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(5*R*)-5,9,9-Trimethyl-5,6,7,8-tetrahydro-5,8-methanoquinoline: a chiral Mills–Nixon pyrazine¹

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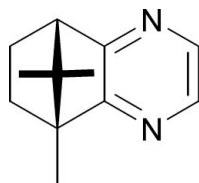
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Key indicators: single-crystal X-ray study; $T = 168$ K; mean $\sigma(\text{C}–\text{C}) = 0.002$ Å; R factor = 0.034; wR factor = 0.092; data-to-parameter ratio = 9.7.

The bond lengths within the pyrazine ring of the title compound, $\text{C}_{12}\text{H}_{16}\text{N}_2$, provide evidence for Mills–Nixon bond localization.

Related literature

For related literature, see: Fitchett & Steel (2000, 2006*b,c*); Northolt & Palm (1966); Stanger (1991); Baldrige & Siegel (1992); Siegel (1994); Steel (1983, 2005); de With *et al.* (1976). For preparation details, see: Elguero & Shimizu (1988); Fitchett & Steel (2006*a*). For discussion of absolute structure, see: Flack & Bernardinelli (1999, 2000).



Experimental

Crystal data

 $\text{C}_{12}\text{H}_{16}\text{N}_2$ $M_r = 188.27$ Orthorhombic, $P2_12_12_1$ $a = 6.7201$ (16) Å $b = 12.069$ (3) Å $c = 12.880$ (3) Å $V = 1044.6$ (4) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.07$ mm⁻¹ $T = 168$ (2) K $0.49 \times 0.48 \times 0.39$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002) $T_{\min} = 0.902$, $T_{\max} = 0.973$

10747 measured reflections

1245 independent reflections

1182 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.025$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.035$ $wR(F^2) = 0.092$ $S = 1.13$

1245 reflections

128 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.14$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.25$ e Å⁻³

Table 1

Selected bond lengths (Å).

N1–C10	1.327 (2)	C3–N4	1.367 (2)
N1–C2	1.361 (2)	N4–C5	1.325 (2)
C2–C3	1.377 (2)	C5–C10	1.413 (2)

Data collection: *SMART* (Bruker 1997); cell refinement: *SAINT* (Bruker 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LW2042).

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¹ Chiral heterocyclic ligands. Part XV.

supplementary materials

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(5*R*)-5,9,9-Trimethyl-5,6,7,8-tetrahydro-5,8-methanoquinoxaline: a chiral Mills-Nixon pyrazine

C. M. Fitchett and P. J. Steel

Comment

We have long been interested in the synthesis and study of chiral heterocyclic ligands derived from the readily available monoterpene (+)-camphor (Steel, 1983; Steel, 2005). More recently, we have reported the preparations of a number of chiral pyrazines derived from (+)-camphor that contain one or two bornane units fused to the sides of a pyrazine ring (Fitchett & Steel, 2000; Fitchett & Steel, 2006*a*; Fitchett & Steel, 2006*b*; Fitchett & Steel, 2006*c*). The title ligand (1) is one such compound that we have shown to form both discrete (Fitchett & Steel, 2006*a*) and polymeric (Fitchett & Steel, 2006*b*) metallosupramolecular assemblies. We were also interested in the possibility that this compound might exhibit the Mills-Nixon effect (Stanger, 1991; Baldrige & Siegel, 1992; Siegel, 1994). This effect refers to bond localization in aromatic systems and is well studied for benzene derivatives, but less so for heterocyclic analogues. One of the best ways to induce this effect is to fuse bridged bicyclic systems to aromatic rings as is the case in (1). We now report the crystal structure of (1).

The molecule crystallizes in the orthorhombic space group $P2_12_12_1$ with a single molecule in the asymmetric unit (Fig. 1). Inspection of the bond lengths within the pyrazine ring (Table 1) shows clear evidence for bond localization. In particular, the internal C—N bonds are significantly shorter than the external ones and the external C—C bond is significantly shorter than the internal one. This suggests that the resonance contributor shown in the schematic is the major contributor to the structure. For comparison the bond lengths for pyrazine itself are 1.388 (1) and 1.333 (1) Å for the C—N and C—C bonds, respectively (de With *et al.*, 1976).

Inspection of the packing shows that there are no short intermolecular contacts between molecules.

Experimental

The title compound was prepared by a literature procedure (Fitchett & Steel, 2006*a*; Elguero & Shimizu, 1988) and was recrystallized from petroleum ether.

Refinement

Due to the structure only containing atoms lighter than Si, no reasonable Flack parameter (Flack & Bernardinelli, 1999 and Flack & Bernardinelli, 2000) was obtained and hence the Freidel pairs were averaged. The absolute configuration was assigned from the known configuration of the precursor (+)-camphor (Northolt & Palm, 1966). All H atoms were introduced in calculated positions as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for other carbons.

Figures

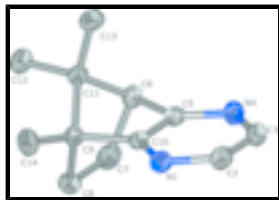


Fig. 1. The molecular structure of (1), showing displacement ellipsoids at the 50% probability level. All H atoms have been omitted for clarity.

(5*R*)-5,9,9-Trimethyl-5,6,7,8-tetrahydro-5,8-methanoquinoxaline

Crystal data

$C_{12}H_{16}N_2$	$F_{000} = 408$
$M_r = 188.27$	$D_x = 1.197 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
Hall symbol: P 2ac 2ab	$\lambda = 0.71073 \text{ \AA}$
$a = 6.7201 (16) \text{ \AA}$	Cell parameters from 7694 reflections
$b = 12.069 (3) \text{ \AA}$	$\theta = 2.3\text{--}26.3^\circ$
$c = 12.880 (3) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$V = 1044.6 (4) \text{ \AA}^3$	$T = 168 (2) \text{ K}$
$Z = 4$	Block, colourless
	$0.49 \times 0.48 \times 0.39 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	1245 independent reflections
Radiation source: fine-focus sealed tube	1182 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.025$
$T = 168(2) \text{ K}$	$\theta_{\text{max}} = 26.3^\circ$
phi and ω scans	$\theta_{\text{min}} = 2.3^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	$h = -8 \rightarrow 6$
$T_{\text{min}} = 0.902$, $T_{\text{max}} = 0.973$	$k = -14 \rightarrow 15$
10747 measured reflections	$l = -15 \rightarrow 16$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 0.1417P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.092$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.13$	$\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
1245 reflections	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$
128 parameters	Extinction correction: none
	Absolute structure: Friedel pairs merged

Primary atom site location: structure-invariant direct methods Flack parameter: ?

Secondary atom site location: difference Fourier map Rogers parameter: ?

Hydrogen site location: inferred from neighbouring sites

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.3716 (2)	0.21301 (11)	0.38303 (10)	0.0252 (3)
C2	0.5047 (3)	0.19406 (13)	0.46067 (12)	0.0277 (4)
H2A	0.5083	0.2442	0.5175	0.033*
C3	0.6345 (3)	0.10575 (14)	0.46071 (13)	0.0294 (4)
H3A	0.7228	0.0979	0.5178	0.035*
N4	0.6431 (2)	0.02876 (11)	0.38304 (11)	0.0284 (3)
C5	0.5156 (2)	0.04882 (12)	0.30684 (12)	0.0226 (3)
C6	0.4787 (3)	-0.01425 (13)	0.20715 (12)	0.0244 (4)
H6A	0.5889	-0.0639	0.1835	0.029*
C7	0.2718 (3)	-0.07056 (14)	0.22311 (14)	0.0306 (4)
H7A	0.2414	-0.1225	0.1657	0.037*
H7B	0.2667	-0.1112	0.2898	0.037*
C8	0.1253 (2)	0.02917 (14)	0.22333 (13)	0.0285 (4)
H8A	0.0527	0.0336	0.2901	0.034*
H8B	0.0275	0.0224	0.1662	0.034*
C9	0.2605 (2)	0.13326 (12)	0.20758 (11)	0.0221 (4)
C10	0.3819 (2)	0.13925 (12)	0.30680 (11)	0.0211 (3)
C11	0.4257 (2)	0.08475 (12)	0.13282 (12)	0.0226 (3)
C12	0.3468 (3)	0.04913 (15)	0.02580 (13)	0.0318 (4)
H12A	0.4568	0.0200	-0.0160	0.048*
H12B	0.2879	0.1132	-0.0094	0.048*
H12C	0.2455	-0.0085	0.0347	0.048*
C13	0.6004 (3)	0.16434 (15)	0.11496 (13)	0.0314 (4)
H13A	0.6973	0.1297	0.0683	0.047*
H13B	0.6644	0.1811	0.1815	0.047*
H13C	0.5512	0.2331	0.0837	0.047*
C14	0.1535 (3)	0.23901 (14)	0.17711 (14)	0.0328 (4)
H14A	0.0562	0.2583	0.2308	0.049*

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H14B	0.0848	0.2279	0.1108	0.049*
H14C	0.2504	0.2992	0.1700	0.049*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0277 (7)	0.0248 (6)	0.0231 (6)	0.0003 (6)	0.0018 (6)	-0.0022 (5)
C2	0.0321 (9)	0.0299 (8)	0.0211 (7)	-0.0044 (7)	-0.0015 (7)	-0.0047 (6)
C3	0.0282 (8)	0.0368 (9)	0.0232 (8)	-0.0037 (8)	-0.0037 (7)	0.0016 (7)
N4	0.0276 (7)	0.0312 (7)	0.0264 (7)	0.0030 (6)	-0.0033 (6)	0.0020 (6)
C5	0.0241 (7)	0.0225 (7)	0.0213 (7)	-0.0004 (6)	0.0021 (7)	0.0010 (6)
C6	0.0278 (8)	0.0226 (7)	0.0227 (7)	0.0035 (7)	-0.0013 (7)	-0.0015 (6)
C7	0.0397 (10)	0.0232 (7)	0.0288 (8)	-0.0073 (8)	-0.0017 (8)	0.0007 (6)
C8	0.0235 (8)	0.0335 (9)	0.0285 (8)	-0.0064 (8)	-0.0009 (7)	-0.0002 (7)
C9	0.0221 (7)	0.0233 (8)	0.0209 (7)	-0.0002 (7)	-0.0013 (7)	0.0000 (6)
C10	0.0206 (7)	0.0223 (7)	0.0202 (7)	-0.0017 (6)	0.0023 (6)	0.0017 (6)
C11	0.0244 (8)	0.0230 (7)	0.0204 (7)	-0.0013 (6)	0.0004 (7)	-0.0008 (6)
C12	0.0360 (9)	0.0374 (9)	0.0219 (8)	-0.0005 (8)	-0.0032 (7)	-0.0013 (7)
C13	0.0308 (9)	0.0367 (9)	0.0265 (8)	-0.0073 (8)	0.0037 (8)	0.0017 (7)
C14	0.0342 (9)	0.0315 (9)	0.0327 (8)	0.0089 (8)	-0.0064 (8)	0.0011 (7)

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

N1—C10	1.327 (2)	C8—H8A	0.9900
N1—C2	1.361 (2)	C8—H8B	0.9900
C2—C3	1.377 (2)	C9—C14	1.516 (2)
C2—H2A	0.9500	C9—C10	1.518 (2)
C3—N4	1.367 (2)	C9—C11	1.582 (2)
C3—H3A	0.9500	C11—C13	1.535 (2)
N4—C5	1.325 (2)	C11—C12	1.538 (2)
C5—C10	1.413 (2)	C12—H12A	0.9800
C5—C6	1.513 (2)	C12—H12B	0.9800
C6—C7	1.561 (2)	C12—H12C	0.9800
C6—C11	1.572 (2)	C13—H13A	0.9800
C6—H6A	1.0000	C13—H13B	0.9800
C7—C8	1.555 (2)	C13—H13C	0.9800
C7—H7A	0.9900	C14—H14A	0.9800
C7—H7B	0.9900	C14—H14B	0.9800
C8—C9	1.564 (2)	C14—H14C	0.9800
C10—N1—C2	113.35 (14)	C10—C9—C8	103.97 (12)
N1—C2—C3	123.13 (15)	C14—C9—C11	119.12 (13)
N1—C2—H2A	118.4	C10—C9—C11	98.80 (12)
C3—C2—H2A	118.4	C8—C9—C11	100.92 (12)
N4—C3—C2	123.56 (15)	N1—C10—C5	123.43 (14)
N4—C3—H3A	118.2	N1—C10—C9	128.80 (14)
C2—C3—H3A	118.2	C5—C10—C9	107.76 (13)
C5—N4—C3	113.00 (14)	C13—C11—C12	107.72 (13)
N4—C5—C10	123.52 (14)	C13—C11—C6	113.18 (13)

N4—C5—C6	129.98 (14)	C12—C11—C6	114.30 (13)
C10—C5—C6	106.50 (13)	C13—C11—C9	113.37 (13)
C5—C6—C7	104.66 (13)	C12—C11—C9	114.03 (13)
C5—C6—C11	99.88 (12)	C6—C11—C9	94.00 (12)
C7—C6—C11	102.07 (12)	C11—C12—H12A	109.5
C5—C6—H6A	116.0	C11—C12—H12B	109.5
C7—C6—H6A	116.0	H12A—C12—H12B	109.5
C11—C6—H6A	116.0	C11—C12—H12C	109.5
C8—C7—C6	103.14 (13)	H12A—C12—H12C	109.5
C8—C7—H7A	111.1	H12B—C12—H12C	109.5
C6—C7—H7A	111.1	C11—C13—H13A	109.5
C8—C7—H7B	111.1	C11—C13—H13B	109.5
C6—C7—H7B	111.1	H13A—C13—H13B	109.5
H7A—C7—H7B	109.1	C11—C13—H13C	109.5
C7—C8—C9	104.68 (12)	H13A—C13—H13C	109.5
C7—C8—H8A	110.8	H13B—C13—H13C	109.5
C9—C8—H8A	110.8	C9—C14—H14A	109.5
C7—C8—H8B	110.8	C9—C14—H14B	109.5
C9—C8—H8B	110.8	H14A—C14—H14B	109.5
H8A—C8—H8B	108.9	C9—C14—H14C	109.5
C14—C9—C10	115.63 (13)	H14A—C14—H14C	109.5
C14—C9—C8	115.73 (14)	H14B—C14—H14C	109.5
C10—N1—C2—C3	-1.2 (2)	C14—C9—C10—N1	17.8 (2)
N1—C2—C3—N4	0.2 (3)	C8—C9—C10—N1	-110.20 (17)
C2—C3—N4—C5	1.0 (2)	C11—C9—C10—N1	146.14 (16)
C3—N4—C5—C10	-1.1 (2)	C14—C9—C10—C5	-162.58 (14)
C3—N4—C5—C6	179.32 (15)	C8—C9—C10—C5	69.43 (15)
N4—C5—C6—C7	108.58 (18)	C11—C9—C10—C5	-34.23 (14)
C10—C5—C6—C7	-71.02 (15)	C5—C6—C11—C13	65.16 (16)
N4—C5—C6—C11	-146.06 (16)	C7—C6—C11—C13	172.61 (13)
C10—C5—C6—C11	34.34 (15)	C5—C6—C11—C12	-171.03 (13)
C5—C6—C7—C8	68.53 (14)	C7—C6—C11—C12	-63.58 (17)
C11—C6—C7—C8	-35.19 (15)	C5—C6—C11—C9	-52.38 (13)
C6—C7—C8—C9	-0.01 (15)	C7—C6—C11—C9	55.07 (13)
C7—C8—C9—C14	164.82 (14)	C14—C9—C11—C13	60.42 (19)
C7—C8—C9—C10	-67.24 (15)	C10—C9—C11—C13	-65.54 (15)
C7—C8—C9—C11	34.80 (15)	C8—C9—C11—C13	-171.73 (13)
C2—N1—C10—C5	1.0 (2)	C14—C9—C11—C12	-63.32 (18)
C2—N1—C10—C9	-179.43 (14)	C10—C9—C11—C12	170.71 (13)
N4—C5—C10—N1	0.2 (2)	C8—C9—C11—C12	64.53 (15)
C6—C5—C10—N1	179.81 (14)	C14—C9—C11—C6	177.81 (14)
N4—C5—C10—C9	-179.48 (14)	C10—C9—C11—C6	51.84 (12)
C6—C5—C10—C9	0.15 (16)	C8—C9—C11—C6	-54.34 (13)

Fig. 1

