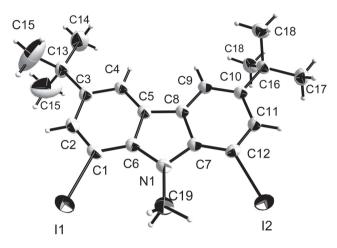
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The crystal structure of 3,6-di-*tert*-butyl-1,8-diiodo-9-methyl-9H-carbazole, $C_{21}H_{25}I_2N$



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Abstract

C₂₁H₂₅I₂N, monoclinic, $P2_1/m$ (no. 11), a=10.2277(18) Å, b=7.6698(13) Å, c=13.142(2) Å, $\beta=93.819(2)^{\circ}$, V=1028.6(3) Å³, Z=2, $R_{\rm gt}(F)=0.0261$, $wR_{\rm ref}(F^2)=0.0680$, T=296(2) K.

CCDC no.: 1985680

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.

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-9H-carbazole (3.58 mmol) and 0.115 g of tetrabutylammoniumbromid in 14 mL of DMSO. After stirred for half an hour, 0.33 mL of CH₃I (5.37 mmol) was added dropwise. Then the mixture was warmed to 80 °C and stirred for 5 h. The reaction was quenched by ice water, and extracted by

Table 1: Data collection and handling.

Crystal:	Yellow prism	
Size:	$0.42\times0.32\times0.21~\text{mm}$	
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)	
μ:	3.06 mm ⁻¹	
Diffractometer, scan mode:	Bruker APEX-II, $oldsymbol{arphi}$ and $oldsymbol{\omega}$	
$\theta_{\sf max}$, completeness:	27.4°, >99%	
N(hkl) _{measured} , N(hkl) _{unique} , R _{int} :	11161, 2494, 0.019	
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{\rm obs} > 2 \ \sigma(I_{\rm obs})$, 2311	
N(param) _{refined} :	157	
Programs:	Bruker [1], SHELX [2]	

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\mathring{A}^2).

Atom	X	у	z	$U_{iso}*/U_{eq}$
<u>C1</u>	0.4434(3)	0.2500	0.2539(3)	0.0338(7)
C2	0.5181(3)	0.2500	0.1695(3)	0.0367(7)
H2	0.4747	0.2500	0.1050	0.044*
C3	0.6557(4)	0.2500	0.1763(3)	0.0356(7)
C4	0.7181(3)	0.2500	0.2733(3)	0.0329(7)
H4	0.8091	0.2500	0.2812	0.039*
C5	0.6449(3)	0.2500	0.3591(3)	0.0312(7)
C6	0.5068(3)	0.2500	0.3520(3)	0.0311(6)
C7	0.5706(3)	0.2500	0.5201(3)	0.0314(7)
C8	0.6856(3)	0.2500	0.4660(2)	0.0299(6)
C9	0.8104(3)	0.2500	0.5162(3)	0.0325(7)
Н9	0.8842	0.2500	0.4786	0.039*
C10	0.8247(3)	0.2500	0.6218(3)	0.0306(6)
C11	0.7100(3)	0.2500	0.6750(3)	0.0333(7)
H11	0.7184	0.2500	0.7459	0.040*
C12	0.5849(3)	0.2500	0.6271(3)	0.0322(7)
C13	0.7312(4)	0.2500	0.0796(3)	0.0451(9)
C14	0.8782(5)	0.2500	0.1012(4)	0.086(2)
H14A	0.9096(10)	0.1483(7)	0.1405(12)	0.103*
H14B	0.9259(14)	0.2500	0.0397(12)	0.103*
C15	0.6955(6)	0.0888(9)	0.0174(4)	0.131(3)
H15A	0.6022	0.0840	0.0038	0.197*
H15B	0.7245	-0.0132	0.0548	0.197*
H15C	0.7372	0.0934	-0.0459	0.197*
C16	0.9617(3)	0.2500	0.6761(3)	0.0329(7)
C17	0.9589(4)	0.2500	0.7928(3)	0.0470(9)
H17A	0.9152(17)	0.1481(7)	0.8160(19)	0.056*
H17B	1.0466(17)	0.2500	0.827(3)	0.056*
C18	1.0369(3)	0.4121(4)	0.6448(2)	0.0452(6)
H18A	1.0473	0.4087	0.5728	0.068*

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Table 2 (continued)

Atom	X	у	Z	$m{U}_{iso}$ * $/m{U}_{eq}$
H18B	1.1215	0.4144	0.6810	0.068*
H18C	0.9888	0.5149	0.6610	0.068*
C19	0.3263(4)	0.2500	0.4745(4)	0.087(2)
H19A	0.2726(8)	0.1489(7)	0.4465(13)	0.104*
H19B	0.3080(17)	0.2500	0.5464(10)	0.104*
l1	0.23957(2)	0.2500	0.21878(2)	0.05099(11)
12	0.43329(2)	0.2500	0.72794(2)	0.04864(11)
N1	0.4623(3)	0.2500	0.4499(2)	0.0346(6)

dichloromethane (3×50 mL). The organic layer was dried with Na₂SO₄ anhydride. The solvent was removed *in vacuo*. The residue was purified by recrystallization using ethanol to yield 3,6-di-*tert*-butyl-9-methyl-9*H*-carbazole as a white solid. To a solution of 3,6-di-*tert*-butyl-9-methyl-9*H*-carbazole (0.743 g, 1.47 mmol) in CH₂Cl₂ (5 mL) and CH₃COOH (5 mL), *N*-iodosuccinimide (0.682 g, 3.03 mmol) was added, and the mixture was stirred at 20 °C for 16 h. CH₂Cl₂ was added, and the organic phase was washed with aqueous NaHCO₃ and water. After drying over Na₂SO₄, 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. Crystals of the title compound were obtained by slow evaporation in CH₂Cl₂ within 1 week.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. There is a disorder of one of the t-butyl groups (C14/C5; about 20%), which was not included in the refinement.

Comment

Carbazoles have been widely used as building blocks to construct organic light-emitting devices (OLEDs) and phosphorescence materials [3–6]. Polycabazoles which are substituated at different positions showed completely different properties. Poly(2,7-carbazole)s generally have smaller band gaps than the corresponding poly(3,6-carbazole)s because of the linear conjugation of the 2,7-positions. Thus, the promising applications are in optoelectronic devices, such as organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), and organic photovoltaics. Poly(1,8-carbazole)s showed blue-light emission [7, 8]. Efficient synthetic routes for the 2,7-dihalogenocarbazole derivatives are reported [9, 10]. However, the synthesis of 1,8-dihalogenocarbazole

derivatives have rarely been reported [11]. Herein, we reported the synthesis of 3,6-di-tert-butyl-1,8-diiodo-9-methyl-9*H*-carbazole, which is a educt for the syntheses of complex systems [12]. The single crystal structure (see the figure) verifies that all bond lengths are in normal ranges.

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