9-Benzyl-3,6-dibromo-9*H*-carbazole

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Key indicators

Single-crystal X-ray study
$T = 294$ K
Mean σ(C–C) = 0.012 Å
R factor = 0.045
wR factor = 0.095
Data-to-parameter ratio = 14.4

For details of how these key indicators were
automatically derived from the article, see
http://journals.iucr.org/e.

Two independent molecules comprise the asymmetric unit of
the title compound, $C_{19}H_{13}Br_2N$, which was synthesized by *N*-
alkylation of benzyl bromide with 3,6-dibromo-9*H*-carbazole.
The carbazole ring system is essentially planar and forms a
dihedral angle with the pendant phenyl ring of 66.0 (2)°
[70.6 (2)° for the second molecule]. In the crystal structure, π–
π interactions and weak C—H···Br interactions are observed.

Comment

Carbazole derivatives substituted by *N*-alkylation possess
valuable pharmaceutical properties (Buu-Hoï & Royer, 1950;
Harfenist & Joyner, 1983; Caulfield *et al.*, 2002; Harper *et al.*,
2002). In this paper, the structure of 9-benzyl-3,6-dibromo-9*H*-
carbazole, (I), is reported; the compound was synthesized by
N-alkylation of benzyl bromide with 3,6-dibromo-9*H*-carba-
zole.

(I)
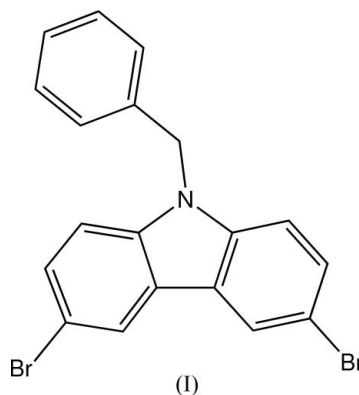
The asymmetric unit of (I) comprises two independent but
similar molecules (Fig. 1). The carbazole ring in each is
essentially planar, with mean deviations of 0.030 and 0.016 Å,
respectively, for the two molecules. The dihedral angles
formed between the carbazole ring and the plane through the
pendant phenyl ring is 66.0 (2)° [70.6 (2)° for the second
molecule]. The C—Br distances fall in the range 1.903 (7)–
1.925 (8) Å, which is consistent with the literature (Allen *et al.*,
1987). In the crystal structure, there are π–π interactions; the
closest, 3.66 Å, is formed between the N1/C1/C2/C7/C8 and
C7–C12 rings of translationally related molecules (x, $-1 + y$,
z). In addition, there are C—H···Br interactions, as shown in
Fig. 2 and as detailed in Table 1.

Experimental

The title compound was prepared according to the procedure of
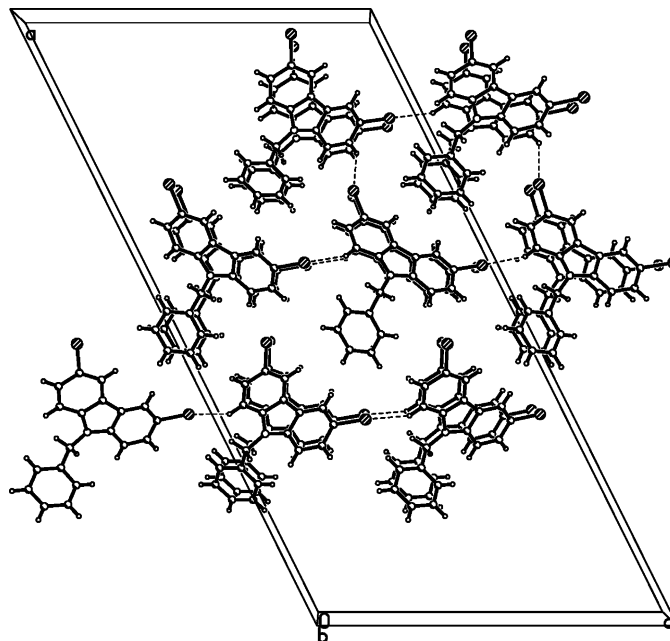Duan *et al.* (2005). A solution of potassium hydroxide (7.0 g) in
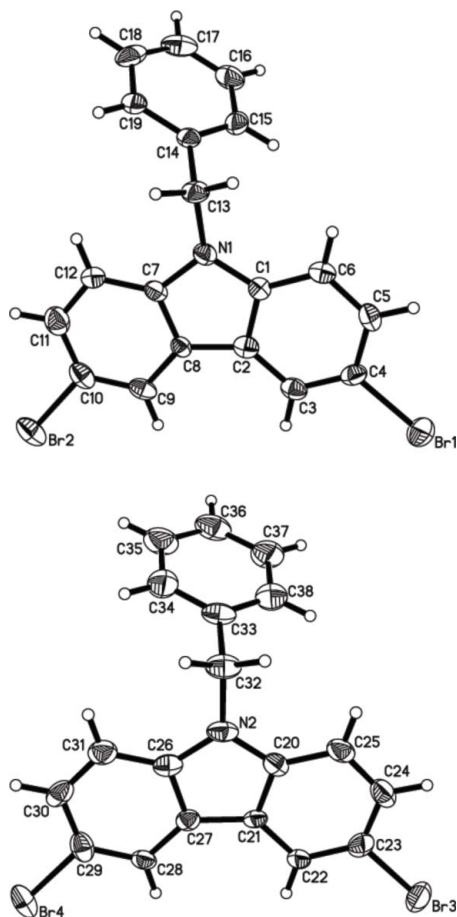
Figure 1
A view of the two independent molecules of (I); displacement ellipsoids are drawn at the 30% probability level.

dimethylformamide (50 ml) was stirred at room temperature for 20 min. 3,6-Dibromocarbazole (6.5 g, 20 mmol), prepared according to Smith *et al.* (1992), was added and the mixture stirred for a further 40 min. A solution of benzyl bromide (5.1 g, 30 mmol) in dimethylformamide (50 ml) was added dropwise with stirring. The resulting mixture was then stirred at room temperature for 10 h and poured into water (500 ml), yielding a white precipitate. The solid product was filtered off, washed with cold water and recrystallized from EtOH, giving crystals of (I) (yield: 7.51 g, 90.5%; m.p. 430–432 K). ^{1}H NMR (DMSO-d_6): δ 5.6 (s, 2H), 7.2–7.6 (m, 9H), 8.5 (m, 2H); ^{13}C NMR (DMSO-d_6): δ 46.8, 112.4, 112.9, 124.1, 124.5, 127.4, 128.3, 129.6, 129.9, 138.2, 140.2. Compound (I) (40 mg) was dissolved in a mixture of chloroform (5 ml) and ethanol (5 ml) and the solution was kept at room temperature for 16 d. Natural evaporation of the solution gave colourless crystals suitable for X-ray analysis.

Crystal data

$C_{19}H_{13}Br_2N$	$D_x = 1.707$ Mg m^{-3}
$M_r = 415.12$	Mo $K\alpha$ radiation
Monoclinic, Cc	Cell parameters from 1791
$a = 39.113$ (6) Å	reflections
$b = 4.5063$ (7) Å	$\theta = 2.3$–$21.4°$
$c = 20.469$ (3) Å	$\mu = 5.01$ mm^{-1}
$\beta = 116.449$ (2)°	$T = 294$ (2) K
$V = 3230.1$ (9) Å^3	Rod, colourless
$Z = 8$	$0.24 \times 0.18 \times 0.14$ mm

Figure 2
A portion of the crystal packing in (I), viewed down the *b*-axis direction. Dashed lines indicate C—H⋯Br interactions.

Data collection

Bruker SMART CCD area-detector diffractometer	5698 independent reflections
	3115 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.043$
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)	$\theta_{max} = 26.4°$
	$h = -48 \rightarrow 44$
$T_{min} = 0.310$, $T_{max} = 0.496$	$k = -3 \rightarrow 5$
8574 measured reflections	$l = -24 \rightarrow 25$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0127P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.095$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.94$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
5698 reflections	$\Delta\rho_{min} = -0.40$ e Å^{-3}
397 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	2371 Friedel pairs.
	Flack parameter: 0.010 (11)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C5—H5⋯Br3^i	0.93	3.00	3.800 (4)	146
C12—H12⋯Br1^{ii}	0.93	3.01	3.724 (4)	135
C25—H25⋯Br4^{iii}	0.93	2.97	3.852 (4)	158

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

All H atoms were included in the riding-model approximation, with C—H = 0.93 (aromatic) and 0.97 Å (methylene), and with U_{iso}(H) = 1.2U_{eq}(C).

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

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Bruker (1997). *SADABS*, *SMART*, *SAINT* and *SHELXTL*. Versions 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Buu-Hoï, N. P. & Royer, R. (1950). *J. Org. Chem.* **15**, 123–130.

Caulfield, T., Cherrier, M. P., Combeau, C. & Mailliet, P. (2002). European Patent No. 1 253 141.

Duan, X. M., Han, J., Chen, L. G., Xu, Y. J. & Li, Y. (2005). *Fine Chemicals*, **22**, 39–40, 52.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Harfenist, M. & Joyner, C. T. (1983). US Patent No. 4 379 160.

Harper, R. W., Lin, H. S. & Richett M. E. (2002). World Patent No. 02 079 154.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Smith, K., James, D. M., Mistry, A. G., Bye, M. R. & Faulkner, D. J. (1992). *Tetrahedron*, **48**, 7479–7488.