organic compounds

2,3,3-Trimethyl-1-[4-(2,3,3-trimethyl-3H-indol-1-ium-1-yl)butyl]-3H-indol-1-ium diiodide

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In the crystal of the title salt, $C_{26}H_{34}N_2^{2+}\cdot2I^-$, the dication lies on a center of inversion that exists along the mid-point of the butyl chain; its five-membered ring is approximately planar (r.m.s. deviation = 0.011 Å). In the crystal, the iodide anion is disordered over two positions in a 1:1 ratio.

Related literature

For the synthesis, see: Yang et al. (2005). For industrial applications of Mannich products, see: Su et al. (2005).
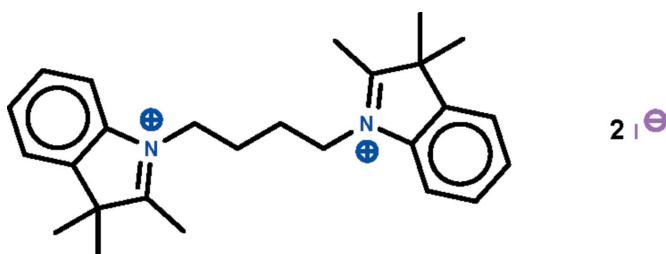
Experimental

Crystal data

$C_{26}H_{34}N_2^{2+}\cdot2I^-$	$V = 1348.6$ (2) Å^3
$M_r = 628.35$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 13.9414$ (14) Å	$\mu = 2.35$ mm^{-1}
$b = 7.6013$ (8) Å	$T = 293$ K
$c = 13.8261$ (15) Å	$0.35 \times 0.30 \times 0.25$ mm
$\beta = 113.011$ (2)°	

Data collection

Bruker SMART APEX diffractometer	8426 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3077 independent reflections
	2602 reflections with $I > 2\sigma(I)$
$T_{min} = 0.494$, $T_{max} = 0.592$	$R_{int} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	146 parameters
$wR(F^2) = 0.087$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{max} = 0.94$ e Å^{-3}
3077 reflections	$\Delta\rho_{min} = -0.37$ e Å^{-3}

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: publCIF (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5603).

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supplementary materials

2,3,3-Trimethyl-1-[4-(2,3,3-trimethyl-3*H*-indol-1-ium-1-yl)butyl]-3*H*-indol-1-ium diiodide

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Comment

The salt (Scheme I) can be synthesized in several steps from benzohydrazine, methyl isopropyl ketone and 1,4-diiodo-butane, and is an intermediate in the synthesis of a bis-spironaphthoxazine (Yang *et al.*, 2005). It is available commercially in milligram quantities. The methyl group on the carbon atom adjacent to the quarternary nitrogen is acidic, and the methyl group undergoes a Mannich-type of reaction to yield compounds that have been patented for use as high-density recording media (Su *et al.*, 2005).

In the salt, $C_{26}H_{34}N_2^+$ 2I⁻, the dicationic species lies on a center-of-inversion that exists along the mid-point of the butyl chain; its five-membered ring is planar (r.m.s. deviation 0.011 Å). The iodide anion is disordered over two positions in a 1:1 ratio (Fig. 1).

Experimental

3,3-Dimethyl-3*H*-indole (40 mmol, 5.81 g), 1,4-dibromobutane (20 mmol, 4.32 g) and potassium iodide (50 mmol, 8.310) were added to acetonitrile (40 ml). The mixture was heated under reflux for 4 days. The mixture was collected and the yellow solid recrystallized from a methanol-ether mixture; yield 40%. The salt is soluble in most organic solvents.

Refinement

Carbon-, nitrogen- and oxygen-bound H-atoms were placed in calculated positions (C–H 0.93 to 0.97, N–H 0.88, O–H 0.84 Å) and were included in the refinement in the riding model approximation, with U(H) set to 1.2 to $1.5U$(C,*N*,*O*).

The iodine atom is disordered over two positions; as the disorder refined to a nearly 1:1 ratio, the occupancy was then fixed as exactly 0.5.

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).
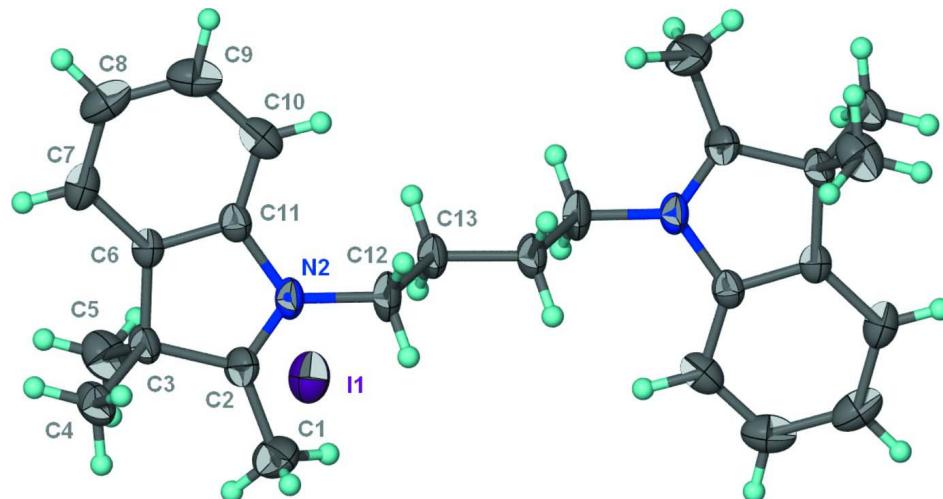
Figure 1

Thermal ellipsoid plot (Barbour, 2001) of $C_{26}H_{34}N_2{}^{2+}$ $2I^-$ at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. The disorder in the iodine atom is not shown.

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Crystal data
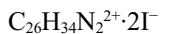
$C_{26}H_{34}N_2{}^{2+}\cdot2I^-$	$F(000) = 620$
$M_r = 628.35$	$D_x = 1.547$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 3950 reflections
$a = 13.9414$ (14) Å	$\theta = 3.0$–$28.3°$
$b = 7.6013$ (8) Å	$\mu = 2.35$ mm^{-1}
$c = 13.8261$ (15) Å	$T = 293$ K
$\beta = 113.011$ (2)°	Prism, colorless
$V = 1348.6$ (2) Å^3	$0.35 \times 0.30 \times 0.25$ mm
$Z = 2$	

Data collection

Bruker SMART APEX diffractometer	8426 measured reflections
Radiation source: fine-focus sealed tube	3077 independent reflections
Graphite monochromator	2602 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.017$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
$T_{min} = 0.494$, $T_{max} = 0.592$	$h = -13 \rightarrow 17$
	$k = -8 \rightarrow 9$
	$l = -17 \rightarrow 14$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.027$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.087$	
$S = 1.04$	Hydrogen site location: inferred from neighbouring sites
3077 reflections	
146 parameters	H-atom parameters constrained
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.3658P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.94$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
I1	0.3111 (2)	0.6289 (3)	0.77695 (19)	0.0536 (2)	0.50
I1′	0.3220 (2)	0.6038 (3)	0.7930 (2)	0.0800 (6)	0.50
N2	0.31190 (14)	0.3641 (2)	0.55053 (14)	0.0382 (4)	
C1	0.3943 (2)	0.1407 (5)	0.6859 (3)	0.0789 (11)	
H1A	0.3772	0.0208	0.6943	0.118*	
H1B	0.4081	0.2039	0.7501	0.118*	
H1C	0.4550	0.1435	0.6693	0.118*	
C2	0.30596 (17)	0.2235 (3)	0.59984 (18)	0.0437 (5)	
C3	0.19566 (18)	0.1564 (3)	0.56180 (19)	0.0398 (5)	
C4	0.1613 (2)	0.1429 (3)	0.6543 (2)	0.0514 (6)	
H4A	0.1669	0.2562	0.6867	0.077*	
H4B	0.2051	0.0604	0.7049	0.077*	
H4C	0.0902	0.1035	0.6292	0.077*	
C5	0.1875 (3)	−0.0238 (4)	0.5086 (2)	0.0621 (7)	
H5A	0.2092	−0.0131	0.4510	0.093*	
H5B	0.1166	−0.0640	0.4830	0.093*	
H5C	0.2316	−0.1067	0.5586	0.093*	
C6	0.13926 (16)	0.2961 (3)	0.48332 (16)	0.0358 (4)	
C7	0.03506 (19)	0.3190 (3)	0.4208 (2)	0.0484 (5)	
H7	−0.0147	0.2402	0.4239	0.058*	
C8	0.0064 (2)	0.4603 (4)	0.3539 (2)	0.0585 (7)	
H8	−0.0635	0.4773	0.3112	0.070*	
C9	0.0803 (3)	0.5787 (4)	0.3488 (2)	0.0585 (7)	
H9	0.0590	0.6731	0.3025	0.070*	
C10	0.1846 (2)	0.5586 (3)	0.41111 (19)	0.0475 (5)	
H10	0.2345	0.6375	0.4084	0.057*	
C11	0.21086 (17)	0.4165 (3)	0.47728 (16)	0.0352 (4)	
C12	0.40689 (18)	0.4695 (4)	0.56978 (19)	0.0491 (6)	
H12	0.4593	0.4384	0.6380	0.059*	
H12B	0.3904	0.5931	0.5719	0.059*	
C13	0.45182 (18)	0.4435 (3)	0.48771 (18)	0.0435 (5)	
H13	0.4001	0.4747	0.4191	0.052*	
H13B	0.4699	0.3206	0.4858	0.052*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0481 (5)	0.0585 (3)	0.0626 (3)	−0.0023 (3)	0.0307 (3)	−0.0126 (3)
I1′	0.0531 (7)	0.0987 (14)	0.1030 (14)	−0.0154 (8)	0.0466 (9)	−0.0430 (8)
N2	0.0294 (9)	0.0511 (10)	0.0395 (9)	−0.0101 (7)	0.0193 (7)	−0.0044 (7)
C1	0.0413 (16)	0.107 (3)	0.083 (2)	0.0150 (15)	0.0190 (15)	0.0413 (18)
C2	0.0320 (11)	0.0575 (14)	0.0466 (12)	0.0011 (9)	0.0206 (9)	0.0075 (10)
C3	0.0342 (11)	0.0396 (11)	0.0514 (12)	−0.0026 (8)	0.0230 (9)	0.0066 (9)

C4	0.0516 (15)	0.0559 (14)	0.0590 (15)	−0.0019 (11)	0.0348 (12)	0.0082 (11)
C5	0.0748 (19)	0.0467 (14)	0.0763 (19)	0.0018 (13)	0.0420 (16)	−0.0007 (13)
C6	0.0317 (10)	0.0376 (10)	0.0406 (10)	−0.0031 (8)	0.0168 (8)	−0.0027 (8)
C7	0.0343 (12)	0.0543 (13)	0.0556 (14)	−0.0054 (10)	0.0166 (10)	−0.0083 (11)
C8	0.0460 (15)	0.0679 (17)	0.0498 (14)	0.0172 (13)	0.0058 (11)	−0.0049 (12)
C9	0.075 (2)	0.0531 (14)	0.0478 (14)	0.0189 (13)	0.0246 (13)	0.0090 (11)
C10	0.0623 (15)	0.0396 (11)	0.0493 (12)	−0.0011 (11)	0.0313 (11)	0.0025 (10)
C11	0.0354 (11)	0.0383 (10)	0.0365 (10)	−0.0052 (8)	0.0191 (8)	−0.0036 (8)
C12	0.0368 (12)	0.0683 (16)	0.0487 (12)	−0.0237 (11)	0.0237 (10)	−0.0136 (11)
C13	0.0343 (11)	0.0568 (13)	0.0459 (12)	−0.0135 (10)	0.0226 (9)	−0.0053 (10)

Geometric parameters (Å, º)

N2—C2	1.287 (3)	C6—C11	1.381 (3)
N2—C11	1.433 (3)	C6—C7	1.381 (3)
N2—C12	1.480 (3)	C7—C8	1.371 (4)
C1—C2	1.478 (4)	C7—H7	0.9300
C1—H1A	0.9600	C8—C9	1.390 (4)
C1—H1B	0.9600	C8—H8	0.9300
C1—H1C	0.9600	C9—C10	1.378 (4)
C2—C3	1.507 (3)	C9—H9	0.9300
C3—C6	1.502 (3)	C10—C11	1.370 (3)
C3—C4	1.535 (3)	C10—H10	0.9300
C3—C5	1.538 (4)	C12—C13	1.508 (3)
C4—H4A	0.9600	C12—H12	0.9700
C4—H4B	0.9600	C12—H12B	0.9700
C4—H4C	0.9600	C13—C13[i]	1.517 (4)
C5—H5A	0.9600	C13—H13	0.9700
C5—H5B	0.9600	C13—H13B	0.9700
C5—H5C	0.9600		
C2—N2—C11	110.85 (18)	C11—C6—C7	119.1 (2)
C2—N2—C12	126.3 (2)	C11—C6—C3	109.00 (19)
C11—N2—C12	122.67 (19)	C7—C6—C3	131.9 (2)
C2—C1—H1A	109.5	C8—C7—C6	118.6 (2)
C2—C1—H1B	109.5	C8—C7—H7	120.7
H1A—C1—H1B	109.5	C6—C7—H7	120.7
C2—C1—H1C	109.5	C7—C8—C9	121.0 (2)
H1A—C1—H1C	109.5	C7—C8—H8	119.5
H1B—C1—H1C	109.5	C9—C8—H8	119.5
N2—C2—C1	125.0 (2)	C10—C9—C8	121.2 (2)
N2—C2—C3	111.39 (19)	C10—C9—H9	119.4
C1—C2—C3	123.5 (2)	C8—C9—H9	119.4
C6—C3—C2	100.79 (17)	C11—C10—C9	116.5 (2)
C6—C3—C4	113.8 (2)	C11—C10—H10	121.8
C2—C3—C4	109.9 (2)	C9—C10—H10	121.8
C6—C3—C5	111.4 (2)	C10—C11—C6	123.5 (2)
C2—C3—C5	110.1 (2)	C10—C11—N2	128.6 (2)
C4—C3—C5	110.5 (2)	C6—C11—N2	107.90 (18)
C3—C4—H4A	109.5	N2—C12—C13	113.52 (18)

C3—C4—H4B	109.5	N2—C12—H12	108.9
H4A—C4—H4B	109.5	C13—C12—H12	108.9
C3—C4—H4C	109.5	N2—C12—H12B	108.9
H4A—C4—H4C	109.5	C13—C12—H12B	108.9
H4B—C4—H4C	109.5	H12—C12—H12B	107.7
C3—C5—H5A	109.5	C12—C13—C13ⁱ	110.4 (2)
C3—C5—H5B	109.5	C12—C13—H13	109.6
H5A—C5—H5B	109.5	C13ⁱ—C13—H13	109.6
C3—C5—H5C	109.5	C12—C13—H13B	109.6
H5A—C5—H5C	109.5	C13ⁱ—C13—H13B	109.6
H5B—C5—H5C	109.5	H13—C13—H13B	108.1
C11—N2—C2—C1	−175.6 (3)	C3—C6—C7—C8	−178.7 (2)
C12—N2—C2—C1	−0.1 (4)	C6—C7—C8—C9	−0.1 (4)
C11—N2—C2—C3	2.1 (3)	C7—C8—C9—C10	−0.4 (4)
C12—N2—C2—C3	177.6 (2)	C8—C9—C10—C11	0.2 (4)
N2—C2—C3—C6	−2.7 (3)	C9—C10—C11—C6	0.3 (4)
C1—C2—C3—C6	175.0 (3)	C9—C10—C11—N2	−179.6 (2)
N2—C2—C3—C4	−123.1 (2)	C7—C6—C11—C10	−0.7 (3)
C1—C2—C3—C4	54.6 (3)	C3—C6—C11—C10	178.7 (2)
N2—C2—C3—C5	114.9 (2)	C7—C6—C11—N2	179.17 (19)
C1—C2—C3—C5	−67.3 (3)	C3—C6—C11—N2	−1.4 (2)
C2—C3—C6—C11	2.4 (2)	C2—N2—C11—C10	179.5 (2)
C4—C3—C6—C11	120.0 (2)	C12—N2—C11—C10	3.7 (3)
C5—C3—C6—C11	−114.4 (2)	C2—N2—C11—C6	−0.4 (3)
C2—C3—C6—C7	−178.3 (2)	C12—N2—C11—C6	−176.17 (19)
C4—C3—C6—C7	−60.7 (3)	C2—N2—C12—C13	104.5 (3)
C5—C3—C6—C7	65.0 (3)	C11—N2—C12—C13	−80.5 (3)
C11—C6—C7—C8	0.6 (4)	N2—C12—C13—C13ⁱ	179.6 (3)

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