# Carbocyclic molecular clefts incorporating hydrogen bonding features

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Chiral carbocyclic cleft molecules incorporating carbonyl, hydroxy, oxime, *o*-phenol and *m*-nitroaryl groups have been synthesised from dibenzobicyclo[*b*,*f*][3.3.1]nona-5a,6a-diene-6,12-dione, a carbocyclic analogue of Tröger's base. These clefts contain similar features to Tröger's base but in addition contain carbonyl groups, which are readily modified, on the chiral bridge that forms the molecular cleft. The oxime and *m*-nitroaryl derivatives have been characterised by single crystal X-ray diffraction. The dihedral angles between the two aromatic rings of these two molecules and those of previously reported related molecules are compared. Two crystal packing motifs are identified and found to influence the size of the dihedral cleft angle of this type of molecule.

Molecular clefts have attracted significant interest in supramolecular chemistry due to their ability to allow functional groups to be oriented in defined geometries.[1,2] Tröger's base (Fig. 1),[3] has attracted particular interest as a building block in supramolecular chemistry due to the chiral diazocine bridge that orients two aryl rings in a tweezer-like structure. Functionalisation of the aromatic rings in Tröger's base has allowed the development of a range of receptors for the recognition of compounds, including nucleic bases, barbiturates and amino acids.[4–12]

We recently reported[13,14] the synthesis and resolution of new functionalised molecular clefts based on a carbocyclic analogue of Tröger's base, dibenzobicyclo[*b*,*f*][3.3.1]nona-5a,6a-diene-6,12-dione, **1**.[15] The chiral carbocyclic bridge provides access to new molecular clefts compared with Tröger's base, with the cleft dimensions being dependent on the nature of the R substituents (Fig. 1). These carbocyclic cleft molecules are readily synthesised in three steps from a substituted benzyl nitrile, can be resolved using chiral HPLC, are able to be synthesised containing deactivating groups on the aromatic rings (R = Br, $NO_2$ in Fig. 1), and contain carbonyl groups in the bridge as additional handles that may be utilised in the design of receptors incorporating the molecular cleft **1**.[13,14]

In order to illustrate the versatility of **1** as a building block in supramolecular chemistry we now report the synthesis of new derivatives of **1** in which hydrogen bonding donor and acceptor recognition sites have been introduced, or are readily accessible *via* standard chemistry, by modification of the dione groups and functionalisation of the aryl rings. Two derivatives have been characterised by single crystal X-ray diffraction analysis. These structures, along with previously published ones,[13,14] have allowed the geometric features of the new clefts to be established and have revealed trends in the packing features of the molecular clefts in the solid state.

## Results and discussion

Reactions involving the carbonyl groups and functionalisation of the aromatic rings of **1** were used to incorporate hydrogen bonding features into the molecular cleft **1** (Schemes 1 and 2). Treatment of the dione **1** with excess hydroxylamine hydrochloride and sodium hydroxide in ethanol afforded the dioxime **2** as a crystalline solid (Scheme 1). The formation of **2** shows that hydroxylamine is able to undergo a nucleophilic addition reaction to the carbonyl groups, presumably from the top face of the cleft, as the lower face is sterically hindered.

Single crystals of the dioxime **2** suitable for analysis by X-ray diffraction were obtained from a methanol solution (Tables 1 and 2). The crystal structure was found to contain two crystallographically independent molecules (**2a** and **2b**) and a methanol solvate molecule; an ORTEP[16,17] depiction of the three molecules is provided in Fig. 2. The three molecules are linked together in a moderately strong oligomeric hydrogen bond network (Table 3). There are three distinct link types in the hydrogen bond chain; one involves two hydrogen bonds between opposing H(1O)–O(1)–N(1) oxime residues on adjacent **2a** molecules. The two molecules are also linked to two crystallographically independent **2b** molecules by two hydrogen bonds between opposing H(2O)–O(2)–N(2) and H(4O)–O(4)–N(4) residues. Two methanol molecules then form a hydrogen bond 'bridge' between the H(3O)–O(3)–N(3) residue of the **2b** molecule and that of an adjacent **2b** molecule. The network is illustrated in Fig. 3. The hydroxy groups in both

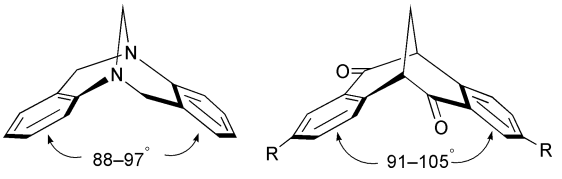
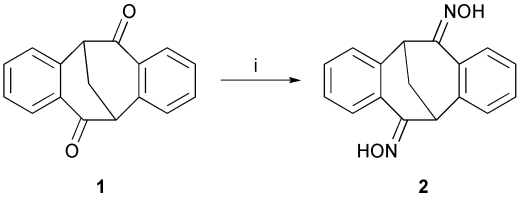



**Fig. 1** Comparison of structural features in Tröger's base (left) and substituted carbocyclic diones (right).




**Scheme 1** *Reagents and conditions*: (i) $NH_2OH{\cdot}HCl$, NaOH, EtOH–$H_2O$

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**Table 1** Crystal data and structure refinement details for **2** and **5**

| | **2** | **5** |
|---|---|---|
| Formula | $C_{17.50}H_{16}N_2O_{2.50}$ | $C_{29}H_{18}N_2O_6$ |
| Molecular weight | 294.32 | 490.45 |
| Crystal system | Triclinic | Orthorhombic |
| Space group | $P\bar{1}$(#2) | $P2_12_12_1$(#19) |
| $a$/Å | 10.282(4) | 7.434(2) |
| $b$/Å | 15.615(6) | 9.8560(14) |
| $c$/Å | 9.472(4) | 29.368(9) |
| $\alpha$/° | 98.290(6) | |
| $\beta$/° | 104.372(6) | |
| $\gamma$/° | 84.571(6) | |
| $U$/Å$^3$ | 1455.1(10) | 2151.8(10) |
| $Z$ | 4 | 4 |
| $T$/K | 293(2) | 123(2) |
| $\lambda$(MoK$\alpha$)/Å | 0.71073 | 0.56356 |
| $\mu$(MoK$\alpha$)/mm$^{-1}$ | 0.091 | 0.067 |
| $N$ | 12 535 | 36 280 |
| $N_{ind}$ | 6455 | 5131 |
| $R_{int}$ | 0.0827 | 0.1010 |
| $N_{obs}$ [$I > 2\sigma(I)$] | 3730 | 4191 |
| $R_1(F)$ | 0.0636 | 0.0359 |
| $wR_2(F^2$ all data) | 0.1584 | 0.0787 |

**Table 2** Selected bond lengths (Å) and angles (°) for **2** and **5**

| | | | |
|---|---|---|---|
| Compound **2** | | | |
| O(1)–N(1) | 1.430(3) | O(2)–N(2) | 1.404(3) |
| O(3)–N(3) | 1.381(3) | O(4)–N(4) | 1.418(3) |
| N(1)–C(7) | 1.268(3) | N(2)–C(15) | 1.283(3) |
| N(3)–C(24) | 1.291(3) | N(4)–C(32) | 1.289(3) |
| C(7)–N(1)–O(1) | 113.8(2) | C(15)–N(2)–O(2) | 114.2(2) |
| C(24)–N(3)–O(3) | 113.4(3) | C(32)–N(4)–O(4) | 112.3(2) |
| C(7)–C(8)–C(9) | 109.44(19) | C(1)–C(16)–C(15) | 108.82(18) |
| C(24)–C(25)–C(26) | 109.12(19) | C(18)–C(33)–C(32) | 110.25(19) |
| O(2)–N(2)–C(15)–C(16) | −0.2(3) | O(3)–N(3)–C(24)–C(25) | −0.6(4) |
| Compound **5** | | | |
| O(1)–C(7) | 1.210(2) | O(2)–C(15) | 1.208(2) |
| O(3)–N(1) | 1.2185(18) | O(4)–N(1) | 1.2355(17) |
| O(5)–N(2) | 0.2209(18) | O(6)–N(2) | 1.2255(17) |
| N(1)–C(20) | 1.469(2) | N(2)–C(26) | 1.460(2) |
| C(1)–C(16)–C(15) | 104.58(12) | C(7)–C(8)–C(9) | 106.88(12) |
| C(3)–C(4)–C(18)–C(19) | −32.2(2) | C(11)–C(12)–C(24)–C(25) | −145.61(15) |
| O(3)–N(1)–C(20)–C(19) | 7.0(2) | O(5)–N(2)–C(26)–C(25) | −5.8(2) |

oxime functional groups are oriented towards the central bridge presumably to facilitate hydrogen bond interactions and perhaps to minimise steric interactions with the adjacent *ortho* hydrogens on the aryl rings.

Compound **3**, which can be resolved by chiral HPLC and prepared in gram quantities,[13] is a key derivative of **1** that is amenable to further modification by transformations involving the aryl bromides as well as the dione functional groups. Stereoselective reduction of the dione **3** with lithium aluminium hydride, in agreement with reduction of the parent dione **1**,[15] afforded diol **4** in which the two hydroxy groups are oriented towards the interior of the cavity (Scheme 2). The dibromodiol **4**, or the dibromodione **3**, may undergo metal catalysed cross-coupling reactions, which are illustrated by two examples with the dione **3**. Thus, treatment of *m*-nitrophenylboronic acid,[18] or dimethyl *o*-hydroxyphenylboronate ester, and dibromodione **3** with a palladium catalyst in dimethoxyethane afforded the dinitrodione **5** and the diphenol **6**, respectively (Scheme 2). Fig. 4 provides an ORTEP depiction of dinitrodione **5**, derived from a single crystal X-ray diffraction analysis. The nitro groups in **5** may be selectively reduced with iron/acetic acid to give the corresponding bisamine while

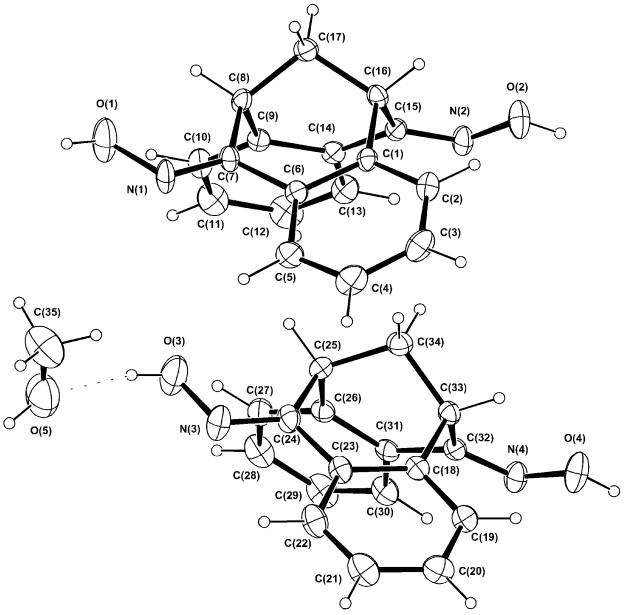



**Fig. 2** ORTEP plot depiction with 20% displacement ellipsoids and numbering scheme for (±)-dioxime **2**. The structure contains two crystallographically independent molecules; **2a** is labelled C(1) to C(17) and **2b** is labelled C(18) to C(34).

**Table 3** Hydrogen bond geometry for dioxime **2**

| Donor | Hydrogen | Acceptor | D–H/Å | H···A/Å | D···A/Å | ∠DHA/° |
|---|---|---|---|---|---|---|
| O(1) | H(1O) | N(1)$^b$ | 0.82 | 2.04 | 2.767(3) | 147.2 |
| O(2) | H(2O) | N(4)$^c$ | 0.82 | 2.20 | 2.915(3) | 145.7 |
| O(3) | H(3O) | O(5)$^a$ | 0.82 | 1.84 | 2.649(3) | 166.7 |
| O(4) | H(4O) | N(2)$^c$ | 0.82 | 2.02 | 2.762(3) | 151.1 |
| O(5)$^a$ | H(5O) | N(3)$^d$ | 0.82 | 2.16 | 2.968(4) | 167.4 |

$^a$ Methanol oxygen. $^b$ Symmetry codes: $1-x$, $2-y$, $-z$; $^c$ $1-x$, $1-y$, $1-z$; $^d$ $1-x$, $2-y$, $-z$.

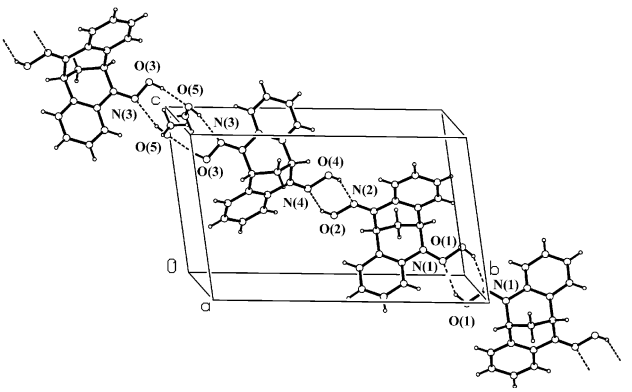
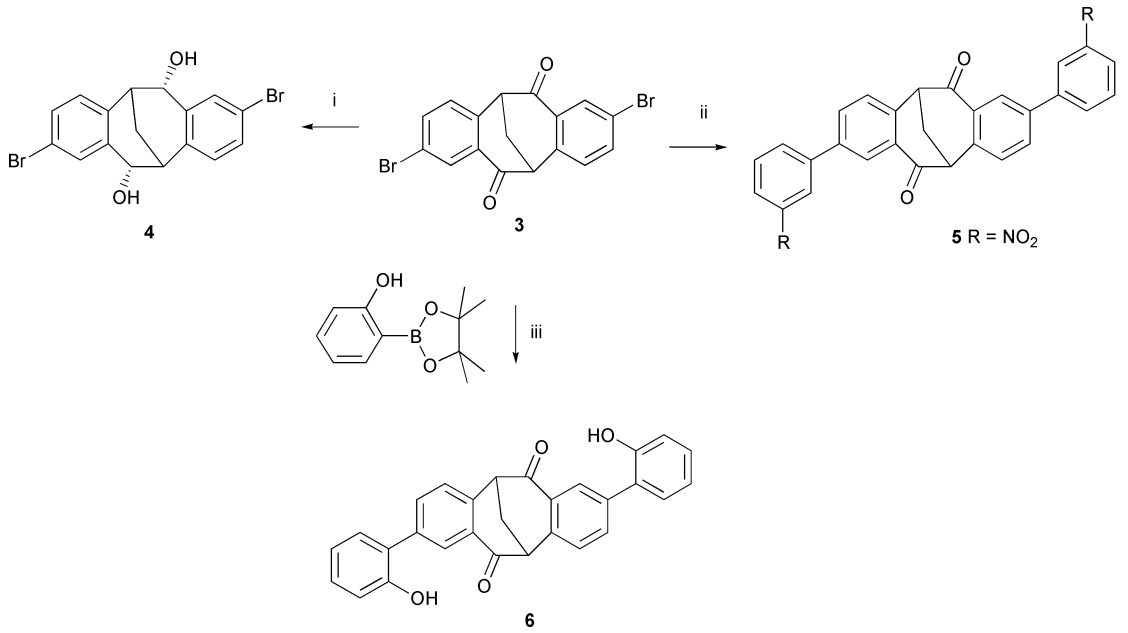



**Fig. 3** The hydrogen bond network in the crystal structure of (±)-dioxime **2**.

catalytic hydrogenation, which has been used in a related system,[13] may be used to reduce both the nitro and carbonyl groups and hence provide entry to receptors containing both amino and hydroxy groups.

A comparison of the interplanar dihedral angles, or cleft angles, between the two aromatic rings of cleft molecules **2** and **5**, and our previously published structures (Table 4),[13,14] shows that the cleft size is influenced by two packing patterns or




**Scheme 2** *Reagents and conditions*: (i) 1 $LiAlH_4$; 2 $H^+/H_2O$. (ii) *m*-$NO_2PhB(OH)_2$, $Pd(PPh_3)_2Cl_2$, $Na_2CO_3$, DME–$H_2O$. (iii) $Pd(dppf)_2Cl_2$, $Na_2CO_3$, DME–$H_2O$.

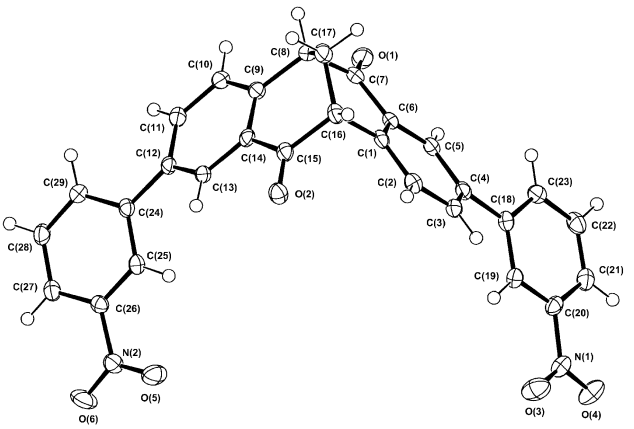



**Fig. 4** ORTEP depiction, with 50% displacement ellipsoids and numbering scheme for (±)-dinitrodione **5**.

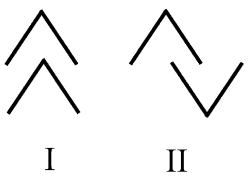



**Fig. 5** Motifs for the two molecular cleft packing types: (I) internal head-to-head, (II) internal tail-to-head.

motifs, schematically illustrated in Fig. 5. For comparsion, Table 4 also lists cleft angles for Tröger's base structures that have the same packing type as the carbocyclic cleft molecules. A cell projection of each motif is shown in Figs. 6 and 7. In the type I structures the apex of one molecule is accommodated in the cleft of another to form columns of apex-to-apex stacked molecules. In the type II structures the terminal residue of one molecule intrudes into the cleft of another. In several cases (FIJTIB and FUPLAD) there is a slight displacement of the two cleft moelcules from the positions indicated in Fig. 5. The cleft angles of the type I structures are larger than those of type II. The apex-to-apex (or bridgehead-to-bridgehead) separation provides a crude measure of the contact between stacked molecules in the type I structures and, as might be expected, there is some correlation between the cleft angle and this distance. The cleft angle dichotomy between type I and type II breaks down for the Tröger's base structures, presumably because of greater variation in the inter-column contact interactions.

In summary, new molecular clefts incorporating hydrogen bonding features have been prepared. The positioning of the hydrogen bond donor/acceptor groups in these receptors can be controlled by the *ortho* or *meta* position on the aryl boronic acid precursor that is coupled with the dibromodione **3**, which is available in optically pure form,[13] thus allowing access to optically pure functionalised clefts. The carbonyl groups may be stereoselectively reduced to the diols, or converted to oximes, and the nitro groups provide entry to amino derivatives. The incorporation of these features into the design of receptors targeted to specific guest molecules is currently under investigation in our laboratory.

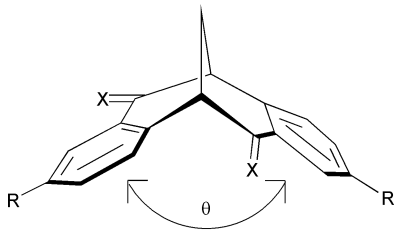
## Experimental

Melting points were measured on a Reichardt hot-stage and are uncorrected. $^1H$ NMR spectra were recorded a Bruker AC200 spectrometer locked on solvent deuterium and referenced to residual solvent peaks. Electron ionisation mass spectra were recorded on an VG Autospec spectrometer at 70 eV. Electrospray (ES) mass spectra were recorded on a LCQ Ion Trap spectrometer, using a capillary voltage of +10 V (positive ion). Values of $m/z$ are quoted with intensities expressed as percentages of the base peak in parentheses. Infrared spectra were recorded on a Perkin Elmer 1600 FT-IR spectrometer. Microanalyses were performed by the Microanalytical Unit at the University of Otago, New Zealand. 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol was purchased from Boron Molecular Pty Ltd, Australia.

### Syntheses

**(±)-Dibenzobicyclo[*b,f*][3.3.1]nona-5a,6a-dien-6,12-dioxime, 2.** Dione **1** (106 mg, 429.8 μmol) was dissolved in ethanol (15 mL) and added to a water solution (6 mL) of hydroxylamine hydrochloride (305 mg, 4.39 mmol) and sodium hydroxide

**Table 4** Interplanar angle $\theta$ between planes defined by benzene rings and packing type in (a) carbocyclic molecular clefts and (b) Tröger's base analogues




(*S*, *S*)-enantiomer

| | $\theta$/degrees | Packing type[a] |
|---|---|---|
| (a) Carbocyclic clefts | | |
| X = NOH, R = H **2** | 101.7(1), 104.3(1)[b] | I [5.594(4), 5.371(4) Å] |
| X = O, R = *p*-$NO_2$Ph **5** | 96.97(5) | I [5.754(2) Å] |
| X = O, R = $CH_3$[14] FIJRUL[c] | 104.3(1), 101.7(1)[b] | I [5.421(5), 5.452(4) Å] |
| X = O, R = $NO_2$ (3-Me deriv)[13] MAZXIU[c] | 102.74(7) | I [5.187(4) Å] |
| X = O, R = Ph[13] MAZWUF[c] | 100.94(7) | I [5.760(3) Å] |
| X = O, R = *p*-MeOPh[13] MAZXAM[c] | 99.74(5) | I [6.040(2) Å] |
| X = O, R = $NO_2$[13] MAZXEQ[c] | 96.09(6)[d] | II |
| X = O, R = Br[14] FIJTIB[c] | 91.4(2) | II |
| (b) Tröger's base analogues from the CSD[c,e] | | |
| DICHIG[c] | 92.7(1) | II |
| FUPLEH[c] | 88.6(2) | I [5.49(1) Å] |
| NIHMEW[c] | 95.9(6) | I [5.13(2) Å] |
| SIRWIZ01[c] | 92.14(3) | I [6.18 Å] |
| DILLEP[c] | 92.9(2), 97.4(2)[b] | I [5.211(7), 5.19(1) Å] |
| FUPLAD[c] | 89.6(7) | II |

[a] See Fig. 5, number in parentheses is the apex to apex distance for type I. [b] Two independent molecules in the asymmetric unit. [c] Cambridge Crystallographic Data Centre database reference code[27]. [d] Reported value was incorrect in reference 13. [e] Other Tröger's base derivatives include DEFQAG, DEGREM, FUPKUW.

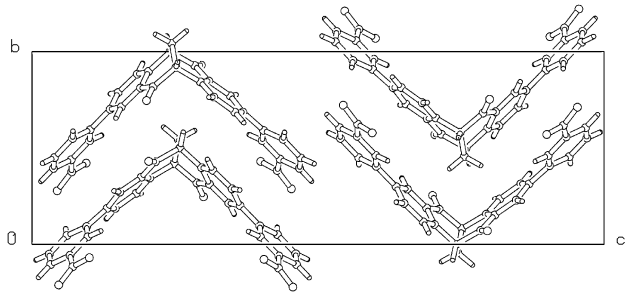



**Fig. 6** Projection along the *a* axis for dioxime **2**, showing the type I motif.

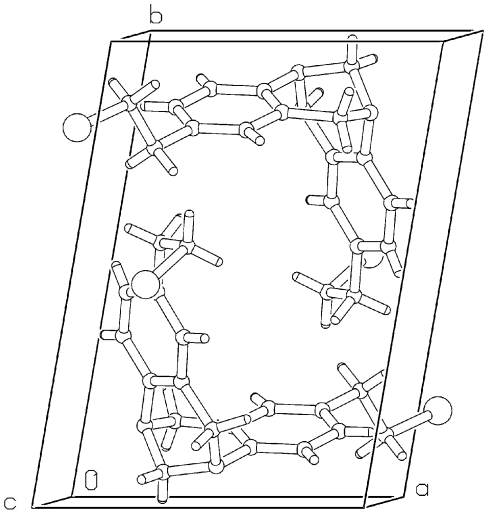



**Fig. 7** Unit cell depiction of the CSD[27] structure DICHIG illustrating the type II motif.

(646 mg, 16.2 mmol). The mixture was stirred at reflux for 24 h, cooled, and acidified with aqueous hydrochloric acid (3 M, 8 mL). The precipitate was filtered, the residue extracted into methanol, evaporated, and recrystallised from methanol to give dioxime **2** (61 mg, 52%) as translucent, off-white plates, mp 156–159 °C (decomp). Anal. found: C, 73.5; H, 4.9; N, 10.2. $C_{17}H_{14}N_2O_2$ requires C, 73.4; H, 5.1; N, 10.1%. $\nu_{max}$(nujol)/cm$^{-1}$ 1596w, 3200s br; $\lambda_{max}$($CH_3OH$)/nm 210 (log $\varepsilon$ 4.82) and 256 (4.56); $\delta_H$ (200 MHz; $CD_3OD$) 2.27 (t, *J* 3.1 Hz, $CH_2$), 5.06 (t, *J* 3.1 Hz, H-5 and H-11), 7.15 (ddd, *J* 7.6, 7.6 and 1.6 Hz, H-2 and H-8), 7.26 (ddd, *J* 7.4, 7.4 and 1.7 Hz, H-3 and H-9), 7.68 (dd, *J* 7.4 and 1.4 Hz, H-4 and H-10) and 7.87 (dd, *J* 7.8, 1.4 Hz, H-1 and -7); *m*/*z* (ES) 279.4 (M + 1, 100%). Crystals suitable for X-ray diffraction were obtained by recrystallisation from methanol.

**(±)-2,8-Dibromodibenzobicyclo[3.3.1]nona-2,6-dien-4,8-diol, 4.** Dibromodione **3** (40 mg, 0.10 mmol) in tetrahydrofuran (1 mL) was added under stirring to a suspension of lithium aluminium hydride (30 mg, 0.79 mmol) in tetrahydrofuran (2 mL) at 0 °C. After stirring for a further 1 h at 0 °C, hydrochloric acid (3 M, 10 mL) was added to the reaction mixture, which was extracted into ether (3 × 15 mL). The combined organic phases were washed with water, saturated sodium bicarbonate solution and brine, dried over anhydrous sodium sulfate and evaporated to dryness. Recrystallisation of the residue from ethyl acetate–hexane (1 : 1) afforded pure diol **4** (35 mg, 88%) as white crystals, mp 225 °C. Anal. found: C, 50.2; H, 3.0. $C_{17}H_{14}O_2Br_2$ requires C, 49.8; H, 3.4%. $\nu_{max}$(nujol)/cm$^{-1}$ 3024 and 2926s; $\lambda_{max}$($CHCl_3$)/nm 244 (log $\varepsilon$

3.19), 274 (2.94) and 282 (2.84); $\delta_H$ (200 MHz; $CD_3OD$) 2.40 (t, *J* 3.2 Hz, $CH_2$), 3.29 (dt, *J* 5.5 and 3.2 Hz, H-5 and H-11), 5.04 (d, *J* 5.5 Hz, H-6 and H-12), 7.14 (d, *J* 8.2 Hz, H-4 and H-10), 7.34 (dd, *J* 8.2 and 2.2 Hz, H-3 and H-9), 7.71 (m, H-1 and H-7); *m*/*z* (EI) 408 ($M^+$, 24%), 406 (37), 392 (33), 390 (29) 111 (38), 109 (26), 97 (58), 95 (39), 83 (58), 57 (100).

**(±)-2,8-Bis(*m*-nitrophenyl)dibenzobicyclo[*b,f*][3.3.1]nona-5a,6a-dien-6,12-dione, 5.** Dibromodione **3** (204 mg, 504 μmol) was dissolved in dimethoxyethane (10 mL) and added to an aqueous solution (5 mL) of *m*-nitrophenylboronic acid (211.7 mg, 1.268 mmol) and sodium carbonate (686 mg, 6.47 mmol). The mixture was stirred at reflux until homogeneous, and dichlorobis(triphenylphosphine)palladium(II) (35.4 mg, 50.4 μmol) was added. The mixture was heated at reflux with vigorous stirring for 45 h, evaporated and partitioned between dichloromethane (100 mL) and water (100 mL). The organic layer was filtered, evaporated and purified by flash chromatography over silica (50–100% dichloromethane–hexane) to dinitrodione **5** (113 mg, 46%) as a white amorphous solid, mp 277–280 °C. Anal. found: C, 70.9; H, 3.4; N, 5.8. $C_{29}H_{18}N_2O_6$ requires C, 71.0; H, 3.7; N, 5.7%. $\nu_{max}(CHCl_3)/cm^{-1}$ 1352s, 1532s, 1687m; $\lambda_{max}(CH_2Cl_2)$/nm 194 (log ε 4.9), 230 (4.9) and 254 (5.0); $\delta_H$ (200 MHz; $CDCl_3$) 3.12 (t, *J* 2.8 Hz, $CH_2$), 4.18 (t, *J* 2.9 Hz, H-5 and H-11), 7.61 (dd, *J* 8.0 and 8.0 Hz, H-5′ and H-5″), 7.65 (d, *J* 8.1 Hz, H-4 and H-10), 7.82 (dd, *J* 8.1 and 2.1 Hz, H-3 and H-9), 7.88 (dm, *J*~7.9 Hz, H-6′ and H-6″), 8.22 (dm, *J*~8.6 Hz, H-4′ and H-4″), 8.26 (d, *J* 2.1 Hz, H-1 and H-7) and 8.41 (m, H-2′ and H-2″); *m*/*z* 491 (M + 1, 33%), 490 (100). Crystals suitable for X-ray diffraction were obtained from a dichloromethane–methanol solution.

**(±)-2,8-Bis(*o*-hydroxyphenyl)dibenzobicyclo[*b,f*][3.3.1]nona-5a,6a-dien-6,12-dione, 6.** Dibromodione **3** (302 mg, 0.739 mmol), 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (0.34 mL, 1.63 mmol), dichlorobis(diphenylphosphinoferrocene)palladium(II) (20.5 mg, 27.9 μmol) and sodium carbonate (238 mg, 2.25 mmol) were stirred at reflux in dimethoxyethane (15 mL) and water (3 mL) for 23 h. The reaction mixture was cooled, diluted with water (50 mL) and extracted with dichloromethane. The combined organic extracts were dried over anhydrous sodium sulfate and evaporated to give the crude product as a brown solid (208 mg, 65%). Purification by flash chromatography over silica (10–20% ethyl acetate–dichloromethane) afforded some mono-substituted product followed by the dione **6**, which was obtained as an off-white solid, mp 292–294 °C/$\lambda_{max}(CHCl_3)$/nm 374 (sh) (ε 702), 354 (sh) (1529), 340 (1760), 296 (sh) (5648), 252 (22 090); $\delta_H$ (300 MHz, $CD_3OD$) 2.99 (t, *J* 3.5, $CH_2$), 3.98 (t, *J* 3.0, H-5 and H-11), 6.75–6.81 (m, 4H-Ar), 7.03–7.14 (m, 4H-Ar), 7.41 (d, *J* 8.0 Hz, H-4 and H-10), 7.70 (dd, *J* 8.0 and 1.9 Hz, H-3 and H-9), 8.03 (d, *J* 2.0 Hz, H-1 and H-7); *m*/*z* (EI) 432 ($M^+$, 42%); 245 (26), 219 (29), 186 (60), 149 (100), 128 (31), 115 (26), 91 (41), 71 (54); HRMS calcd for $C_{29}H_{20}O_4$ 432.1937, found 432.1916.

### Crystallographic data collection and structure determination for 2 and 5

The diffraction data integration and reduction for **2** and **5** were undertaken with SAINT and XPREP,[19] subsequent computations were carried out with the XShell,[20] teXsan[21] and WinGX[22] graphical user interfaces. There was no crystal decay during the data collections. The structures were solved by direct methods with SIR97[23] and extended and refined with SHELXL97.[24] Anisotropic displacement parameters were refined for the non-hydrogen atoms and a riding atom model was used for hydrogen atoms. A very poor quality colourless blade-like crystal of **2** was mounted on a Bruker SMART 1000 CCD diffractometer employing graphite monochromated MoKα radiation generated from a sealed tube. A Gaussian absorption correction was applied to the data.[19,25] for **2**. The asymmetric unit contains two crystallographically independent molecules, together with a methanol solvate molecule. Data for a small crystal of dinitrodione **5** were obtained during commissioning studies at the ChemMatCARS facility at the Advanced Photon Source of the Argonne National Laboratory (Argonne, IL, USA). Double diamond (111) reflections were used to obtain monochromated 0.56356 Å radiation from the synchrotron source, and harmonics were eliminated with mirrors. A colourless columnar crystal was attached to a short length of fibre supported on a thin piece of copper wire inserted in a copper mounting pin. The pin and crystal were mounted on a Bruker Kappa diffractometer equipped with a 4-chip mosaic CCD detector and an Oxford Scientific Cryojet operating at 123(2) Kelvin. The absolute structure could not be reliably determined, with the Flack parameter[26] refining to 0.0(12).

CCDC reference numbers 184112 and 184113. See http://www.rsc.org/suppdata/nj/b1/b109055k/ for crystallographic data in CIF or other electronic format.

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