organic compounds

2,2,8-Trimethyl-2,3-dihydropyrano-[2,3-a]carbazol-4(11H)-one

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The molecule of the title compound, $C_{18}H_{17}NO_2$, is essentially planar: the r.m.s. deviation for all non-H atoms excluding the $C(CH_3)$ group of the 2,2-dimethyl-2H-pyran-4(3H)-one unit is 0.045 Å. Intermolecular N—H⋯O hydrogen bonds are formed to the keto O atom, and C—H⋯π contacts are observed between methyl H atoms and the π system of the pyrrole ring. While the flat molecules are in part parallel to each other, no strong π–π stacking interactions are found. The molecules lie in layers parallel to the (001) planes, with the c axis spanning two such layers.

Related literature

A low-yield synthesis of the title compound has been reported previously by Patel (1982). Rajendra Prasad & Vijayalakshmi (1994) describe the synthesis of the 1-oxo/1-hydroxycarbazole starting materials. The use of trifluoroacetic acid as an acylating agent is described in Sowmithran & Rajendra Prasad (1986).
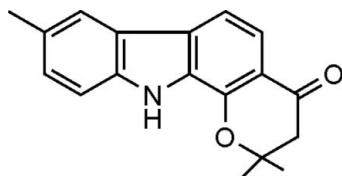
Experimental

Crystal data

$C_{18}H_{17}NO_2$
M_r = 279.33
Monoclinic, $P2_1/n$
a = 6.7323 (3) Å
b = 14.3303 (7) Å
c = 15.6502 (8) Å
β = 99.152 (1)°

V = 1490.65 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 298 (2) K
$0.47 \times 0.43 \times 0.17$ mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2007)
T_{min} = 0.906, T_{max} = 0.986

11129 measured reflections
3676 independent reflections
2866 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.150
S = 1.06
3676 reflections

193 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

$Cg1$ is the centroid of the pyrrole ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O2[i]	0.86	2.09	2.8093 (17)	141
C14—H14A⋯$Cg1$[ii]	0.97	2.58	3.534 (2)	168
C18—H18B⋯$Cg1$[iii]	0.96	3.00	3.881 (2)	153

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

Data collection: SMART (Bruker, 2003); cell refinement: SAINT-Plus (Bruker, 2003); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Bruker, 2003); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2241).

References

Bruker (2003). SMART (Version 5.630), SAINT-Plus (Version 6.45) and SHELXTL (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). SADABS. Version 2/2007. Bruker AXS Inc., Madison, Wisconsin, USA.
Patel, B. P. J. (1982). Indian J. Chem. **21B**, 20–23.
Rajendra Prasad, K. J. & Vijayalakshmi, C. S. (1994). Indian J. Chem. **33B**, 481–482.
Sowmithran, D. & Rajendra Prasad, K. J. (1986). Heterocycles, **24**, 711–717.

supplementary materials

2,2,8-Trimethyl-2,3-dihydropyrano[2,3-*a*]carbazol-4(11*H*)-one

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Comment

A low-yield synthesis of the title compound has been reported previously by Patel (1982). Using trifluoroacetic acid as the acylating agent (Rajendra Prasad & Vijayalakshmi (1994); Sowmithran & Rajendra Prasad (1986)), we have prepared the compound in excellent yield as the sole product of a one-step synthesis (Fig. 1). Crystallization from ethanol yielded crystals suitable for X-ray diffraction analysis. In the crystal, the molecule is essentially planar (Fig. 2), with only atom C15 and the adjacent two methyl groups (C16, C17) of the 2,2-dimethyl-2*H*-pyran-4(3*H*)-one unit deviating significantly from the mean plane of the other atoms. The RMS deviation for all non-H atoms excluding C15, C16 and C17 is 0.045 Å and the deviation from the plane is −0.590 (2), 2.102 (2) and −0.221 (2) Å for C15, C16 and C17, respectively.

Intermolecular N—H···O hydrogen bonds are formed, with the keto oxygen atom O2 acting as the acceptor, and C—H···π contacts are observed between C14 and the π system of the pyrrole ring, with a C—H···Cg^{ii} distance of 2.58 Å (symmetry code: (ii) $1 + x, y, z$). The other face of the pyrrole ring accepts another significantly longer C—H···π contact from the methyl group C18, with a C—H···Cg^{iii} distance of 3.00 Å (symmetry code (iii): $−1 + x, y, z$). While the flat molecules are in part parallel to each other, no strong π..π stacking interactions are observed.

The N—H···O hydrogen bonds connect individual molecules into infinite chains along the *b*-axis. The two types of C—H···π contacts are formed between molecules adjacent along the *a*-axis. Both types of highlighted interactions are formed between molecules lying within layers parallel to the (001) planes, and the *c*-axis spans two such layers (Fig. 3).

Experimental

6-Methyl-1-hydroxy carbazole (0.001 mol) dissolved in 10 ml of trifluoroacetic acid was heated with 3,3-dimethylacrylic acid (0.001 mol) at 323 K for 5 h. After completion of the reaction (as monitored by TLC), the excess trifluroacetic acid was removed using rotary evaporation. A solid precipitated out and the residue was poured onto ice water, then extracted using ethyl acetate and washed with water. The combined organic layers were dried over anhydrous sodium sulfate and filtered, then the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using petroleum ether / ethyl acetate (95:5) as eluant. Evaporation of the solvent afforded yellow crystals which were recrystallized from ethanol to yield the title compound in 91% yield (m.p. 489–491 K).

Refinement

H atoms were added in calculated positions with C—H = 0.96 or 0.97 Å, N—H = 0.86 Å, and refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C/N)$.

supplementary materials

Figures

Fig. 1. Synthesis of the title compound.
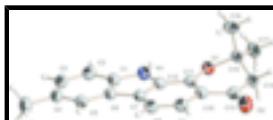
Fig. 2. Molecular structure showing displacement ellipsoids at 30% probablity for non-H atoms.
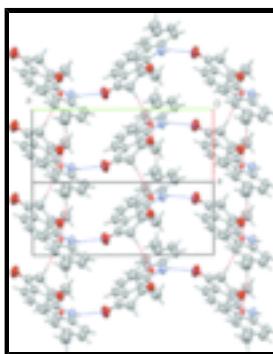
Fig. 3. View along [101] showing a segment of one of the layers formed by N—H···O hydrogen bonds (blue lines) and C—H···π contacts (red lines). Small red spheres are the centroids of the pyrrole rings.

2,2,8-Trimethyl-2,3-dihydropyrano[2,3-*a*]carbazol-4(11*H*)-one

Crystal data

$C_{18}H_{17}NO_2$	$F_{000} = 592$
$M_r = 279.33$	$D_x = 1.245$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 5575 reflections
$a = 6.7323$ (3) Å	$\theta = 2.6–30.5°$
$b = 14.3303$ (7) Å	$\mu = 0.08$ mm^{-1}
$c = 15.6502$ (8) Å	$T = 298$ (2) K
$\beta = 99.152$ (1)°	Plate, yellow
$V = 1490.65$ (12) Å^3	$0.47 \times 0.43 \times 0.17$ mm
$Z = 4$	

Data collection

Bruker SMART APEX CCD diffractometer	3676 independent reflections
Radiation source: fine-focus sealed tube	2866 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.027$
$T = 298(2)$ K	$\theta_{max} = 28.3°$
ω scans	$\theta_{min} = 1.9°$
Absorption correction: multi-scan (SADABS; Bruker, 2007)	$h = -8 \rightarrow 8$
$T_{min} = 0.906$, $T_{max} = 0.986$	$k = -18 \rightarrow 19$
11129 measured reflections	$l = -20 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.055$	H-atom parameters constrained
$wR(F^2) = 0.150$	$w = 1/[\sigma^2(F_o^2) + (0.0715P)^2 + 0.208P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
3676 reflections	$\Delta\rho_{max} = 0.20$ e Å^{-3}
193 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2sigma(F^2)$ 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	$U_{iso}*/U_{eq}$
C1	−0.2265 (2)	0.28205 (10)	0.33056 (10)	0.0548 (4)
C2	−0.3687 (3)	0.21301 (11)	0.33728 (12)	0.0634 (4)
H2	−0.3726	0.1582	0.3052	0.076*
C3	−0.5030 (3)	0.22888 (12)	0.39311 (12)	0.0668 (4)
H3	−0.5999	0.1837	0.3978	0.080*
C4	−0.5010 (2)	0.31017 (12)	0.44367 (11)	0.0629 (4)
C5	−0.3611 (2)	0.37843 (11)	0.43512 (10)	0.0584 (4)
H5	−0.3591	0.4332	0.4671	0.070*
C6	−0.2224 (2)	0.36555 (10)	0.37862 (10)	0.0526 (3)
C7	−0.0635 (2)	0.42209 (10)	0.35340 (10)	0.0516 (3)
C8	0.0111 (3)	0.51209 (10)	0.37606 (11)	0.0588 (4)
H8	−0.0448	0.5482	0.4155	0.071*
C9	0.1672 (3)	0.54513 (10)	0.33884 (11)	0.0598 (4)
H9	0.2182	0.6042	0.3540	0.072*
C10	0.2537 (2)	0.49222 (10)	0.27784 (10)	0.0529 (4)
C11	0.1767 (2)	0.40375 (9)	0.25316 (9)	0.0493 (3)
C12	0.0202 (2)	0.36987 (9)	0.29234 (9)	0.0507 (3)
C13	0.4290 (2)	0.52526 (10)	0.24281 (11)	0.0586 (4)

C14	0.5098 (2)	0.46048 (12)	0.18106 (11)	0.0624 (4)
H14A	0.6162	0.4230	0.2133	0.075*
H14B	0.5690	0.4975	0.1397	0.075*
C15	0.3540 (2)	0.39582 (11)	0.13186 (10)	0.0572 (4)
C16	0.1999 (3)	0.44889 (14)	0.06790 (12)	0.0786 (5)
H16A	0.1010	0.4061	0.0397	0.118*
H16B	0.2665	0.4788	0.0254	0.118*
H16C	0.1353	0.4951	0.0983	0.118*
C17	0.4503 (3)	0.31758 (13)	0.08771 (13)	0.0752 (5)
H17A	0.5383	0.2825	0.1302	0.113*
H17B	0.5262	0.3435	0.0464	0.113*
H17C	0.3474	0.2773	0.0585	0.113*
C18	−0.6477 (3)	0.32132 (15)	0.50596 (15)	0.0853 (6)
H18A	−0.6206	0.2752	0.5508	0.128*
H18B	−0.7823	0.3133	0.4757	0.128*
H18C	−0.6340	0.3825	0.5312	0.128*
N1	−0.0805 (2)	0.28588 (8)	0.27825 (9)	0.0576 (3)
H1	−0.0560	0.2432	0.2428	0.069*
O1	0.24620 (16)	0.34866 (7)	0.19360 (7)	0.0575 (3)
O2	0.5125 (2)	0.59946 (8)	0.26454 (10)	0.0843 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0618 (8)	0.0458 (7)	0.0563 (8)	0.0020 (6)	0.0083 (7)	0.0034 (6)
C2	0.0711 (10)	0.0477 (8)	0.0707 (10)	−0.0062 (7)	0.0087 (8)	0.0035 (7)
C3	0.0645 (9)	0.0586 (9)	0.0762 (11)	−0.0068 (7)	0.0081 (8)	0.0147 (8)
C4	0.0586 (9)	0.0653 (9)	0.0652 (10)	0.0051 (7)	0.0107 (7)	0.0141 (8)
C5	0.0636 (9)	0.0545 (8)	0.0574 (9)	0.0066 (7)	0.0109 (7)	0.0028 (7)
C6	0.0583 (8)	0.0455 (7)	0.0530 (8)	0.0029 (6)	0.0054 (6)	0.0024 (6)
C7	0.0578 (8)	0.0451 (7)	0.0514 (8)	0.0021 (6)	0.0070 (6)	−0.0006 (6)
C8	0.0713 (9)	0.0454 (7)	0.0608 (9)	0.0019 (7)	0.0139 (7)	−0.0093 (7)
C9	0.0726 (10)	0.0404 (7)	0.0656 (10)	−0.0044 (6)	0.0088 (8)	−0.0068 (6)
C10	0.0609 (8)	0.0419 (7)	0.0549 (8)	0.0009 (6)	0.0062 (7)	0.0029 (6)
C11	0.0567 (8)	0.0410 (7)	0.0495 (8)	0.0053 (5)	0.0062 (6)	0.0007 (5)
C12	0.0585 (8)	0.0395 (7)	0.0532 (8)	0.0019 (6)	0.0059 (6)	−0.0004 (6)
C13	0.0664 (9)	0.0450 (7)	0.0635 (9)	−0.0008 (6)	0.0076 (7)	0.0111 (7)
C14	0.0604 (9)	0.0648 (9)	0.0630 (10)	0.0008 (7)	0.0126 (7)	0.0067 (7)
C15	0.0622 (9)	0.0571 (8)	0.0527 (8)	0.0067 (7)	0.0109 (7)	0.0043 (7)
C16	0.0902 (13)	0.0816 (12)	0.0591 (10)	0.0178 (10)	−0.0030 (9)	0.0066 (9)
C17	0.0800 (12)	0.0753 (11)	0.0736 (12)	0.0118 (9)	0.0231 (10)	−0.0075 (9)
C18	0.0736 (12)	0.0920 (14)	0.0956 (15)	0.0030 (10)	0.0295 (11)	0.0134 (11)
N1	0.0692 (8)	0.0410 (6)	0.0644 (8)	−0.0036 (5)	0.0167 (6)	−0.0077 (5)
O1	0.0684 (6)	0.0458 (5)	0.0607 (6)	0.0031 (5)	0.0174 (5)	−0.0034 (4)
O2	0.0984 (10)	0.0509 (6)	0.1084 (11)	−0.0191 (6)	0.0310 (8)	−0.0011 (6)

Geometric parameters (Å, °)

C1—N1	1.377 (2)	C11—C12	1.388 (2)

C1—C2	1.392 (2)	C12—N1	1.3816 (18)
C1—C6	1.411 (2)	C13—O2	1.2254 (19)
C2—C3	1.372 (3)	C13—C14	1.503 (2)
C2—H2	0.930	C14—C15	1.515 (2)
C3—C4	1.407 (3)	C14—H14A	0.970
C3—H3	0.930	C14—H14B	0.970
C4—C5	1.379 (2)	C15—O1	1.4628 (19)
C4—C18	1.502 (3)	C15—C17	1.516 (2)
C5—C6	1.397 (2)	C15—C16	1.525 (2)
C5—H5	0.930	C16—H16A	0.960
C6—C7	1.446 (2)	C16—H16B	0.960
C7—C12	1.401 (2)	C16—H16C	0.960
C7—C8	1.409 (2)	C17—H17A	0.960
C8—C9	1.364 (2)	C17—H17B	0.960
C8—H8	0.930	C17—H17C	0.960
C9—C10	1.415 (2)	C18—H18A	0.960
C9—H9	0.930	C18—H18B	0.960
C10—C11	1.4006 (19)	C18—H18C	0.960
C10—C13	1.457 (2)	N1—H1	0.860
C11—O1	1.3600 (17)		
N1—C1—C2	129.63 (15)	O2—C13—C14	121.16 (16)
N1—C1—C6	109.13 (13)	C10—C13—C14	116.04 (13)
C2—C1—C6	121.18 (16)	C13—C14—C15	114.35 (14)
C3—C2—C1	117.43 (16)	C13—C14—H14A	108.7
C3—C2—H2	121.3	C15—C14—H14A	108.7
C1—C2—H2	121.3	C13—C14—H14B	108.7
C2—C3—C4	123.17 (16)	C15—C14—H14B	108.7
C2—C3—H3	118.4	H14A—C14—H14B	107.6
C4—C3—H3	118.4	O1—C15—C14	108.85 (12)
C5—C4—C3	118.55 (16)	O1—C15—C17	104.62 (13)
C5—C4—C18	121.14 (17)	C14—C15—C17	111.85 (14)
C3—C4—C18	120.31 (17)	O1—C15—C16	107.87 (14)
C4—C5—C6	120.24 (15)	C14—C15—C16	111.86 (14)
C4—C5—H5	119.9	C17—C15—C16	111.43 (15)
C6—C5—H5	119.9	C15—C16—H16A	109.5
C5—C6—C1	119.41 (15)	C15—C16—H16B	109.5
C5—C6—C7	134.19 (14)	H16A—C16—H16B	109.5
C1—C6—C7	106.40 (13)	C15—C16—H16C	109.5
C12—C7—C8	119.66 (14)	H16A—C16—H16C	109.5
C12—C7—C6	106.39 (12)	H16B—C16—H16C	109.5
C8—C7—C6	133.94 (14)	C15—C17—H17A	109.5
C9—C8—C7	118.57 (14)	C15—C17—H17B	109.5
C9—C8—H8	120.7	H17A—C17—H17B	109.5
C7—C8—H8	120.7	C15—C17—H17C	109.5
C8—C9—C10	121.97 (14)	H17A—C17—H17C	109.5
C8—C9—H9	119.0	H17B—C17—H17C	109.5
C10—C9—H9	119.0	C4—C18—H18A	109.5
C11—C10—C9	119.82 (14)	C4—C18—H18B	109.5
C11—C10—C13	118.46 (14)	H18A—C18—H18B	109.5

C9—C10—C13	121.64 (13)	C4—C18—H18C	109.5
O1—C11—C12	117.89 (12)	H18A—C18—H18C	109.5
O1—C11—C10	124.19 (14)	H18B—C18—H18C	109.5
C12—C11—C10	117.92 (13)	C1—N1—C12	108.56 (12)
N1—C12—C11	128.43 (13)	C1—N1—H1	125.7
N1—C12—C7	109.52 (13)	C12—N1—H1	125.7
C11—C12—C7	122.03 (13)	C11—O1—C15	116.44 (11)
O2—C13—C10	122.73 (16)		
N1—C1—C2—C3	−177.57 (15)	O1—C11—C12—N1	−1.0 (2)
C6—C1—C2—C3	−0.7 (2)	C10—C11—C12—N1	179.38 (14)
C1—C2—C3—C4	−0.8 (3)	O1—C11—C12—C7	−178.97 (13)
C2—C3—C4—C5	1.8 (2)	C10—C11—C12—C7	1.4 (2)
C2—C3—C4—C18	−177.69 (17)	C8—C7—C12—N1	−177.97 (13)
C3—C4—C5—C6	−1.3 (2)	C6—C7—C12—N1	0.88 (16)
C18—C4—C5—C6	178.20 (15)	C8—C7—C12—C11	0.4 (2)
C4—C5—C6—C1	−0.1 (2)	C6—C7—C12—C11	179.20 (12)
C4—C5—C6—C7	178.32 (15)	C11—C10—C13—O2	−175.96 (15)
N1—C1—C6—C5	178.62 (13)	C9—C10—C13—O2	0.9 (2)
C2—C1—C6—C5	1.2 (2)	C11—C10—C13—C14	1.0 (2)
N1—C1—C6—C7	−0.24 (16)	C9—C10—C13—C14	177.85 (14)
C2—C1—C6—C7	−177.66 (14)	O2—C13—C14—C15	−155.34 (16)
C5—C6—C7—C12	−178.99 (15)	C10—C13—C14—C15	27.62 (19)
C1—C6—C7—C12	−0.39 (16)	C13—C14—C15—O1	−51.15 (17)
C5—C6—C7—C8	−0.4 (3)	C13—C14—C15—C17	−166.25 (14)
C1—C6—C7—C8	178.22 (16)	C13—C14—C15—C16	67.95 (19)
C12—C7—C8—C9	−1.4 (2)	C2—C1—N1—C12	177.92 (16)
C6—C7—C8—C9	−179.89 (16)	C6—C1—N1—C12	0.78 (17)
C7—C8—C9—C10	0.7 (2)	C11—C12—N1—C1	−179.23 (14)
C8—C9—C10—C11	1.0 (2)	C7—C12—N1—C1	−1.04 (17)
C8—C9—C10—C13	−175.75 (15)	C12—C11—O1—C15	158.45 (12)
C9—C10—C11—O1	178.33 (13)	C10—C11—O1—C15	−21.94 (19)
C13—C10—C11—O1	−4.8 (2)	C14—C15—O1—C11	48.52 (16)
C9—C10—C11—C12	−2.1 (2)	C17—C15—O1—C11	168.22 (13)
C13—C10—C11—C12	174.82 (13)	C16—C15—O1—C11	−73.05 (16)

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2[i]	0.86	2.09	2.8093 (17)	141
C14—H14A···Cg1[ii]	0.97	2.58	3.534 (2)	168
C18—H18B···Cg1[iii]	0.96	3.00	3.881 (2)	153

Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+1/2; (ii) *x*+1, *y*, *z*; (iii) *x*−1, *y*, *z*.

Fig. 1

Fig. 2

Fig. 3