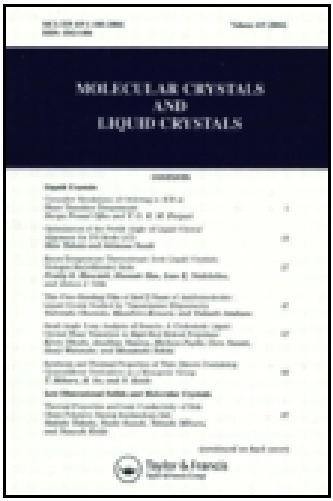

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Effect of Adding Bromine Sensors to the Central Linker of New Diquinoline Derivative

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Effect of Adding Bromine Sensors to the Central Linker of New Diquinoline Derivative

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Designing a selective lattice inclusion host had been challenging and fulfilling. Using **3** *as a building block, we introduced bromine sensors to the central linker and investigate its effect on inclusion properties. An unexpected result was obtained when a pure sample of the diquinoline derivative* **4** *was crystallised from tetrahydrofuran. Unlike host* **3***, the diquinoline* **4** *did not include any guest molecules.*

Keywords: bromine sensors; inclusion compounds; supramolecular synthon; X-ray crystal structure

INTRODUCTION

Recently, we have been investigating the design and properties of new lattice inclusion hosts based on racemic V-shaped diheteroaromatic structures that are unable to employ strong hydrogen bonding interactions during crystal formation using the general crystal engineering design illustrated in Fig. 1 [1–4]. The target molecules are constructed from three distinct structural components; two planar aromatic wings, a flexible central linker group able to provide molecular C_2 symmetry, and two *exo*-oriented sensor groups. The synthetic methodology used to prepare such compounds, comprises a simple modular process whereby the two aromatic wings are condensed onto the central cyclic linker group, and then the synthesis is completed by substitution of the benzylic sensor groups.

This new family of host molecules does not contain functional groups (such as OH, NH_2, or CO_2H) that are capable of strong

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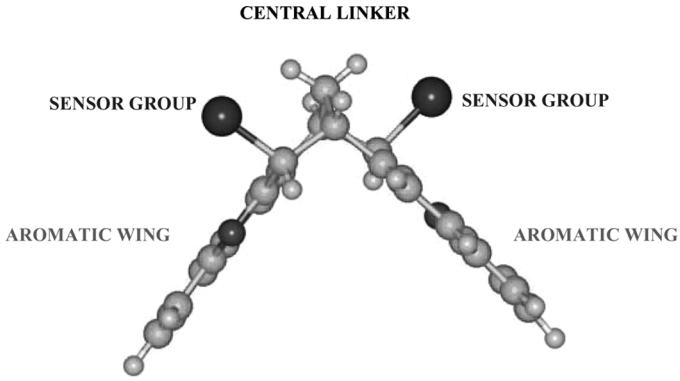


FIGURE 1 General schematic design for new lattice inclusion hosts, involving three structural sub-units: aromatic wings, central linker group, and *exo*-sensor groups.

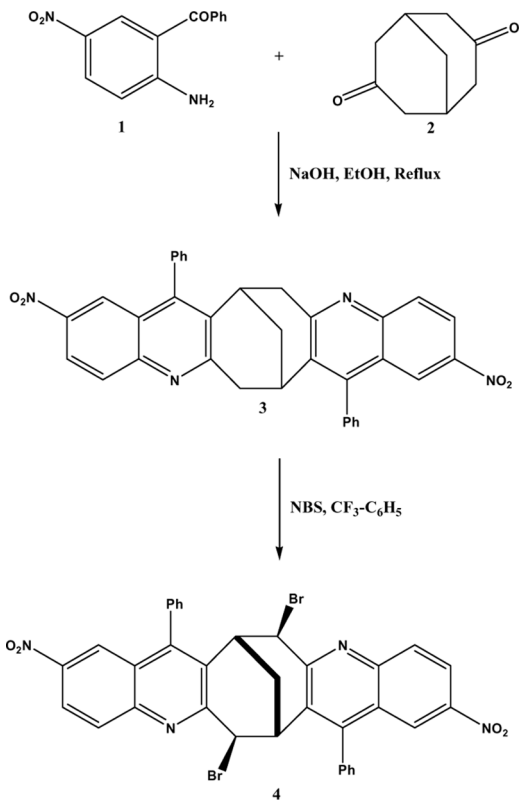
hydrogen bonding. Instead, weak host-host and host-guest noncovalent bonds (such as aryl face-face and edge-face, halogen-halogen, halogen-nitrogen, and edge-edge C-H N dimer interactions) can occur. Competition between these weak interactions results in the best overall net energy that affords the observed lattice inclusion structure. Hence these new host molecules, and their various inclusion compounds, provide an excellent means of probing the interdependence of many of the weaker supramolecular synthons [5–7].

In this work, we started with **3** as the basic building block. It was a host for polar guest molecules [8]. By adding bromine sensors to the central linker, we had been successful in synthesizing compound **4**. Substitution on the central linker in this case provided efficient packing of the diquinoline molecules without the need of presence any guest molecules resulting in the formation of non-host **4**.

RESULTS AND DISCUSSION

Synthesis of Dinitrodiphenyldiquinoline 3

Compound **3** was synthesized according to Scheme 1 using Friedländer condensation [9,10]. 2 equivalents of 2-amino-5-nitrobenzophenone **1** and 1 equivalent of racemic bicyclo[3.3.1]nonane-3,7-dione **2** [11] were dissolved in ethanol with catalytic amount of NaOH and refluxed overnight to produce a light brown powder of **3** [8].



SCHEME 1 Synthetic route for diquinolines **3** and **4**.

Synthesis of Dibromodinitrodiphenyldiquinoline 4

Radical bromination at the benzylic positions of diquinoline **3** was achieved using *N*-bromosuccinimide (NBS) in trifluoromethylbenzene to give the racemic dibromodinitrodiquinoline **4** in 75% yield (Scheme 1). The highly regio- and stereo-selective outcomes of such NBS substitution reactions have been discussed in recent publications [12,13].

Crystallization of Compound 4

A solvent free sample of diquinoline **4** was obtained after crystallization from tetrahydrofuran. Crystallization from a variety of other solvents also gave no evidence of guest inclusion by **4** (confirmed by ^{1}H NMR and FTIR). The crystal data for inclusion compounds and structure refinements were shown in Table 1.

TABLE 1 Crystal Data and Structure Refinements

Empirical formula	$C_{35}H_{22}Br_2N_4O_4$	
Formula weight	722.39	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 17.2093(13) Å	$\alpha = 90^\circ$.
	b = 10.7231(8) Å	$\beta = 116.942(2)^\circ$.
	c = 18.1962(13) Å	$\gamma = 90^\circ$.
Volume	2993.4(4) Å^3	
Z	4	
Density (calculated)	1.603 Mg/m^3	
Absorption coefficient	2.756 mm^{-1}	
F(000)	1448	
Crystal size	0.60 × 0.08 × 0.03 mm^3	
Theta range for data collection	2.32 to 27.50°	
Index ranges	$-22 \le n \le 10$, $-13 \le k \le 13$, $-23 \le \le 23$	
Reflections collected	10368	
Independent reflections	3440 [R(int) = 0.0410]	
Completeness to theta = 27.50°	100.0%	
Absorption correction	Sadabs, (Sheldrick 2001)	
Max. and min. transmission	0.9219 and 0.2886	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3440/0/204	
Goodness-of-fit on F^2	1.057	
Final R indices [I > 2sigma(I)]	R1 = 0.0559, wR2 = 0.1429	
R indices (all data)	R1 = 0.0830, wR2 = 0.1563	
Largest diff. peak and hole	1.609 and −0.340 e.Å^{-3}	

Crystal Structure of 4

Crystallization of **4** from tetrahydrofuran yielded crystals of the solvent free compound in the monoclinic space group C2/c with z = 4. The asymmetric unit contains one half of the molecule $C_{35}H_{22}Br_2N_4O_4$. The whole molecule is generated by the 2-fold rotation. Analysis of the crystal structure of solid **4** indicated aryl-nitrogen interactions with C-H N and C-H N distances of 3.00 and 3.83 Å, respectively. Figure 2 illustrates two molecules of **4** interacting together.

Further analysis of the crystal structure of **4** revealed the absence of the ubiquitous edge-edge aryl C-H N dimer interaction frequently observed in crystal structures of our previous diquinoline derivatives [14]. This interaction was replaced with the previously unobserved Centrosymmetric double Br H-C-Ar hydrogen interaction between

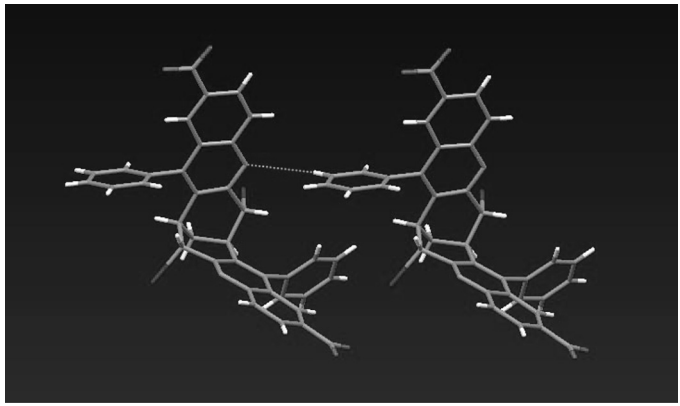


FIGURE 2 Part of the crystal structure of **4** showing two molecules of **4** interacting together. Color code: C = gray, N = blue, H = white, O = red, and Br = dark red.

opposite enantiomers of **4**. This gave a dimer between two host molecules of opposite chirality with C-H Br distances of 3.22 and 3.05 Å in each motif (Fig. 3).

In addition, bromine atoms were found to interact with the oxygen atoms of the nitro group with Br O distance of 3.45 Å which should provide extra packing stability between the diquinoline molecules (Fig. 4).

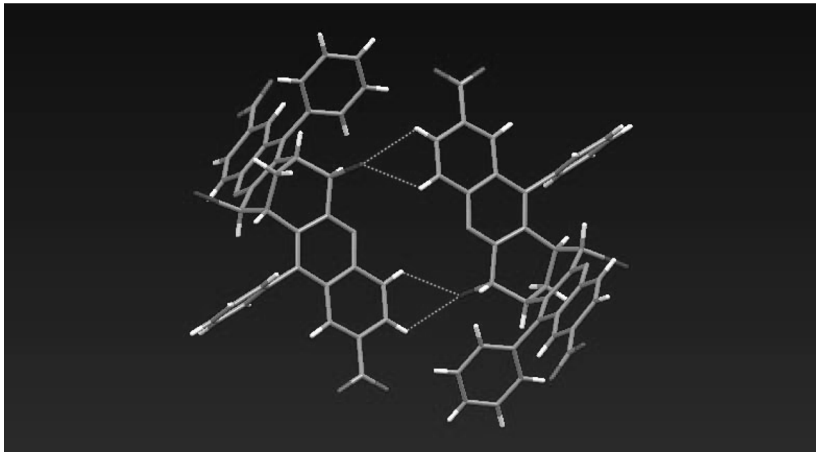


FIGURE 3 Centrosymmetric double Br H-C-Ar hydrogen interaction between opposite enantiomers of 4 with C-H---Br distances of 3.22 and 3.05 Å in each motif. Color code: C = gray, N = blue, H = white, O = red, and Br = dark red.

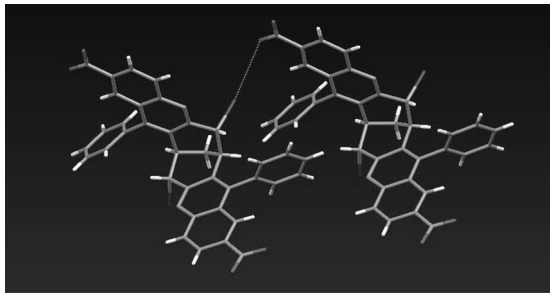


FIGURE 4 Two molecules of **4** with same chirality interact via Br O with a distance of 3.45 Å.

CONCLUSIONS

In this article we synthesised compound **4** in which we expected that it would behave in a similar manner to **3** perhaps even giving isostructural outcomes, but this proved not to be the case. In moving from compound **3** to **4** the only molecular change is replacement of a benzylic hydrogen atom by a bromine atom. This minor alteration results in considerable supramolecular change and molecules of **4** pack quite differently. Indeed compound **4** no longer includes the guests trapped by **3**. On a supramolecular level the bromine atom offers new possibilities for intermolecular attractions and as a result, this potential host molecule is able to adopt new efficient lattice packing without guest inclusion.

EXPERIMENTAL

Melting points were determined using a Büchi melting point B-540 apparatus. NMR spectra were recorded using a Bruker 400 MHz standard bore instrument with Quad Nuclear Probe (QNP) and carbon substitution information was determined using the Distortionless Enhancement of Polarization Transfer (DEPT) procedure. Mass spectrometry data were recorded using a Finnigan TSQ 7000 machine. Elemental analyses for C, H, N, O, and Br were determined using a Perkin-Elmer PE 2400 or platinum sample pans.

7α,15α-Dibromo-2,10-dinitro-8,16-diphenyl-6,7,14,15-tetrahydro-7,15-methanocycloocta[1,2-b:5,6-b′]diquinoline (4)

A solution of NBS (0.45 g, 2.54 mmol) and **3** (0.58 g, 1.02 mmol) in trifluoromethylbenzene (40 mL) was refluxed overnight and then the

resulting mixture was allowed to cool. Succinimide was filtered off, washed with additional trifluoromethylbenzene (20 mL), and then the combined filtrate was evaporated under reduced pressure to give a lightyellow solid. Crystallization from THF gave colourless crystals of **4** (0.56 g, 75%), mp 168 170°C. Elemental analysis: experimental (calculated), %C: 58.19(58.14), %H: 3.07 (3.03), %N: 7.76 (7.70), %Br: 22.12 (22.20), %O: 8.86 (8.90). ^{1}H NMR (DMSO) δ 2.95 (s, 2H), 4.04 (d, 2H), 5.28 (d, 2H), 7.415–7.474 (m, 4H), 7.714–7.829 (m, 6H), 8.089–8.113 (m, 2H), 8.302–8.307 (m, 2H), 8.377–8.383 (m, 2H); ^{13}C NMR (CD_3SOCD_3) δ 19.78 (CH_2), 38.01(CH), 52.76 (CH), 123.25 (CH), 123.43 (CH), 126.97 (C), 128.45 (CH), 128.59 (C), 129.25 (CH), 129.75 (CH), 129.85 (CH), 129.90 (CH), 130.99 (CH), 133.47 (C), 146.05 (C), 149.44 (C), 152.08 (C), 157.43 (C); MS (ESI, m/z +>10%): 630.2 (10), 710.1 (31), 712.1 (75), 723.1 (100), 725.0 (45), 726.1 (20).

Solution and Refinement of the Crystal Structure

Single-crystal X-ray diffraction experiments were carried out on a Bruker SMART Apex 1000 diffractometer equipped with a CCD detector and Mo-Kα sealed tube at 223(2) K. SMART [14] was used for collecting frame data, indexing reflection, and determination of lattice parameters. SAINT [15] was used for integration of intensity of reflections and scaling. SADABS [16] was used for absorption correction and SHELXTL [17] for space group, structure determination, and least-square refinements on F^2. All hydrogen atoms were placed in calculated positions for the purpose of structure factor calculation. All nonhydrogen atoms were refined anisotropically [17], and all hydrogen atoms were included in calculated positions with isotropic thermal motion linked to that of the bonded atom.

SUPPORTING INFORMATION AVALIABLE

Crystallographic data (cif) have been deposited with the Cambridge Structural Data Centre (CCDC), CCDC reference number 684344. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)-1223 336033 or E-mail: deposit@ccdc.cam.ac.uk).

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