organic compounds

A second monoclinic polymorph of 2-(diformylmethylidene)-3,3-dimethyl-2,3-dihydro-1*H*-indole

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The crystal structure of the title compound, $C_{13}H_{13}NO_2$, is a polymorph of the structure first reported by Helliwell *et al.* [*Acta Cryst.* (2006), E**62**, o737-o738]. It is also monoclinic (space group $P2_1/c$), but with completely different cell constants. The molecular conformations of these polymorphs differ by a 180° rotation of one formyl group. The present molecule is planar [maximum deviation 0.089 (2) Å] with the exception of the two methyl groups which lie on either side of the plane. There are strong intra- and intermolecular N—H⋯O hydrogen bonds. The latter link pairs of molecules across crystallographic centers of symmetry. Two aldehyde O atoms are brought close together [2.896 (4) Å in this arrangement but are not hydrogen bonded. In the earlier polymorph, one formyl group is rotated by 180° to yield intermolecular hydrogen bonding and an infinite polymeric chain. The other formyl group is involved in the same intramolecular hydrogen bonding as has been found here.

Related literature

For the crystal structure of the other polymorph, see: Helliwell *et al.* (2006). For a discussion of crystal growth conditions that can affect the occurrence of polymorphs, see: Hulliger *et al.* (1994). For chemistry involving 2-(diformylmethylidene)-3,3-dimethyl-2,3-dihydro-1*H*-indole, see: Baradarani *et al.* (2006).
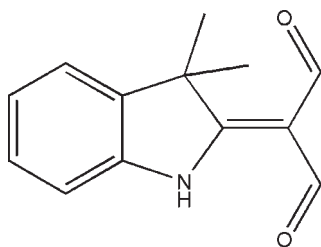
Experimental

Crystal data

$C_{13}H_{13}NO_2$	$V = 1072.8$ (3) Å³
$M_r = 215.24$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 6.9877$ (10) Å	$\mu = 0.09$ mm⁻¹
$b = 18.688$ (3) Å	$T = 103$ K
$c = 8.2154$ (12) Å	$0.57 \times 0.37 \times 0.03$ mm
$\beta = 90.291$ (3)°	

Data collection

Bruker APEXII CCD diffractometer	4763 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1865 independent reflections
	1123 reflections with $I > 2\sigma(I)$
$T_{min} = 0.950$, $T_{max} = 0.997$	$R_{int} = 0.072$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.103$	
$S = 0.92$	
1865 reflections	$\Delta\rho_{max} = 0.26$ e Å⁻³
151 parameters	$\Delta\rho_{min} = -0.22$ e Å⁻³

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O1	0.93 (3)	1.93 (3)	2.642 (3)	132 (2)
N1—H1⋯O1^i	0.93 (3)	2.19 (3)	2.946 (2)	138 (2)

Symmetry code: (i) $-x + 1, -y + 1, -z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2009).

References

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supplementary materials

A second monoclinic polymorph of 2-(diformylmethylidene)-3,3-dimethyl-2,3-dihydro-1*H*-indole

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Experimental

A solution of trimethylindolenine, (5.57 g, 35 mmol), in anhydrous dimethylformamide (15 ml) was cooled in an ice bath. A solution of phosphoryl chloride (10 ml) in dimethylformamide (15 ml) was added dropwise with stirring over a period of 1 h at below 283 K. The cooling bath was removed and the reaction mixture was stirred at 363 K for 2 h. The resulting solution was poured onto ice water (400 ml), the pH was adjusted to 9.0 by the addition of aqueous NaOH (35%) whereupon the solid product was precipitated. It was filtered, washed with hot water, dried and recrystallized from n-hexane/ethyl acetate to give a yellow solid in 4.35 g, 58% yield. Further recrystallization, from ethanol/water (3:1 *v/v*), led to a mixture of lath and prismatic habits. The prism cell dimensions confirmed the form reported earlier but the laths appeared new.

Refinement

C-bound hydrogen atoms were placed at calculated positions (C–H = 0.95–0.98 Å) and refined as riding with U(H) = 1.2–1.5 times U_{eq}(C). The N-bound hydrogen atom was located from a difference map, and freely refined to give a bond length of 0.93 (3) Å.

Figures
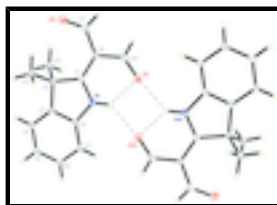
Fig. 1. A perspective drawing of two molecules of the title compound showing dimerization through intermolecular H-bonds. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: A = 1-x, 1-y, -z

2-(diformylmethylidene)-3,3-dimethyl-2,3-dihydro-1*H*-indole

Crystal data

$C_{13}H_{13}NO_2$	$F_{000} = 456$
$M_r = 215.24$	$D_x = 1.333$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 864 reflections
$a = 6.9877$ (10) Å	$\theta = 2.2–24.7°$
$b = 18.688$ (3) Å	$\mu = 0.09$ mm^{-1}
$c = 8.2154$ (12) Å	$T = 103$ K
$\beta = 90.291$ (3)°	Lath, yellow
$V = 1072.8$ (3) Å^3	$0.57 \times 0.37 \times 0.03$ mm
$Z = 4$	

supplementary materials

Data collection

Bruker APEXII CCD diffractometer	1865 independent reflections
Radiation source: fine-focus sealed tube	1123 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.072$
$T = 103$ K	$\theta_{max} = 25.1°$
ω scans	$\theta_{min} = 2.2°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -5\rightarrow8$
$T_{min} = 0.950$, $T_{max} = 0.997$	$k = -21\rightarrow22$
4763 measured reflections	$l = -9\rightarrow9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.103$	$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.92$	$(\Delta/\sigma)_{max} < 0.001$
1865 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
151 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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_{iso}*/U_{eq}
O1	0.4035 (3)	0.49657 (9)	0.1554 (2)	0.0308 (5)
O2	0.4628 (3)	0.65460 (9)	0.6032 (2)	0.0346 (5)
N1	0.7133 (3)	0.57750 (10)	0.1457 (2)	0.0192 (5)
H1	0.637 (4)	0.5445 (14)	0.092 (3)	0.054 (9)*

C1	0.6569 (3)	0.60337 (11)	0.2893 (3)	0.0195 (5)
C2	0.8061 (3)	0.65754 (12)	0.3488 (3)	0.0199 (6)
C3	0.9518 (3)	0.65385 (12)	0.2146 (3)	0.0197 (6)
C4	1.1227 (3)	0.68961 (12)	0.1934 (3)	0.0225 (6)
H4	1.1673	0.7228	0.2725	0.027*
C5	1.2281 (4)	0.67584 (12)	0.0535 (3)	0.0253 (6)
H5	1.3459	0.7002	0.0373	0.030*
C6	1.1650 (4)	0.62761 (12)	−0.0621 (3)	0.0259 (6)
H6	1.2405	0.6190	−0.1560	0.031*
C7	0.9931 (3)	0.59154 (12)	−0.0434 (3)	0.0221 (6)
H7	0.9479	0.5585	−0.1226	0.027*
C8	0.8906 (3)	0.60609 (11)	0.0965 (3)	0.0196 (5)
C9	0.4879 (3)	0.57998 (12)	0.3639 (3)	0.0192 (6)
C10	0.3723 (4)	0.52662 (12)	0.2862 (3)	0.0258 (6)
H10	0.2591	0.5128	0.3415	0.031*
C11	0.4105 (4)	0.60552 (13)	0.5160 (3)	0.0257 (6)
H11	0.3018	0.5801	0.5539	0.031*
C12	0.7221 (4)	0.73372 (12)	0.3575 (3)	0.0262 (6)
H12A	0.8248	0.7679	0.3812	0.039*
H12B	0.6261	0.7359	0.4438	0.039*
H12C	0.6621	0.7458	0.2530	0.039*
C13	0.8926 (3)	0.63454 (12)	0.5131 (3)	0.0241 (6)
H13A	0.9436	0.5859	0.5039	0.036*
H13B	0.7932	0.6357	0.5968	0.036*
H13C	0.9961	0.6674	0.5433	0.036*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0343 (11)	0.0320 (10)	0.0261 (10)	−0.0086 (9)	−0.0002 (8)	−0.0040 (8)
O2	0.0367 (12)	0.0377 (11)	0.0295 (10)	−0.0023 (9)	0.0058 (9)	−0.0071 (9)
N1	0.0143 (12)	0.0217 (11)	0.0215 (11)	−0.0051 (9)	0.0010 (9)	−0.0019 (9)
C1	0.0213 (15)	0.0178 (12)	0.0192 (12)	0.0006 (11)	−0.0039 (11)	0.0024 (10)
C2	0.0234 (15)	0.0187 (12)	0.0176 (12)	−0.0011 (11)	0.0010 (11)	−0.0001 (10)
C3	0.0223 (15)	0.0183 (12)	0.0185 (12)	0.0021 (11)	0.0003 (11)	0.0028 (10)
C4	0.0205 (15)	0.0230 (13)	0.0239 (13)	−0.0023 (11)	−0.0024 (11)	0.0018 (10)
C5	0.0198 (15)	0.0262 (14)	0.0299 (14)	−0.0006 (11)	0.0033 (12)	0.0067 (11)
C6	0.0292 (17)	0.0253 (13)	0.0233 (13)	0.0041 (12)	0.0055 (12)	0.0039 (11)
C7	0.0227 (15)	0.0237 (13)	0.0201 (12)	−0.0017 (11)	0.0009 (11)	0.0000 (10)
C8	0.0208 (14)	0.0157 (12)	0.0223 (12)	0.0028 (11)	0.0000 (11)	0.0031 (10)
C9	0.0154 (14)	0.0216 (13)	0.0204 (12)	−0.0019 (11)	−0.0005 (11)	0.0033 (10)
C10	0.0235 (16)	0.0267 (14)	0.0271 (14)	−0.0004 (12)	0.0010 (12)	0.0077 (11)
C11	0.0207 (15)	0.0278 (14)	0.0286 (14)	0.0045 (12)	−0.0003 (12)	0.0040 (12)
C12	0.0313 (16)	0.0215 (13)	0.0259 (13)	0.0023 (12)	0.0020 (12)	−0.0006 (10)
C13	0.0214 (15)	0.0301 (14)	0.0207 (13)	−0.0033 (11)	−0.0011 (11)	0.0016 (10)

Geometric parameters (Å, °)

O1—C10	1.233 (3)	C5—H5	0.9500

O2—C11	1.219 (3)	C6—C7	1.387 (3)
N1—C1	1.336 (3)	C6—H6	0.9500
N1—C8	1.410 (3)	C7—C8	1.384 (3)
N1—H1	0.93 (3)	C7—H7	0.9500
C1—C9	1.403 (3)	C9—C10	1.431 (3)
C1—C2	1.531 (3)	C9—C11	1.445 (3)
C2—C3	1.506 (3)	C10—H10	0.9500
C2—C13	1.538 (3)	C11—H11	0.9500
C2—C12	1.542 (3)	C12—H12A	0.9800
C3—C4	1.380 (3)	C12—H12B	0.9800
C3—C8	1.384 (3)	C12—H12C	0.9800
C4—C5	1.392 (3)	C13—H13A	0.9800
C4—H4	0.9500	C13—H13B	0.9800
C5—C6	1.380 (3)	C13—H13C	0.9800
C1—N1—C8	112.3 (2)	C6—C7—H7	121.7
C1—N1—H1	119.3 (17)	C3—C8—C7	123.3 (2)
C8—N1—H1	128.4 (17)	C3—C8—N1	108.2 (2)
N1—C1—C9	121.7 (2)	C7—C8—N1	128.5 (2)
N1—C1—C2	108.5 (2)	C1—C9—C10	119.8 (2)
C9—C1—C2	129.8 (2)	C1—C9—C11	126.5 (2)
C3—C2—C1	101.40 (18)	C10—C9—C11	113.8 (2)
C3—C2—C13	111.46 (19)	O1—C10—C9	127.1 (2)
C1—C2—C13	111.06 (18)	O1—C10—H10	116.4
C3—C2—C12	109.57 (18)	C9—C10—H10	116.4
C1—C2—C12	111.51 (19)	O2—C11—C9	130.1 (2)
C13—C2—C12	111.43 (18)	O2—C11—H11	114.9
C4—C3—C8	119.2 (2)	C9—C11—H11	114.9
C4—C3—C2	131.2 (2)	C2—C12—H12A	109.5
C8—C3—C2	109.6 (2)	C2—C12—H12B	109.5
C3—C4—C5	118.4 (2)	H12A—C12—H12B	109.5
C3—C4—H4	120.8	C2—C12—H12C	109.5
C5—C4—H4	120.8	H12A—C12—H12C	109.5
C6—C5—C4	121.4 (2)	H12B—C12—H12C	109.5
C6—C5—H5	119.3	C2—C13—H13A	109.5
C4—C5—H5	119.3	C2—C13—H13B	109.5
C5—C6—C7	121.0 (2)	H13A—C13—H13B	109.5
C5—C6—H6	119.5	C2—C13—H13C	109.5
C7—C6—H6	119.5	H13A—C13—H13C	109.5
C8—C7—C6	116.7 (2)	H13B—C13—H13C	109.5
C8—C7—H7	121.7		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.93 (3)	1.93 (3)	2.642 (3)	132 (2)
N1—H1···O1[i]	0.93 (3)	2.19 (3)	2.946 (2)	138 (2)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*.

Fig. 1