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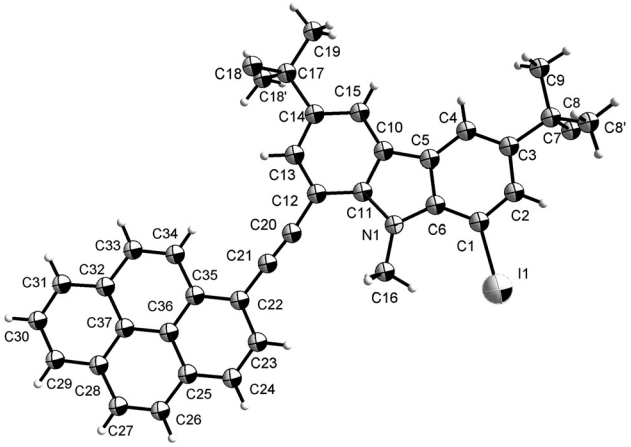
Crystal structure of 3,6-di-*tert*-butyl-1-iodo-9-methyl-8-(pyren-1-ylethynyl)-9*H*-carbazole, $C_{39}H_{34}IN$



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Abstract

$C_{39}H_{34}IN$, monoclinic, $P2_1/m$ (no. 11), a = 11.651(2) Å, b = 7.0023(14) Å, c = 18.716(4) Å, β = 97.5°, V = 1513.8(5) Å^3, Z = 2, $R_{gt}(F)$ = 0.0410, w$R_{ref}(F^2)$ = 0.1056, T = 296(2) K.

CCDC no.: 2154302

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.42 × 0.36 × 0.16 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.09 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17,067, 3700, 0.051
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 2478
$N(param)_{refined}$:	243
Programs:	Bruker [1], SHELX [2]

Source of material

At room temperature 0.5 ml of KOH (50%, 8.95 mmol) was added to a stirred solution of 1.0 g of 3,6-di-*tert*-butyl-9*H*-carbazole (3.58 mmol) and 0.115 g of TBAB in 14 ml of DMSO. After stirred for half an hour, 0.33 ml of CH_3I (5.37 mmol) was added dropwise. The mixture was warmed to 80 °C and stirred for 5 h. The reaction was quenched by ice water, and extracted by dichloromethane (3 × 50 ml). The organic layer was dried with Na_2SO_4. The solvent was removed *in vacuo*. The residue was purified by purified by recrystallization using ethanol to yield 3,6-di-*tert*-butyl-9-methyl-9*H*-carbazole as white solid. To a solution of 3,6-di-*tert*-butyl-9-methyl-9*H*-carbazole (0.743 g, 1.47 mmol) in CH_2Cl_2 (5 ml) and CH_3COOH (5 ml), *N*-iodosuccinimide (0.682 g, 3.03 mmol) was added, and the mixture was stirred at 20 °C for 16 h. CH_2Cl_2 was added, and the organic phase was washed with aqueous $NaHCO_3$ and water. After drying over Na_2SO_4, the solution was filtered. Removal of the solvent *in vacuo* and column chromatography (hexane) afforded 3,6-di-*tert*-butyl-1,8-diiodo-9-methyl-9*H*-carbazole as a white solid. The mixture of 3,6-di-*tert*-butyl-1,8-diiodo-9-methyl-9*H*-carbazole (0.36 g, 0.66 mmol) and 1-ethynylpyrene (0.15 g, 0.66 mmol) was dissolved in NEt_3 at room temperature under argon atmosphere. Then, $PdCl_2(PPh_3)_2$ (2.3 mg, 0.33 mmol) and CuI (0.31 mg, 0.17 mmol) were added to the solution. The mixture was then stirred at 70 °C for 22 h. Following evaporation, the residue was purified by flash column chromatography on silica gel to afford the title compound as yellow solid (217 mg, 51%). Crystals of the title compound were obtained by slow evaporation in CH_2Cl_2 within one week.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
I1	0.44251 (3)	0.250000	0.91533 (2)	0.06237 (16)
N1	0.6342 (3)	0.250000	0.77418 (18)	0.0369 (8)
C1	0.6216 (4)	0.250000	0.9103 (2)	0.0398 (10)
C2	0.6905 (4)	0.250000	0.9763 (2)	0.0434 (11)
H2	0.654128	0.250000	1.017666	0.052*
C3	0.8115 (3)	0.250000	0.9848 (2)	0.0343 (9)
C4	0.8634 (4)	0.250000	0.9230 (2)	0.0380 (10)
H4	0.943783	0.250000	0.926736	0.046*
C5	0.7989 (3)	0.250000	0.8549 (2)	0.0362 (10)
C6	0.6759 (4)	0.250000	0.8473 (2)	0.0368 (10)
C7	0.8768 (4)	0.250000	1.0609 (2)	0.0430 (11)
C8	0.8456 (3)	0.4285 (6)	1.10182 (19)	0.0635 (11)
H8A	0.862445	0.540634	1.075541	0.095*
H8B	0.890222	0.430642	1.148709	0.095*
H8C	0.764644	0.426078	1.106782	0.095*
C9	1.0081 (4)	0.250000	1.0610 (3)	0.0544 (13)
H9A	1.045756	0.250000	1.109763	0.082*
H9B[a]	1.030477	0.138060	1.036598	0.082*
H9C[a]	1.030477	0.361940	1.036599	0.082*
C10	0.8315 (3)	0.250000	0.7842 (2)	0.0349 (9)
C11	0.7283 (4)	0.250000	0.7356 (2)	0.0375 (10)
C12	0.7349 (4)	0.250000	0.6609 (2)	0.0391 (10)
C13	0.8442 (4)	0.250000	0.6393 (2)	0.0459 (11)
H13	0.849205	0.250000	0.590073	0.055*
C14	0.9472 (4)	0.250000	0.6865 (2)	0.0434 (11)
C15	0.9397 (4)	0.250000	0.7600 (2)	0.0400 (10)
H15	1.006672	0.250000	0.793043	0.048*
C16	0.5128 (4)	0.250000	0.7422 (3)	0.0529 (13)
H16A	0.464126	0.250000	0.779846	0.079*
H16B[a]	0.497335	0.361940	0.712962	0.079*
H16C[a]	0.497334	0.138060	0.712962	0.079*
C17	1.0635 (4)	0.250000	0.6563 (3)	0.0528 (13)
C18	1.0726 (4)	0.0716 (8)	0.6096 (3)	0.0972 (17)
H18A	1.064630	−0.040797	0.637901	0.146*
H18B	1.146578	0.070034	0.592228	0.146*
H18C	1.012257	0.074031	0.569416	0.146*
C19	1.1672 (5)	0.250000	0.7144 (3)	0.101 (3)
H19A	1.237110	0.250000	0.692320	0.152*
H19B[a]	1.165074	0.361940	0.743785	0.152*
H19C[a]	1.165074	0.138060	0.743784	0.152*
C20	0.6369 (4)	0.250000	0.6061 (2)	0.0435 (11)
C21	0.5621 (4)	0.250000	0.5555 (3)	0.0454 (11)
C22	0.4706 (4)	0.250000	0.4963 (2)	0.0411 (10)
C23	0.3553 (4)	0.250000	0.5103 (3)	0.0511 (12)
H23	0.339715	0.250000	0.557794	0.061*
C24	0.2653 (4)	0.250000	0.4554 (3)	0.0523 (13)
H24	0.189526	0.250000	0.466116	0.063*
C25	0.2858 (4)	0.250000	0.3835 (2)	0.0440 (11)
C26	0.1939 (4)	0.250000	0.3250 (3)	0.0529 (13)
H26	0.117628	0.250000	0.334800	0.063*
C27	0.2149 (5)	0.250000	0.2566 (3)	0.0680 (17)
H27	0.153083	0.250000	0.219774	0.082*
C28	0.3288 (5)	0.250000	0.2390 (3)	0.0572 (14)
C29	0.3531 (7)	0.250000	0.1676 (3)	0.0767 (19)
H29	0.292442	0.250000	0.129963	0.092*
C30	0.4630 (8)	0.250000	0.1527 (3)	0.088 (2)
H30	0.476780	0.250000	0.104890	0.105*
C31	0.5559 (7)	0.250000	0.2066 (3)	0.0753 (19)
H31	0.630905	0.250000	0.194594	0.090*
C32	0.5385 (5)	0.250000	0.2790 (3)	0.0577 (14)
C33	0.6308 (5)	0.250000	0.3386 (3)	0.0627 (15)
H33	0.707261	0.250000	0.329254	0.075*
C34	0.6085 (4)	0.250000	0.4070 (3)	0.0508 (12)
H34	0.670130	0.250000	0.444024	0.061*
C35	0.4940 (4)	0.250000	0.4247 (2)	0.0422 (11)
C36	0.4008 (4)	0.250000	0.3681 (2)	0.0389 (10)
C37	0.4229 (4)	0.250000	0.2959 (2)	0.0443 (11)

[a]Occupancy: 0.5.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Comment

Carbazoles are frequently found in pharmaceuticals and bioactive molecules [3, 4]. Because of their superior electrical and optical properties, carbazoles have been widely used as building blocks to construct organic light-emitting devices (OLEDs) and phosphorescence materials [5, 6]. Consequently, numerous approaches have been developed to synthesize carbazoles in recent decades [7–9]. However, the synthesis of 1,8-dihalogenocarbazole derivatives were rarely been reported [10]. Previously, Zhang and Zeng reported the synthesis and crystal structure of 3,6-di-*tert*-butyl-1,8-diiodo-9-methyl-9*H*-carbazole [11]. Herein, we reported the synthesis of 3,6-di-*tert*-butyl-1-iodo-9-methyl-8-(pyren-1-ylethynyl)-9*H*-carbazole, which may enriched the application of carbazoles in materials chemistry. The title compound, built up by the $C_{39}H_{34}I_1N_1$ molecules. The molecule is located on the mirror plane of the space group $P21/m$ (see the Figure, and Table 2). The single-crystal structure verifies that all bond lengths are in normal ranges.

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