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1,3,6-Tribromo-9-ethyl-9*H*-carbazole

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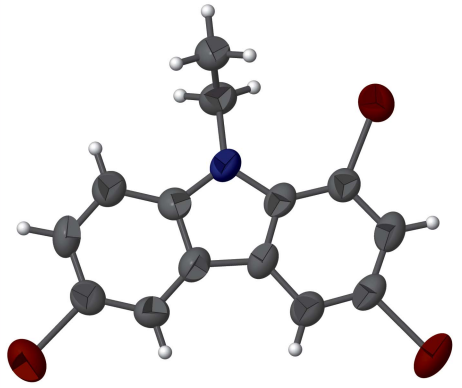
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{14}H_{10}Br_3N$, the carbazole ring system is almost planar, with an r.m.s. deviation of 0.023 Å from the best fit mean plane of the 13 non-H atoms of the three rings. The methyl C atom lies 1.232 (3) Å out of this plane. No hydrogen bonds are found in the crystal structure but weak C—Br$\cdots\pi$ contacts at approximately 3.721 Å may stabilize the structure.

3D view



Chemical scheme

Structure description

N-substituted carbazole derivatives are important in cancer research (Caulfield *et al.*, 2002) and as materials for opto-electronic devices (Niu *et al.*, 2011; Miyazaki *et al.*, 2014; Grigalevicius *et al.*, 2003). The crystal structures of 3-bromo- and 1,3,6,8-tetrabromo-9-ethyl-*9H*-carbazole have been described previously (Bezuglyi *et al.*, 2015*a*,*b*). We report here the structure of the title tri-bromocarbazole derivative (Fig. 1).

The tricyclic carbazole ring system is almost planar with an r.m.s. deviation of 0.023 Å from the best-fit plane through its 13 non-hydrogen atoms. C13 and C14 deviate from the carbazole ring plane by 0.111 (2) and 1.232 (3) Å, respectively, while the best fit plane through N1/C13/C14 is inclined to the carbazole ring plane by 86.97 (7)°.

In the crystal there are no significant hydrogen bonds but Br$\cdots\pi$ contacts between Br3 and the mid-point of the C5—C6 bond of the C1–C6 ring are found. These are close to the Br$\cdots$C van der Waals contact distance of 3.70 Å. The packing is illustrated in Fig. 2.

Synthesis and crystallization

Ethylcarbazole was brominated with *N*-bromosuccinimide in dichloromethane in the presence of silica by a procedure described by Smith *et al.* (1992). The crude product was purified by column chromatography (silica, eluent hexane) to isolate the product as white needle-like crystals. Yield 90%, m.p. 146–148°C.

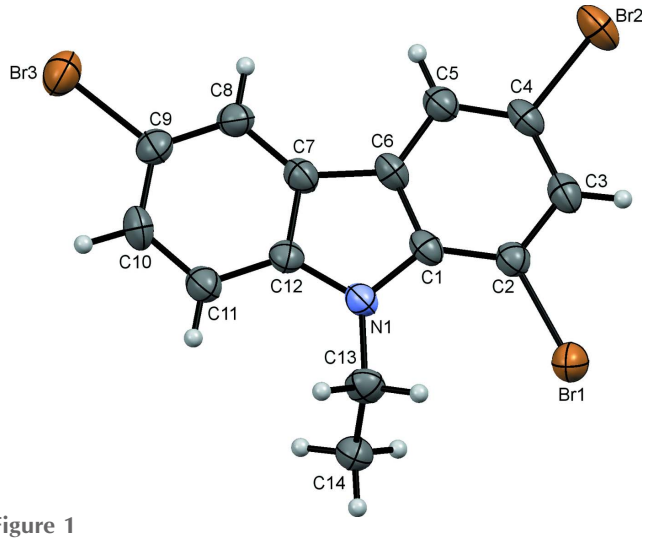


Figure 1
The molecular structure of the title molecule with displacement ellipsoids drawn at the 50% probability level.

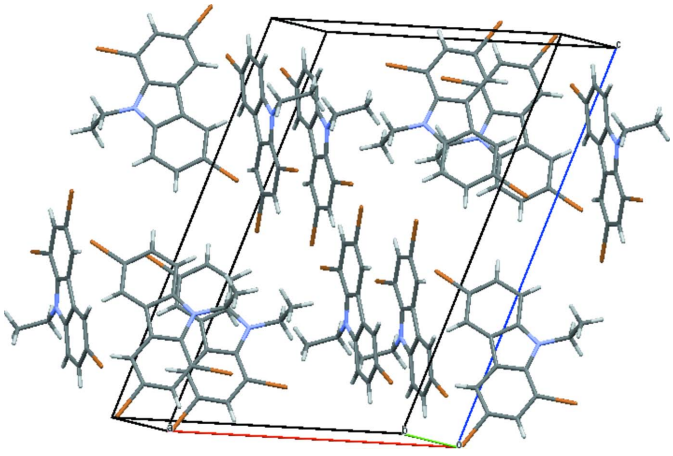


Figure 2
The crystal packing of the title compound viewed along the *b*-axis direction.

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.01 (*d*, *J* = 1.8 Hz, 1H) 7.97 (*d*, *J* = 1.8 Hz, 1H), 7.65 (*d*, *J* = 1.8 Hz, 1H), 7.51 (*dd*, *J* = 8.7, 1.9 Hz, 1H), 7.22 (*d*, *J* = 8.7 Hz, 1H), 4.65 (*q*, *J* = 7.2 Hz, 2H), 1.35 (*t*, *J* = 7.2 Hz, 3H).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Acknowledgements

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Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{10}Br_3N$
M_r	431.95
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	273
a, *b*, *c* (Å)	17.17 (6), 4.267 (13), 20.22 (6)
β (°)	108.45 (4)
V (Å^3)	1405 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	8.62
Crystal size (mm)	0.19 × 0.12 × 0.06
Data collection	
Diffractometer	Rigaku XtaLAB mini
Absorption correction	Multi-scan (*REQAB*; Rigaku, 1998)
T_{min}, T_{max}	0.258, 0.596
No. of measured, independent and observed [$F^2 > 2.0\sigma(F^2)$] reflections	11828, 3226, 1894
R_{int}	0.075
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.652
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.084, 0.249, 1.09
No. of reflections	3226
No. of parameters	163
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.65, −1.14

Computer programs: *CrystalClear-SM Expert* (Rigaku, 2011), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008) and *CrystalStructure* (Rigaku, 2010).

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full crystallographic data

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Crystal data

$C_{14}H_{10}Br_3N$
M_r = 431.95
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 17.17 (6) Å
b = 4.267 (13) Å
c = 20.22 (6) Å
β = 108.45 (4)°
V = 1405 (7) Å^3
Z = 4
$F(000)$ = 824.00
D_x = 2.042 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 2508 reflections
θ = 3.0–27.5°
μ = 8.62 mm^{-1}
T = 273 K
Prism, colorless
0.19 × 0.12 × 0.06 mm

Data collection

Rigaku XtaLAB mini diffractometer
Detector resolution: 13.653 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*REQAB*; Rigaku, 1998)
T_{min} = 0.258, T_{max} = 0.596
11828 measured reflections
3226 independent reflections
1894 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.075
θ_{max} = 27.6°
h = −22→22
k = −5→5
l = −26→26

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.084
$wR(F^2)$ = 0.249
S = 1.09
3226 reflections
163 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.125P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.65 e Å^{-3}
$\Delta\rho_{min}$ = −1.14 e Å^{-3}

Special details

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0$ sigma(F^2) is used only for calculating R-factor (gt).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.46805 (6)	0.1221 (3)	0.39247 (5)	0.0742 (4)
Br2	0.28015 (8)	0.7910 (3)	0.52805 (5)	0.0877 (5)
Br3	−0.04827 (6)	0.7559 (3)	0.10482 (6)	0.0872 (5)
N1	0.2882 (4)	0.2353 (15)	0.2548 (4)	0.0548 (16)
C1	0.3000 (5)	0.3408 (18)	0.3221 (4)	0.0531 (18)
C2	0.3653 (5)	0.3157 (19)	0.3841 (4)	0.0548 (18)
C3	0.3591 (6)	0.448 (2)	0.4461 (4)	0.063 (2)
C4	0.2875 (6)	0.6122 (19)	0.4423 (4)	0.061 (2)
C5	0.2229 (6)	0.655 (2)	0.3825 (5)	0.061 (2)
C6	0.2314 (5)	0.5147 (18)	0.3219 (4)	0.0548 (18)
C7	0.1732 (5)	0.5137 (19)	0.2516 (4)	0.0577 (19)
C8	0.0957 (5)	0.641 (2)	0.2208 (5)	0.061 (2)
C9	0.0579 (5)	0.589 (2)	0.1500 (5)	0.063 (2)
C10	0.0965 (6)	0.416 (2)	0.1098 (5)	0.066 (3)
C11	0.1739 (6)	0.287 (2)	0.1401 (5)	0.065 (2)
C12	0.2124 (5)	0.3377 (18)	0.2128 (4)	0.0522 (17)
C13	0.3414 (6)	0.0232 (19)	0.2280 (5)	0.062 (2)
C14	0.3969 (6)	0.204 (2)	0.1982 (5)	0.065 (3)
H8	0.0698	0.3881	0.0624	0.0790*
H9A	0.3743	−0.1074	0.2658	0.0742*
H9B	0.3068	−0.1133	0.1923	0.0742*
H13	0.1766	0.7696	0.3819	0.0737*
H14	0.4013	0.4273	0.4881	0.0761*
H15	0.0699	0.7573	0.2468	0.0728*
H20	0.1996	0.1720	0.1139	0.0774*
H21A	0.4300	0.0607	0.1819	0.0782*
H21B	0.4318	0.3369	0.2335	0.0782*
H21C	0.3646	0.3294	0.1600	0.0782*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0664 (7)	0.0917 (9)	0.0627 (7)	0.0080 (5)	0.0178 (5)	0.0103 (4)
Br2	0.1242 (10)	0.0949 (9)	0.0498 (6)	−0.0041 (6)	0.0361 (6)	−0.0109 (5)
Br3	0.0636 (7)	0.1003 (10)	0.0863 (9)	0.0060 (5)	0.0075 (6)	0.0070 (6)
N1	0.058 (4)	0.067 (5)	0.042 (4)	−0.003 (3)	0.019 (3)	−0.004 (3)
C1	0.065 (5)	0.055 (5)	0.043 (4)	−0.010 (4)	0.023 (4)	0.001 (3)
C2	0.057 (5)	0.060 (5)	0.050 (5)	−0.003 (4)	0.019 (4)	0.002 (4)
C3	0.074 (6)	0.072 (6)	0.043 (5)	−0.014 (4)	0.016 (4)	−0.001 (4)
C4	0.080 (6)	0.066 (6)	0.043 (5)	−0.008 (4)	0.029 (4)	−0.001 (4)
C5	0.065 (6)	0.070 (6)	0.052 (5)	−0.006 (4)	0.023 (4)	−0.003 (4)
C6	0.071 (5)	0.055 (5)	0.040 (4)	−0.003 (4)	0.019 (4)	−0.004 (3)
C7	0.064 (5)	0.064 (5)	0.046 (5)	−0.005 (4)	0.019 (4)	−0.007 (4)
C8	0.052 (5)	0.069 (6)	0.063 (6)	0.000 (4)	0.022 (4)	−0.008 (4)
C9	0.051 (5)	0.072 (6)	0.065 (6)	−0.007 (4)	0.018 (4)	−0.001 (4)

C10	0.071 (6)	0.073 (6)	0.041 (5)	−0.005 (4)	0.002 (4)	−0.003 (4)
C11	0.062 (6)	0.078 (6)	0.054 (5)	−0.007 (4)	0.021 (4)	−0.002 (4)
C12	0.051 (5)	0.058 (5)	0.051 (5)	−0.005 (4)	0.021 (4)	0.006 (4)
C13	0.068 (6)	0.054 (5)	0.067 (6)	0.006 (4)	0.026 (4)	−0.011 (4)
C14	0.061 (6)	0.081 (7)	0.057 (6)	0.000 (4)	0.024 (4)	0.003 (4)

Geometric parameters (Å, º)

Br1—C2	1.907 (10)	C8—C9	1.389 (13)
Br2—C4	1.934 (10)	C9—C10	1.411 (15)
Br3—C9	1.900 (9)	C10—C11	1.389 (13)
N1—C1	1.386 (11)	C11—C12	1.424 (12)
N1—C12	1.381 (10)	C13—C14	1.492 (15)
N1—C13	1.504 (13)	C3—H14	0.930
C1—C2	1.396 (10)	C5—H13	0.930
C1—C6	1.392 (13)	C8—H15	0.930
C2—C3	1.410 (13)	C10—H8	0.930
C3—C4	1.394 (14)	C11—H20	0.930
C4—C5	1.370 (11)	C13—H9A	0.970
C5—C6	1.413 (13)	C13—H9B	0.970
C6—C7	1.456 (10)	C14—H21A	0.960
C7—C8	1.388 (12)	C14—H21B	0.960
C7—C12	1.403 (13)	C14—H21C	0.960
C1—N1—C12	108.6 (7)	N1—C12—C7	110.5 (7)
C1—N1—C13	129.2 (6)	N1—C12—C11	128.8 (9)
C12—N1—C13	122.1 (7)	C7—C12—C11	120.7 (7)
N1—C1—C2	133.2 (8)	N1—C13—C14	111.9 (7)
N1—C1—C6	108.0 (6)	C2—C3—H14	121.129
C2—C1—C6	118.7 (8)	C4—C3—H14	121.141
Br1—C2—C1	124.7 (7)	C4—C5—H13	122.194
Br1—C2—C3	115.0 (6)	C6—C5—H13	122.203
C1—C2—C3	120.2 (8)	C7—C8—H15	121.002
C2—C3—C4	117.7 (7)	C9—C8—H15	121.015
Br2—C4—C3	117.0 (6)	C9—C10—H8	119.650
Br2—C4—C5	118.3 (8)	C11—C10—H8	119.639
C3—C4—C5	124.7 (9)	C10—C11—H20	121.210
C4—C5—C6	115.6 (9)	C12—C11—H20	121.204
C1—C6—C5	122.9 (7)	N1—C13—H9A	109.227
C1—C6—C7	108.7 (8)	N1—C13—H9B	109.224
C5—C6—C7	128.4 (8)	C14—C13—H9A	109.235
C6—C7—C8	134.5 (9)	C14—C13—H9B	109.231
C6—C7—C12	104.2 (7)	H9A—C13—H9B	107.915
C8—C7—C12	121.3 (7)	C13—C14—H21A	109.471
C7—C8—C9	118.0 (9)	C13—C14—H21B	109.468
Br3—C9—C8	120.1 (8)	C13—C14—H21C	109.476
Br3—C9—C10	118.2 (6)	H21A—C14—H21B	109.470
C8—C9—C10	121.7 (8)	H21A—C14—H21C	109.474

C9—C10—C11	120.7 (8)	H21B—C14—H21C	109.469
C10—C11—C12	117.6 (9)		
C1—N1—C12—C7	0.3 (9)	Br2—C4—C5—C6	−179.0 (5)
C1—N1—C12—C11	180.0 (7)	C3—C4—C5—C6	1.2 (13)
C12—N1—C1—C2	−177.7 (8)	C4—C5—C6—C1	0.6 (12)
C12—N1—C1—C6	−0.8 (9)	C4—C5—C6—C7	178.6 (8)
C1—N1—C13—C14	−96.3 (9)	C1—C6—C7—C8	179.2 (8)
C13—N1—C1—C2	7.1 (14)	C1—C6—C7—C12	−0.9 (9)
C13—N1—C1—C6	−176.0 (7)	C5—C6—C7—C8	0.9 (16)
C12—N1—C13—C14	89.1 (8)	C5—C6—C7—C12	−179.2 (8)
C13—N1—C12—C7	175.9 (7)	C6—C7—C8—C9	179.9 (9)
C13—N1—C12—C11	−4.4 (13)	C6—C7—C12—N1	0.4 (9)
N1—C1—C2—Br1	2.9 (14)	C6—C7—C12—C11	−179.4 (7)
N1—C1—C2—C3	−179.5 (8)	C8—C7—C12—N1	−179.7 (8)
N1—C1—C6—C5	179.5 (7)	C8—C7—C12—C11	0.6 (13)
N1—C1—C6—C7	1.1 (9)	C12—C7—C8—C9	0.0 (13)
C2—C1—C6—C5	−3.1 (12)	C7—C8—C9—Br3	179.7 (7)
C2—C1—C6—C7	178.5 (7)	C7—C8—C9—C10	−0.6 (13)
C6—C1—C2—Br1	−173.8 (7)	Br3—C9—C10—C11	−179.6 (6)
C6—C1—C2—C3	3.9 (12)	C8—C9—C10—C11	0.8 (14)
Br1—C2—C3—C4	175.7 (6)	C9—C10—C11—C12	−0.3 (13)
C1—C2—C3—C4	−2.2 (12)	C10—C11—C12—N1	179.9 (8)
C2—C3—C4—Br2	179.8 (7)	C10—C11—C12—C7	−0.4 (12)
C2—C3—C4—C5	−0.4 (13)		