(C···π) of 3.708 (3) Å and a C—H···π angle of 158°. The interaction leads to the formation inversion dimers arranged in a two-

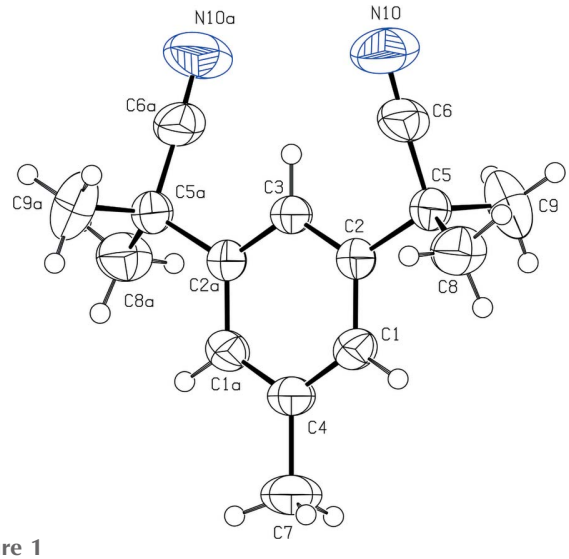


Figure 1
An ellipsoid plot (50% probability) of 1,3-di(dimethylcyanomethyl)-5-methylbenzene (MCMB). Symmetry code: (a) $-x$, y, $\frac{3}{2} - z$.

dimensional supramolecular strand-like architecture, linked by C—H$\cdots\pi$ interactions, as shown in Fig. 2.

An electronic transition takes place in the region of 212 nm because of a π–π^* transition of the C═C benzene and C≡N nitrile bonds of MCMB. The UV spectrum is shown in Fig. 3.

Synthesis and crystallization

The compound MCMB (0.056 mg, 0.25 mmol), obtained as a gift sample, was dissolved in hot methanol and stirred for half an hour. The resulting solution was allowed to cool and stored for slow evaporation. After a week, colorless prismatic crystals were harvested from the mother solution.

IR spectra: ν_{max}(cm^{-1}): (C=C) 1601, 1458, (Ar C—H) 2984, in-plane bending vibration 1001, 1293, out-of-plane bending vibration 707, 867, (C≡N) 2237, (*sym* and *asym* CH_3) 2874, 2942; ^{1}H NMR (500 MHz, DMSO) δ: 1.7 (*s*,12*H*), 2.3 (*s*, 3H), 7.3 (*o*, 2H), 7.4 (*p*, 1H).

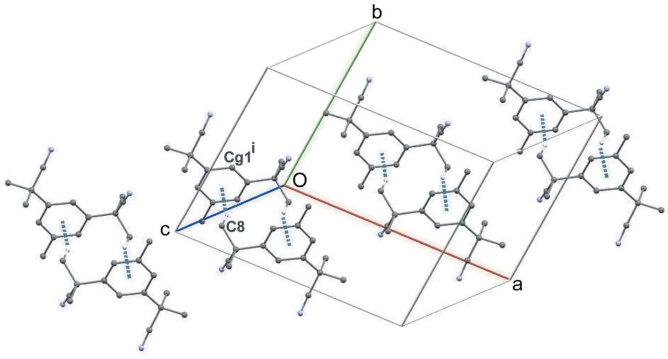


Figure 2
Inversion dimers linked by C—H$\cdots\pi$ bonds [symmetry code: (i) $\frac{1}{2} - x$, 1/2 $- y$, 2 $- z$] forming supramolecular strands. H atoms apart from the one that interacts with the phenyl group have been omitted to enhance the clarity of the figure.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{18}N_2$
M_r	226.31
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	298
a, *b*, *c* (Å)	13.821 (6), 13.138 (3), 9.473 (3)
β (°)	126.133 (8)
V (Å^3)	1389.3 (8)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.06
Crystal size (mm)	0.52 × 0.24 × 0.13
Data collection	
Diffractometer	Rigaku Mercury
Absorption correction	Multi-scan (*CrystalClear*; Rigaku, 2008)
T_{min}, T_{max}	0.653, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5988, 1261, 1012
R_{int}	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.600
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.059, 0.168, 1.06
No. of reflections	1261
No. of parameters	82
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.14

Computer programs: *CrystalClear* (Rigaku, 2008), *SHELXT2015* (Sheldrick, 2015*a*), *SHELXL2015* (Sheldrick, 2015*b*), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008), *POVRay* (Cason, 2004), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 1. The H atoms attached to C7 are disordered over two sets of sites..

Acknowledgements

The authors thank Mr Sunil Kumar, Research Scholar, Department of Chemistry, Periyar Maniammai Institute of Science and Technology, for the gift of a sample.

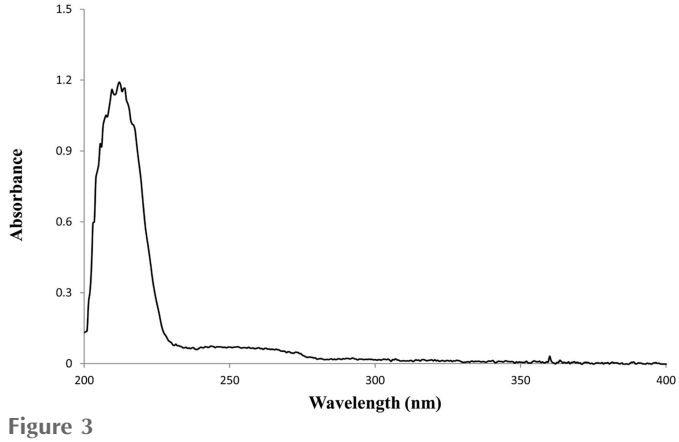


Figure 3
UV absorption spectrum of MCMB.

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full crystallographic data

IUCrData (2019). **4**, x190376 [https://doi.org/10.1107/S2414314619003766]

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2,2′-(5-Methyl-1,3-phenylene)bis(2-methylpropanenitrile)

Crystal data

$C_{15}H_{18}N_2$
M_r = 226.31
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 13.821 (6) Å
b = 13.138 (3) Å
c = 9.473 (3) Å
β = 126.133 (8)°
V = 1389.3 (8) Å^3
Z = 4
F(000) = 488
D_x = 1.082 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 1261 reflections
θ = 2.4–25.2°
μ = 0.06 mm^{-1}
T = 298 K
Prism, colourless
0.52 × 0.24 × 0.13 mm

Data collection

Rigaku Mercury diffractometer
Radiation source: Sealed Tube
Graphite Monochromator monochromator
Detector resolution: 18.4 pixels mm^{-1}
dtprofit.ref scans
Absorption correction: multi-scan (CrystalClear; Rigaku, 2008)
T_{min} = 0.653, T_{max} = 1.000
5988 measured reflections
1261 independent reflections
1012 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 25.3°, θ_{min} = 2.4°
h = −14→16
k = −15→15
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.168
S = 1.06
1261 reflections
82 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0857P)^2 + 0.652P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating -R-factor-obs 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.
All hydrogen atoms were positioned geometrically and were refined using a riding model with C—H bond lengths 0.93–0.96 Å and with U_{iso}(H) = 1.2Ueq(C) for CH (aromatic) or 1.5Ueq(C) for CH_3.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
N10	0.2028 (3)	0.50771 (16)	0.8107 (5)	0.1065 (13)	
C1	0.07549 (16)	0.16087 (13)	0.7249 (2)	0.0490 (6)	
C2	0.07652 (15)	0.26634 (13)	0.7246 (2)	0.0427 (5)	
C3	0.00000	0.31872 (17)	0.75000	0.0422 (7)	
C4	0.00000	0.10686 (19)	0.75000	0.0527 (8)	
C5	0.15448 (16)	0.32323 (13)	0.6845 (2)	0.0476 (6)	
C6	0.1794 (2)	0.42686 (15)	0.7556 (3)	0.0646 (8)	
C7	0.00000	−0.0085 (2)	0.75000	0.0781 (13)	
C8	0.2775 (2)	0.27308 (17)	0.7686 (3)	0.0678 (8)	
C9	0.0871 (2)	0.3299 (2)	0.4854 (3)	0.0848 (10)	
H1	0.12620	0.12544	0.70811	0.0590*	
H3	0.00000	0.38950	0.75000	0.0510*	
H7A	−0.03430	−0.03284	0.80706	0.1170*	0.500
H7B	0.08078	−0.03284	0.81121	0.1170*	0.500
H7C	−0.04647	−0.03284	0.63173	0.1170*	0.500
H8A	0.32525	0.31468	0.74812	0.1020*	
H8B	0.26704	0.20704	0.71796	0.1020*	
H8C	0.31717	0.26621	0.89209	0.1020*	
H9A	0.01218	0.36436	0.43489	0.1270*	
H9B	0.07231	0.26250	0.43753	0.1270*	
H9C	0.13464	0.36694	0.45929	0.1270*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N10	0.128 (2)	0.0523 (12)	0.196 (3)	−0.0193 (12)	0.127 (2)	−0.0238 (14)
C1	0.0539 (10)	0.0420 (10)	0.0613 (11)	0.0052 (7)	0.0396 (9)	0.0001 (7)
C2	0.0467 (9)	0.0415 (9)	0.0463 (9)	0.0003 (7)	0.0310 (7)	0.0004 (6)
C3	0.0464 (12)	0.0355 (11)	0.0489 (12)	0.0000	0.0305 (11)	0.0000
C4	0.0617 (15)	0.0373 (13)	0.0668 (15)	0.0000	0.0422 (13)	0.0000
C5	0.0507 (10)	0.0452 (10)	0.0583 (10)	0.0013 (7)	0.0385 (9)	0.0012 (7)
C6	0.0697 (13)	0.0467 (11)	0.1048 (17)	−0.0001 (9)	0.0666 (13)	0.0035 (10)
C7	0.095 (2)	0.0386 (15)	0.121 (3)	0.0000	0.075 (2)	0.0000
C8	0.0581 (12)	0.0590 (12)	0.0988 (16)	0.0032 (9)	0.0531 (12)	0.0003 (11)
C9	0.0824 (16)	0.116 (2)	0.0638 (13)	−0.0166 (15)	0.0475 (13)	0.0137 (13)

Geometric parameters (Å, º)

N10—C6	1.143 (3)	C7—H7B	0.9600
C1—C2	1.386 (2)	C7—H7C	0.9600
C1—C4	1.393 (3)	C7—H7A^{i}	0.9600
C2—C3	1.396 (3)	C7—H7B^{i}	0.9600
C2—C5	1.532 (3)	C7—H7C^{i}	0.9600
C4—C7	1.516 (4)	C8—H8A	0.9600
C5—C6	1.467 (3)	C8—H8B	0.9600
C5—C8	1.537 (4)	C8—H8C	0.9600
C5—C9	1.537 (3)	C9—H9A	0.9600
C1—H1	0.9300	C9—H9B	0.9600
C3—H3	0.9300	C9—H9C	0.9600
C7—H7A	0.9600		
C2—C1—C4	121.3 (2)	H7A—C7—H7C	109.00
C1—C2—C3	118.9 (2)	H7A—C7—H7A^{i}	141.00
C1—C2—C5	119.87 (19)	H7A—C7—H7B^{i}	56.00
C3—C2—C5	121.14 (16)	H7A—C7—H7C^{i}	56.00
C2—C3—C2^{i}	120.95 (19)	H7B—C7—H7C	109.00
C1—C4—C7	120.62 (12)	H7A^{i}—C7—H7B	56.00
C1—C4—C1^{i}	118.8 (2)	H7B—C7—H7B^{i}	141.00
C1^{i}—C4—C7	120.62 (12)	H7B—C7—H7C^{i}	56.00
C2—C5—C6	110.37 (19)	H7A^{i}—C7—H7C	56.00
C2—C5—C8	112.78 (16)	H7B^{i}—C7—H7C	56.00
C2—C5—C9	109.05 (18)	H7C—C7—H7C^{i}	141.00
C6—C5—C8	105.75 (19)	H7A^{i}—C7—H7B^{i}	109.00
C6—C5—C9	108.60 (17)	H7A^{i}—C7—H7C^{i}	109.00
C8—C5—C9	110.2 (2)	H7B^{i}—C7—H7C^{i}	109.00
N10—C6—C5	177.2 (4)	C5—C8—H8A	109.00
C2—C1—H1	119.00	C5—C8—H8B	109.00
C4—C1—H1	119.00	C5—C8—H8C	110.00
C2—C3—H3	120.00	H8A—C8—H8B	109.00
C2^{i}—C3—H3	120.00	H8A—C8—H8C	109.00
C4—C7—H7A	109.00	H8B—C8—H8C	109.00
C4—C7—H7B	109.00	C5—C9—H9A	109.00
C4—C7—H7C	109.00	C5—C9—H9B	109.00
C4—C7—H7A^{i}	109.00	C5—C9—H9C	109.00
C4—C7—H7B^{i}	109.00	H9A—C9—H9B	109.00
C4—C7—H7C^{i}	109.00	H9A—C9—H9C	109.00
H7A—C7—H7B	109.00	H9B—C9—H9C	109.00
C4—C1—C2—C3	0.0 (2)	C1—C2—C5—C6	−157.97 (17)
C4—C1—C2—C5	−175.93 (12)	C1—C2—C5—C8	−40.0 (2)
C2—C1—C4—C7	−180.00 (12)	C1—C2—C5—C9	82.8 (2)
C2—C1—C4—C1^{i}	0.00 (17)	C3—C2—C5—C6	26.2 (2)

C1—C2—C3—C2^{i}	0.02 (18)	C3—C2—C5—C8	144.25 (15)
C5—C2—C3—C2^{i}	175.86 (12)	C3—C2—C5—C9	−92.99 (19)

Symmetry code: (i) $-x$, y, $-z+3/2$.