Synthesis, crystal structures, and nonlinear optic and thermal properties of two diiodocarbazole derivatives

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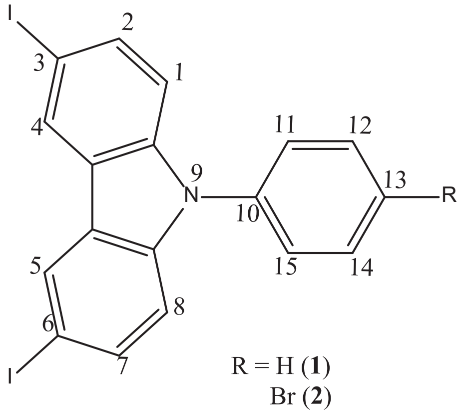
Two 3,6-diiodocarbazole derivatives were prepared from the iodination of the corresponding phenylcarbazole. 3,6-Diiodo-9-phenylcarbazole crystallises in the chiral space group $P2_1$ and shows good second-harmonic generation effects. Thermogravimetric analysis of the two compounds shows high thermal stabilities, in which the decomposition temperature for **1** and **2** are 273 and 308 °C, respectively.

Keywords: phenylcarbazole, iodination, infrared spectra, UV-Vis and NMR spectra, X-ray diffraction, crystal structures, nonlinear optics

Carbazoles are an important type of heterocyclic organic compounds in the field of organic fluorescence materials, gas absorption, and separation and nonlinear optics[1–3] as they have efficient hole-transporting capability and electronic properties.[4–6] More importantly, the synthesis and characterisation of iodocarbazoles are of interest. Most iodocarbazoles are obtained by iodination using a mixture of KI and KIO_3 under acidic conditions.[7,8]

In particular, di- and poly-iodocarbazole derivatives have attracted much attention because they are key intermediates in the design and development of interesting optoelectronic materials.[7–11] Notably, diiodocarbazole compounds play a key role in the design and development of novel optoelectronic materials. However, there is little of knowledge of the relationship between structure and properties for these compounds in solid state. Thus, determining detailed structural information and the structure–property relationships for diiodocarbazoles still remains a formidable challenge.

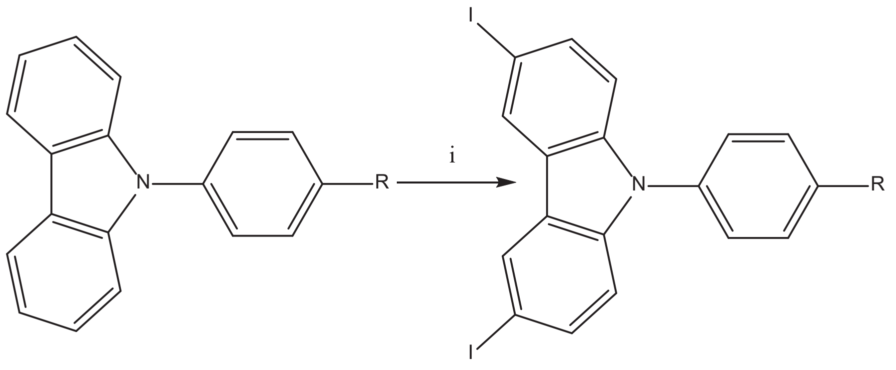


Scheme 1

Prompted by these elegant studies on the interesting properties of carbazole derivatives, and understanding the importance of the structure–property relationships of organic iodo-compounds, we synthesised two derivatives containing a 3,6-diiodocarbazole moiety: 3,6-diiodo-9-phenylcarbazole (**1**) and 9-(4-bromophenyl)-3,6-diiodocarbazole (**2**) (Schemes 1 and 2), and characterised them by FTIR, UV-Vis, ^{1}H NMR, and single-crystal X-ray diffraction. Compounds **1** and **2** crystallised in chiral and centrosymmetric space groups, respectively. In addition, we investigated their thermal properties in detail and the nonlinear optic properties of compound **1** were studied.

X-ray diffraction analysis of compound **1** revealed that it crystallises in the chiral space group $P2_1$. As illustrated in Fig. 1, in an asymmetric unit, there are two unique molecules of **1**. The first molecule contains I1 and I2 groups. The C–I bond distances are 2.124 (9) and 2.054 (10) Å. There is two-fold disorder of the 9-position phenyl group and the dihedral angle between the phenyl group and the five-member ring is about 43.9°. Interestingly, the dihedral angles between the three fused rings Cg1–Cg2, Cg2–Cg3, and Cg1–Cg3 (where Cg1, Cg2 and Cg3 are C1–C2–C3–C4–C5–C6, N1–C6–C1–C7–C12, and C7–C8–C9–C10–C11–C12, respectively) are 2.36°, 6.84°, and 4.6°, respectively, indicating that the whole carbazole moiety is rather planar.

In the second molecule, the C–I bond lengths are 2.043 (9) and 2.120 (9) Å, which are comparable to those in the first molecule. The 9-position phenyl group in the carbazole group



R = H (**1**)
Br (**2**)
Reaction conditions: i) KI, KIO_3, glacial acetic acid, 135 °C, 18 h

Scheme 2

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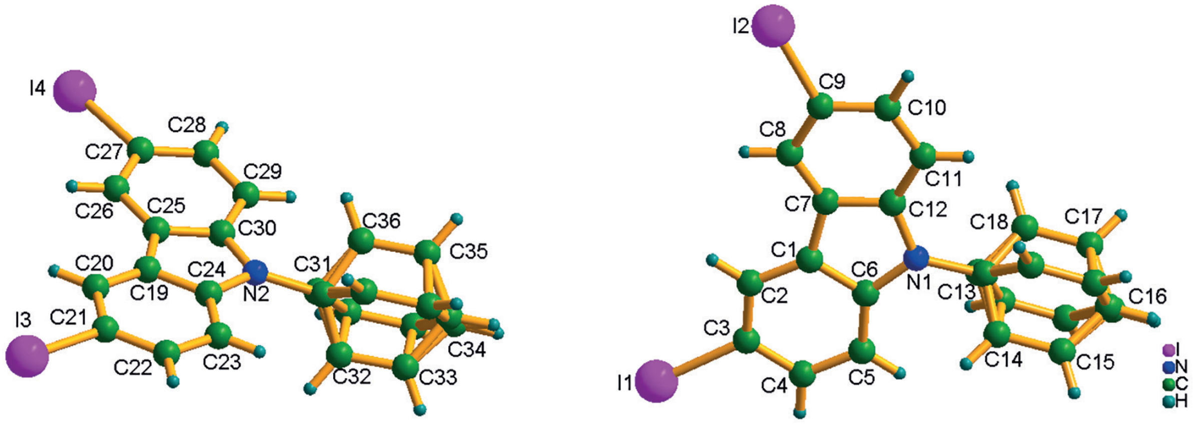

Fig. 1 A perspective of compound **1**.

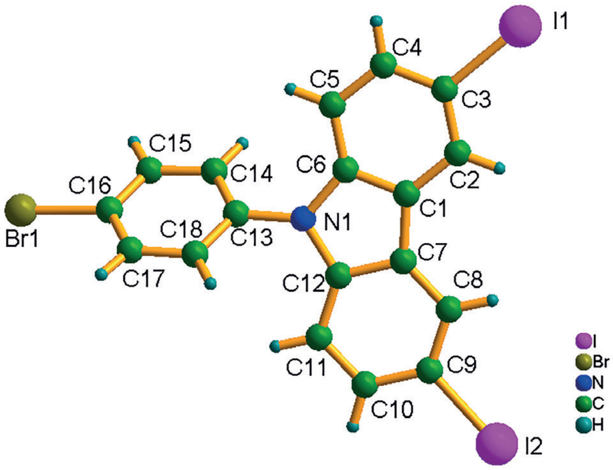

Fig. 2 A perspective of compound **2**.

also occurs in the formation of two-fold disorder. The dihedral angles between the *N*-phenyl group and the five-member ring are observed to be 52.6° and 47.4°. As a result, the average dihedral angle is 50°, which is much higher than that in the first molecule.

X-ray diffraction of compound **2** revealed that it crystallises in the space group $P2_1/c$. As shown in Fig. 2, there is only one molecule of **2** in the asymmetric unit. The molecule contains two kinds of halogen atoms: Br and I. The C–I bond distances are 2.094 (8) and 2.090 (8) Å, which are comparable to those in compound **1**. The Br–C bond length is 1.909 (7) Å. The bond length of N1–C13 (1.422 (9) Å) in the Br-phenyl ring is obviously longer than that of N1–C6 (1.389 (10) Å) or N1–C12 (1.400 (10) Å) in the carbazolyl ring and shorter than the common C–N bond (1.52 Å), which indicates the formation of conjugation between the carbazole group and the Br-phenyl group. In the carbazole group, the dihedral angles of the adjacent aromatic rings are 0.40°, 0.65°, and 0.67° for Cg1–Cg2, Cg2–Cg3, and Cg3–Cg1 (Cg1, Cg2, and Cg3 represent C1–C2–C3–C4–C5–C6, N1–C6–C1–C7–C12, and C7–C8–C9–C10–C11–C12, respectively), respectively. Interestingly, the whole carbazole ring has a co-planar structure, which can be ascribed to the small dihedral angle (average 0.66°) between the three aromatic rings of the carbazole group. Obviously, this dihedral angle is smaller than the corresponding dihedral angle in compound **1**, which may be due to the disordered structure of the *N*-phenyl group. A dihedral angel of 53.8° in compound **2** is observed between the Br-phenyl group and the five-member ring in the carbazole system. This dihedral angle is much larger than the corresponding dihedral angle in compound **1**, which can be attributed to the stereo-hindrance effect of the substituent bromo group. Compared with the structure of compound **1**, the phenyl group at the 9-position of the carbazole ring in **2** does not display disorder.

Given that compound **1** crystallised in the chiral space group $P2_1$, the effect of second-harmonic generation (SHG) for compound **1** was investigated. The primary experimental results revealed that compound **1** is SHG active, and displays a moderate SHG efficiency. The effect of SHG for compound **1** is twice than that of KH_2PO_4, which may be mainly attributed to a good donor–acceptor system (Scheme 1) and the orderly arrangement of the organic moieties. The experimental results further identified the arrangement of the organic moieties obtained by the single-crystal structure mentioned above.

In summary, we successfully obtained two compounds, 3,6-diiodo-9-phenylcarbazole and 9-(4-bromophenyl)-3,6-diiodocarbazole, which were structurally characterised by FTIR, UV-Vis, ^{1}H-NMR, elemental analysis, and single-crystal X-ray diffraction. Both compounds displayed good thermal stability. Single-crystal diffraction analysis revealed packing interactions in the structures of the compounds. Interestingly, the packing interactions in 9-(4-bromophenyl)-3,6-diiodocarbazole with a bromine substituent were obviously stronger than those of 3,6-diiodo-9-phenylcarbazole. Furthermore, compound **1** showed strong SHG efficiency, and may be a promising nonlinear optic material. The design and development of other diiodocarbazole-based derivatives is ongoing in our laboratory.

Experimental

9-Phenylcarbazole and 9-(4-bromophenyl)carbazole were obtained from Zhengzhou HQ material Co., Ltd. and Puyang Chemical Factory, respectively. Potassium iodide and sodium thiosulfate pentahydrate were purchased from The Third Plant of Tianjin Chemical Reagent. Potassium iodate and acetic acid are obtained from Tianjin Bo Di Chemical Co., Ltd. and Jinan Reagent General Factory, respectively. The reagents and solvents employed were used as received without further purification. Elemental analyses were performed on an Elementar Vario EL III microanalyser. The FTIR spectra were recorded from KBr pellets in the range 400–4000 cm^{-1} on a Bruker spectrometer. NMR spectra were recorded using a Bruker Advances 400 spectrometer at 400 MHz for samples dissolved in $CDCl_3$ and held at room temperature. The absorption spectra were recorded with an absorption spectrophotometer model TU-1900/1901. Thermogravimetric analysis data were collected with a TA SDT Q600 analyser in N_2 at a heating rate of 10 °C min^{-1} in the range of 20–750 °C. Kurtz powder SHG measurements were performed on ground samples of crystalline compound **1** with a synchroscan streak camera (Hamamatsu Model C1587, 8 ps resolution) connected to a polychromator as the detector system, and an optical parametric generator (Spectra Physics, Model: OPA-800C) pumped by a mode-locked Ti:sapphire laser oscillator–amplifier system (Spectra Physics, Model: Hurricane) as the pump source. The powder second-harmonic signals were compared with that of KH_2PO_4 to determine the relative SHG efficiencies of compounds **1** and **2**, respectively.

Single-crystal structure determinations of compounds **1** and **2** were measured by a Bruker Smart CCD diffractometer equipped with graphite–monochromator Mo $K\alpha$ radiation (λ = 0.71073 Å). The lattice parameters were obtained by a least-squares refinement of the diffraction data. All the measured independent reflections were used in the structural analysis, and semi-empirical absorption corrections were applied using the SADABS program.[12] The program SAINT was used for integration of the diffraction profiles.[13] The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL.[14,15] All non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for all the non-hydrogen atoms based on F^2. The hydrogen atoms were placed in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. Special computations for the crystal structure discussions were carried out with PLATON for Windows.[16] A summary of the crystallographic data and structure refinements are listed in Table 1. The IR, UV-Vis, ^{1}H-NMR and thermogravimetric analysis data are provided in the Electronic Supplementary Information. Selected bond lengths and angles are given in Table S1 in the Electronic Supplementary Information. Corresponding packing interactions data for compounds **1** and **2** are listed in Tables S2 and S3 in the Electronic Supplementary Information.

Table 1 Crystal data and structure refinement parameters for **1** and **2**

Compound	1	2
Chemical formula	$C_{18}H_{11}I_2N$	$C_{18}H_9BrI_2N$
Formula mass	495.08	573.98
Crystal system	monoclinic	monoclinic
a/Å	12.3621 (9)	4.4724 (4)
b/Å	4.8724 (4)	13.9377 (12)
c/Å	27.031(2)	27.172 (2)
α/°	90.00	90.00
β/°	103.1897 (9)	90.0720 (10)
γ/°	90.00	90.00
Unit cell volume/Å^3	1585.2 (2)	1693.8 (3)
Temperature/K	293 (2)	293 (2)
Space group	$P2_1$	$P2_1/c$
No. of formula units per unit cell, Z	4	4
Radiation type	Mo K	Mo K
Absorption coefficient, μ/mm^{-1}	3.960	6.068
No. of reflections measured	14083	18577
No. of independent reflections	7166	3825
R_{int}	0.0338	0.0567
Final R_1 values ($I > 2\sigma(I)$)[a]	0.0421	0.0468
Final $wR(F^2)$ values ($I > 2\sigma(I)$)[b]	0.0826	0.0919
Final R_1 values (all data)[a]	0.0629	0.0824
Final $wR(F^2)$ values (all data)[b]	0.0934	0.1017
Goodness of fit on F^2	1.026	1.057
CCDC number	1437026	1437027

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.

Synthesis of 3,6-diiodo-9-phenylcarbazole (**1**)

A mixture of 9-phenylcarbazole (0.2433 g, 0.1 mmol), potassium iodide (0.6640 g, 4.0 mmol) and potassium iodate (0.4277 g, 2.0 mmol) was refluxed for 18 h in glacial acetic acid (50 mL). The colour of the solution changed from purple to chocolate brown. After the reaction was completed, the mixture was left to cool naturally. The precipitate was separated and washed with 10% sodium hyposulfite solution (50 mL) and distilled water (30 mL) successively. The white needles obtained were further dried and recrystallised from alcohol to give compound **1** as white crystals: m.p. 185–186 °C; yield 0.3703 g (74.8%); ^{1}H NMR (400 MHz, Chloroform-d_1): δ 8.40 (s, 2H), 7.71–7.58 (m, 4H), 7.50 (t, J = 9.4 Hz, 3H), 7.16 (d, J = 8.6 Hz, 2H); FTIR (KBr) (cm^{-1}): 3134(s), 1595(m), 1500(w), 1463(s), 1427(s), 1400(s), 1278(m), 1228(s), 1014(m), 867(w), 798(m), 756(m), 696(w), 630(w), 565(w), 563(w). Anal. calcd for $C_{18}H_{11}I_2N$: C, 43.67; H, 2.24; N, 2.83; found: C, 43.54; H, 2.23; N, 2.84%.

Synthesis of 9-(4-bromophenyl)-3,6-diiodocarbazole (**2**)

The preparation procedure for compound **2** was similar to that for **1** except that 9-(4-bromophenyl) carbazole took the place of 9-phenylcarbazole. The pink crystals obtained were further dried and recrystallised from alcohol to give compound **2** as pale yellow crystals: yield 0.472 g (82.22%); m.p. 234–235 °C; ^{1}H NMR (400 MHz, Chloroform-d_1): δ 8.39 (s, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.6 Hz, 2H); FTIR (KBr) (cm^{-1}): 3134(s), 1585(w), 1490(s), 1425(s), 1400(s), 1226(m), 1068(m), 933(s), 867(s), 827(s), 794(s), 630(m), 563(m), 497(w). Anal. calcd for $C_{18}H_{10}BrI_2N$: C, 37.67; H, 1.76; N, 2.44; found: C, 37.45; H, 1.75; N, 2.45%.

Acknowledgements

This work was financially supported by J09LB03, BS2011CL034, and NSFC (No. 21276149).

Electronic Supplementary Information

The ESI is available through:
stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data.

Received 10 December 2016; accepted 20 December 2016
Paper 1604476 DOI: 10.3184/174751917X14839766277297

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