Heterocalixarenes Part 3: Bis-oxo-bridged calix[1]cyclicurea[3]arene and calix[1]cyclicurea[1]pyridine[2]arenes. Synthesis, X-ray crystal structure and conformational analysis[1]

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Received (in Cambridge, UK) 24th August 1999, Accepted 19th January 2000

The Friedel–Crafts aroylations of 2- and 4-methylanisole with isophthaloyl dichloride or pyridine-2,6-dicarbonyl dichloride provide respective diones, which on bromination with NBS provide corresponding bisbromomethyl derivatives that undergo simple cyclocondensations with embedded cyclicurea-containing heterocycles, *viz.* benzimidazol-2(1*H*)-one, 5-nitrobenzimidazol-2(1*H*)-one, 5,6-dinitrobenzimidazol-2(1*H*)-one, uracil and quinazoline-2,4(1*H*,3*H*)-dione to form 11 new bis-oxo-bridged heterocalix[4]arenes (**11**–**19**, **24**, **25**). The X-ray crystal structure of the **11**–benzene complex, ^{1}H–^{1}H COSY spectra and energy-minimization studies assign partial cone conformations to these heterocalix[4]arenes. The variation in the cyclicurea moiety controls the flexibility of these heterocalix[4]arenes.

The derivatizations on the upper and/or lower rims of conventional calix[*n*]arenes[2] and replacement of their phenylene units with heterocyclic moieties[3] provide tremendous novel opportunities for generating receptors with unique inclusion/complexation characteristics and related non-covalent host–guest interactions. Whereas extensive work has been done on the modification of hydroxy and *para*-alkyl groups,[2] modifications on the methylene bridge(s) in the backbone of calixarenes have been only recently studied.[4,5] The presence of alkyl and/or aryl group(s) on a methylene carbon creates new stereochemical centres and thus affects the geometries of the resulting calixarenes.[4] The presence of two bridge(s) in calixarenes could further increase their versatility both due to possible participation of carbonyl group in binding and to their being a chemically reactive and prochiral centre. So far the synthesis of oxo-bridged calixarenes through oxidation of preformed calixarenes has not met with much success.[5] The cyclizations of preformed oxo-bridged precursors have provided monooxo-bridged calix[4/5/6]arenes,[4d] which exhibit a strong intramolecular H-bonding between carbonyl oxygen and an adjacent phenolic OH group and result in greater conformational flexibility than the parent calixarenes.

In the present investigations, a simple, high yielding, three-step approach, involving Friedel–Crafts aroylation as a key step, has been used to synthesize eleven new heterocalix[4]arenes (**11**–**19**, **24**, **25**) possessing two carbonyl units in place of methylene spacers and one or two heterocyclic units in place of phenylene rings. The ^{1}H NMR, ^{1}H–^{1}H COSY spectra and energy-minimization studies define partial cone conformations to these calixarenes, which has been confirmed in one case, *i.e.* the **11**–benzene complex, by X-ray crystal-structure determination.

Results and discussion

Synthesis

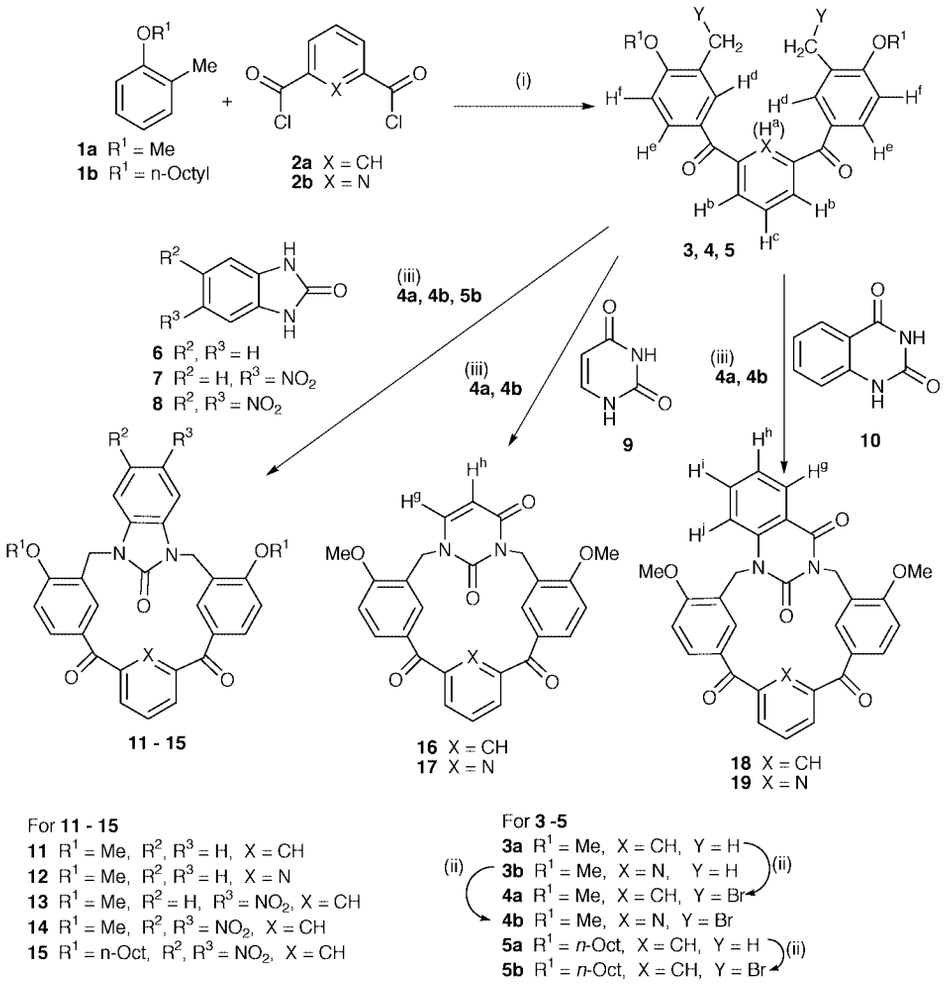
Friedel–Crafts aroylation of 2-methylanisole **1a** with isophthaloyl dichloride **2a** (2:1) in chloroform in the presence of $AlCl_3$ (anhydrous) provides **3a** (65%), mp 136 °C, M^+ 374. The bromination of **3a** with *N*-bromosuccinimide (NBS) provides dibromide **4a** (80%), mp 120 °C, M^+ 530, 532, 534 (1:2:1). The intermolecular cyclocondensation of **4a** with benzimidazol-2(1*H*)-one **6** under solid–liquid phase-transfer catalytic (PTC) conditions [CH_3CN–K_2CO_3–tetrabutylammonium hydrogen sulfate ($TBAHSO_4$)] provides bisoxocalix[1]benzimidazol-2(1*H*)-one[3]arene **11** (70%), mp 352–354 °C, M^+ 504 (Scheme 1). Similarly, **4a** reacts with 5-nitrobenzimidazol-2(1*H*)-one (**7**), 5,6-dinitrobenzimidazol-2(1*H*)-one **8**, uracil **9** and quinazoline-2,4(1*H*,3*H*)-dione **10** under PTC conditions to provide, respectively, heterocalix[4]arenes **13** (35%), mp >355 °C, M^+ 549; **14** (45%), mp >355 °C, M^+ 594; **16** (60%), mp 333–335 °C, M^+ 482 and **18** (65%), mp 337–339 °C, M^+ 532. Similarly, the reaction of 2-methylanisole **1a** with pyridine-2,6-dicarbonyl dichloride **2b** provides **3b** (60%), mp 155 °C, M^+ 375. The bromination of **3b** to **4b** and subsequent cyclizations with heterocycles **6**, **9** and **10** provide, respectively, heterocalix-[4]arenes **12** (45%), mp 299 °C, M^+ 505; **17** (40%), mp 335 °C, M^+ 483 and **19** (45%), mp 320 °C, M^+ 533. Friedel–Crafts aroylation of **1b** with **2a**, subsequent NBS bromination, and cyclization with **8** provides heterocalixarene **15** (12%), mp 319–320 °C, M^++1 791.

Friedel–Crafts aroylation of 4-methylanisole **20** with isophthaloyl dichloride **2a** (2:1) in chloroform in the presence of $AlCl_3$ (anhydrous) provides **21** (17%), thick liquid, M^+ 286 and **22** (28%), mp 80 °C, M^+ 374. The bromination of **22** with NBS provides dibromide **23** (79%), mp 40 °C, M^+ 530, 532, 534 (1:2:1). The intermolecular cyclocondensations of **23** with **6** and **9** provide heterocalix[4]arenes **24** (33%), mp 240 °C, M^+ 504, and **25** (10%), mp 280 °C; M^+ 482 (Scheme 2).

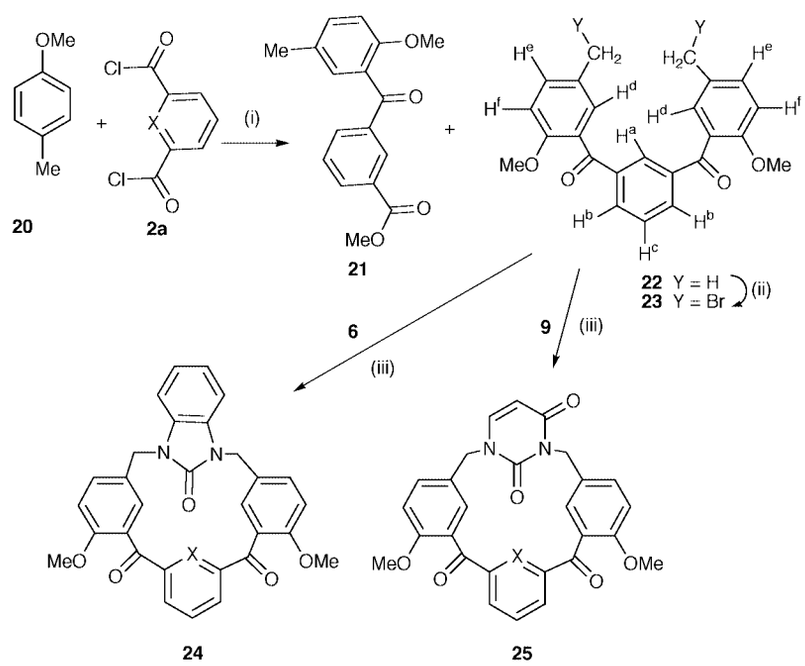
Conformational analysis

(A) Solid state – X-ray. Compound **11**, on recrystallization from chloroform–benzene (1:1 *v*/*v* mixture), forms a **11**–benzene complex of 1:1 stoichiometry. The X-ray crystal structure (Fig. 1) of the **11**–benzene complex reveals a typical calix inclusion complex, where **11** attains partial cone conformation with the isophthaloyl unit (ring A) placed in an opposite (*anti*) direction to the rest of the rings (Fig. 2). The torsion angles[6] φ and χ around connecting methylene and carbonyl carbons C(8), C(16), C(23) and C(31) change their signs as + −, + −, + + and − −, indicating a partial cone conformation[2d] (Table 1). These four connecting carbons deviate approximately ± 0.08 Å from their best fitted mean plane. The interplanar angles between this plane and benzimidazol-2-(1*H*)-one ring (C) and

DOI: 10.1039/a906883j



Scheme 1 *Reagents and conditions*: (i) $AlCl_3$, $CHCl_3$, stirring, 40 °C; (ii) NBS, CCl_4, reflux; (iii) K_2CO_3–CH_3CN–$TBAHSO_4$, reflux.



Scheme 2 *Reagents and conditions*: (i) $AlCl_3$, $CHCl_3$, stirring, 40 °C; (ii) NBS, CCl_4, reflux; (iii) K_2CO_3–CH_3CN–$TBAHSO_4$, reflux.

isophthaloyl ring (A) are 57.7(1)° and 53.7(1)° whereas the two methoxy aryl rings B and B′ are making dihedral angles 42.8(1)° and 48.5(1)°, respectively, The dihedral angle between rings B and B′, and between A and C, are 91.3(2)° and 4.1(1)°, respectively, showing that the two methoxy aryl rings are almost perpendicular whereas the benzimidazol-2-(1*H*)-one ring 'C' and isophthaloyl unit ring 'A' are parallel to each other (Fig. 2). The two rings in pairs A, C and B, B′ are placed 7.4(1) Å and 6.8(1) Å apart, respectively giving rise to an almost square cavity. Both the methoxy groups are *anti* with respect to the aryl ring B and B′ (Table 1) and remain exocyclic to the cavity.

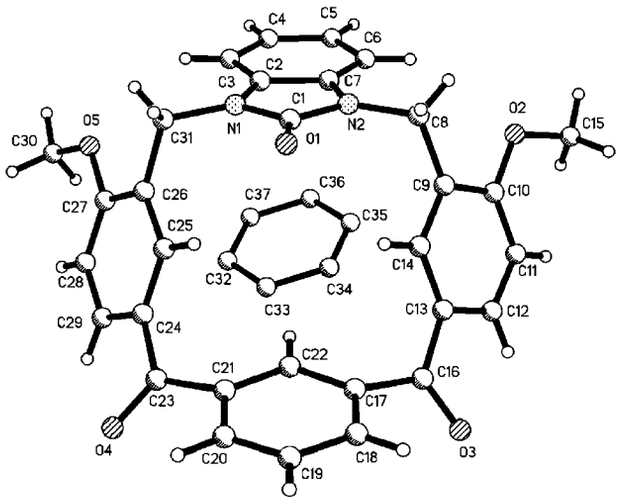


Fig. 1 Prospective view of **11**–benzene complex, showing the atom-labelling scheme.

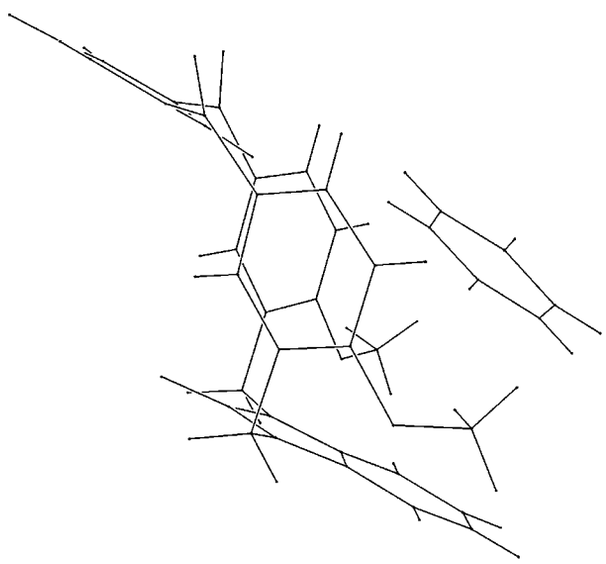


Fig. 2 The side view of the **11**–benzene complex, showing partial cone conformation of **11** and placement of benzene with respect to benzimidazol-2(1*H*)-one of **11**.

Table 1 Important torsion angles (°) for complex **11**–benzene

C(25)–C(26)–C(31)–N(1)	74.6(7)
C(26)–C(31)–N(1)–C(1)	−86.6(6)
C(1)–N(2)–C(8)–C(9)	90.4(6)
N(2)–C(8)–C(9)–C(14)	−71.1(6)
C(14)–C(13)–C(16)–C(17)	21.3(8)
C(13)–C(16)–C(17)–C(22)	52.9(7)
C(22)–C(21)–C(23)–C(24)	−39.7(8)
C(21)–C(23)–C(24)–C(25)	−35.0(8)
C(15)–O(2)–C(10)–C(9)	166.8(5)
C(30)–O(5)–C(27)–C(26)	−179.2(5)

The solvent benzene molecule deviates significantly from planarity, having a maximum rms deviation of 0.09 Å from a least-square plane. This may be due to slight disorder in the ring. The benzene molecule exhibits a face-to-face π–π interaction with the benzimidazol-2(1*H*)-one unit at a distance of 4.08(1) Å (Fig. 3). The dihedral angle between the mean plane of these two rings is 19.7(2)°. The benzimidazol-2(1*H*)-one ring also shows an intermolecular face-to-face π–π interaction with the isophthaloyl ring of the symmetry-related molecule (*x*, *y* + 1, *z*), at 3.67(1) Å. Therefore, the benzimidazol-2(1*H*)-one ring is sandwiched between a benzene molecule on one side and an isophthaloyl ring on other side. This gives a stacking of molecules down the '*b*' axis (Fig. 3).

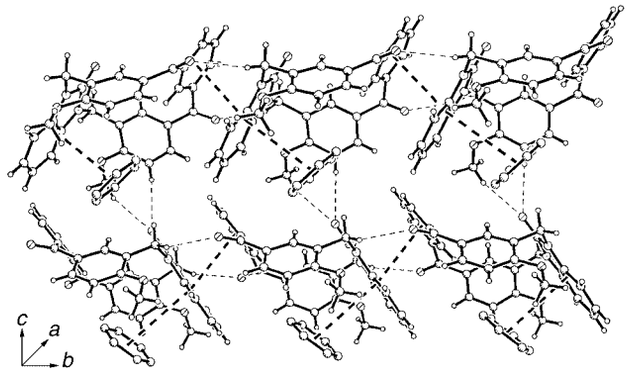


Fig. 3 Packing diagram of **11**–benzene complex showing H-bonding and π–π interactions.

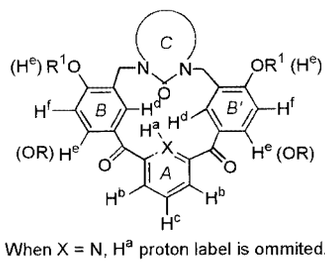


Fig. 4 When X = N, H^a proton label is omitted.

Table 2 H-bonding interactions (distance in Å and angle in °) for complex **11**–benzene

	X···O	H···O	∠X···H···O
C(11)···O(1) (i)	3.42	2.54	158.8
C(15)···O(1) (i)	3.37	2.50	151.5
C(8)···O(3) (ii)	3.36	2.51	146.0
C(31)···O(4) (ii)	3.39	2.62	146.4

(i) $x, -y, z + 1/2$; (ii) $x, y + 1, z$

Apart from these π–π interactions, different molecules are held together by weak C···O intermolecular H-bonds (Fig. 3). Imide carbonyl oxygen O(1) is H-bonded to carbon C(15) of the methoxy group and aromatic carbon C(11) of aryl unit B, whereas the oxygens of the bridging carbonyl groups, O(3) and O(4), are H-bonded to the bridging methylene carbons C(8) and C(31), respectively (Table 2).

(B) Solution phase – ^{1}H NMR. The rationalization of multiplicities and chemical shifts of various proton signals in the ^{1}H NMR spectra and a comparison with their acyclic counterparts provides a useful tool for assigning the geometries of calixarenes. Assignments of the chemical shifts of various protons have been carried out by decoupling experiments and ^{1}H–^{1}H COSY spectra. For presentation of these data, as far as possible a uniform labelling pattern (Fig. 4) has been adopted. In the case of pyridine-containing calixarenes, as one CH has been replaced by =N-, the H^a label has been omitted.

The ^{1}H NMR spectrum of **11** in $CDCl_3$ shows one singlet due to 2 × OMe protons, one broad singlet at δ 5.10 due to two NCH_2 units and signals for ArH. In the aromatic region, irradiation of the triplet (δ 7.54), which is obviously due to the H^c proton, converts the multiplet at δ 7.75–7.81 into a distorted singlet. So, the signals of H^b protons are embedded in this multiplet. Similarly, irradiation of the double doublet at δ 8.03 changes the pattern of the multiplet (δ 7.02–7.13), and thus the signals of H^f protons are embedded into this multiplet. In the ^{1}H–^{1}H COSY spectrum of **11**, the triplet (H^c) shows one cross-peak at δ 7.79 (H^b, doublet). This doublet (δ 7.79) has one

Table 3 Nature of NCH_2 signals and change in the chemical shift of the protons H^a and H^d in heterocalixarenes **11**–**19**, **24** and **25** with respect to acyclic precursors

	Nature of NCH_2 protons	Change in chemical shift of H^a and H^d	
		H^a	H^d
11	Broad singlet	−0.8	−0.1
16	Broad AB quartet	−0.6	−0.5
18	AB quartet	−0.6	−0.9
13	Sharp singlet	−0.6	<−0.1
14	Sharp singlet	−0.6	−0 ± 0.1
15	Sharp singlet	−0.6	<−0.1
12	AB quartet		−0.7 ± 0.1
17	AB quartet		−0.8 ± 0.1
19	AB quartet		−1.3 ± 0.1
24	Sharp singlet	−0.7	−0.3
25	Sharp singlet	−0.7	<−0.1

cross-peak at δ 7.29 (H^a, singlet). The double doublet (δ 8.03), which is obviously due to the H^e proton, has two cross-peaks δ 7.75 (H^d, singlet) and δ 7.03 (H^f, doublet). The ^{1}H NMR spectrum of **11** in $CDCl_3$ + TFA shows an AB quartet (5.03, 5.43, *J* 17 Hz) due to the NCH_2 protons.

The ^{1}H NMR spectrum of **12** in $CDCl_3$ shows one singlet at δ 4.05 due to OMe protons, one AB quartet at δ 4.95, 5.27 due to two NCH_2 groups, one singlet at δ 6.96 due to four benzimidazolone aromatic H^s, three doublets at δ 7.05, 7.41 and 7.53 due to H^f, H^d and H^b, respectively, one triplet at δ 7.87 due to H^c and one double doublet at δ 8.11 due to 2 × H^e protons. The well defined ^{1}H NMR spectrum and presence of one AB quartet due to the NCH_2 groups point toward a rigid conformation in solution phase. Correlation in various proton signals has been determined by decoupling experiments.

The ^{1}H NMR spectrum of **16** in $CDCl_3$ + TFA exhibits two singlets (δ 3.98, 4.01) for OMe, three broad singlets (δ 4.52, 5.05, 5.42) for two NCH_2 groups, two doublets (δ 7.09, 7.13) for two aromatic H^f, one multiplet (δ 8.01–8.10) for four aromatic H^e, $H^{e'}$, H^b and $H^{b'}$, one singlet (δ 7.46) for H^a, one triplet (δ 7.78) for H^c, one broad singlet (δ 7.41) for H^d and $H^{d'}$, and two doublets (δ 6.15, 7.59) for uracil H. Thus the non-equivalence of N-1 and N-3 positions of the uracil creates a dissymmetry in the calixarene.

In the ^{1}H NMR spectrum of **18**, two OMe groups appear as two singlets at δ 4.05 and 4.09, two NCH_2 group constitute two AB quartets, and remaining protons appear in a well defined pattern in the aromatic region. In the ^{1}H–^{1}H COSY spectrum of **18**, two triplets (δ 7.40, 7.74) have cross-peaks against each other. Obviously, these triplets are due to H^h and H^i. Also, both of these triplets have cross-peaks at δ 7.15 and 8.15. These two peaks are, obviously, due to H^g and H^j. Because of H^g being *ortho* to the carbonyl group, the downfield signal (δ 8.15) could be assigned to H^g. Accordingly, the doublet at δ 7.15 is due to H^j, the triplet at δ 7.74 due to H^h and the triplet at δ 7.40 due to H^i. Now the triplet at δ 7.58 (H^c) has one cross-peak at δ 7.85 (m, H^b and $H^{b'}$) and it has one more cross-peak at δ 7.49 (s, H^a). Similarly, the two multiplets δ 7.12–7.22 and 8.11–8.24 have a correlation and the second multiplet has two cross-peaks at δ 6.93 and 7.01, which are obviously due to H^d and $H^{d'}$. The well defined nature of the spectrum and the appearance of two NCH_2 groups as two AB quartets show that the conformation is rigid and the non-equivalence of two cyclic urea nitrogens creates a dissymmetry in the molecule. The heterocalixarenes **17** and **19** show similar patterns in their ^{1}H NMR spectra, which reveal that the conformations are similar.

The change in chemical shifts of H^a and H^d in these calixarenes as compared with those H in their precursors is given in Table 3. It may be seen that in all heterocalix[4]arenes **11**–**19**, **24**, **25**, H^a are shifted upfield by the same order ($\Delta\delta$ −0.7 ± 0.1), which points toward a similar placement of the isophthaloyl unit in these calix[4]arenes. The upfield shift of the protons H^a ($\Delta\delta$ −0.7) as compared with the acyclic precursors revealed that the isophthaloyl ring is perpendicular to the anisole units and thus H^a faces the π-electron ring currents of these adjacent anisole units. Even in **24** and **25** the change in position of the OMe group does not affect their conformations. In the ^{1}H NMR spectra, the NCH_2 signals of benzimidazol-2(1*H*)-one and its nitro derivatives heterocalix[4]arenes (**11**–**15** and **24**), appear as singlets (except for **12**), but in the case of uracil-based heterocalix[4]arenes (**16**, **17** and **25**), NCH_2 appears as two broad singlets or as two AB quartets, and in case of quinazoline-2,4(1*H*,3*H*)-dione-based heterocalix[4]arenes (**18** and **19**) NCH_2 appears as two AB quartets. Apparently, while moving from benzimidazol-2(1*H*)-one ⟶ uracil ⟶ quinazoline-2,4(1*H*,3*H*)-dione moieties, the rigidity in conformations of the respective calixarenes increases. As a result, the anisole rings undergo slow rotation (NMR time scale) and H^d, which faces the π-cloud of the opposite ring, is shifted upfield by δ 0.5–1.3. Therefore, these heterocalix[4]arenes possess variable flexibility depending on the nature of the heterocyclic moiety(ies).

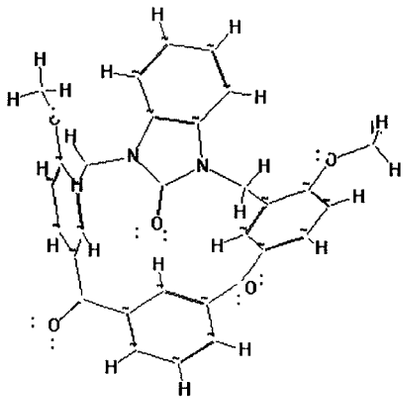


Fig. 5 Energy-minimized partial cone structure of calix[4]arene **11**.

MMX energy-minimization studies[7] on these heterocalix[4]arenes reveal that all of them have by-and-large similar conformations. In these conformations the isophthaloyl ring is placed perpendicular to the adjacent phenylene rings, as shown in their X-ray and ^{1}H NMR spectra. The energy-minimized conformation of the representative case of the heterocalix[4]arenes **11** is shown in Fig. 5.

Therefore, Friedel–Crafts aroylation of 2- or 4-methylanisole or 2-methylphenyl octyl ether with isophthaloyl dichloride or pyridinedicarbonyl dichloride constitutes a key step of the three-step methodology developed for the synthesis of bis-oxo-bridged heterocalix[4]arenes. The X-ray crystal structure of the **11**–benzene complex, as well as ^{1}H NMR and energy-minimization studies, define an inward flattened partial cone conformation to these calixarenes. The flexibility in these heterocalixarenes is affected by the nature of the cyclic urea moiety present.

Experimental

General

For general experimental details see ref. 8. In ^{13}C NMR spectral data, the +ve and −ve signals correspond to a DEPT-135 spectrum, and 'ab' corresponds to quaternary carbon signals, which are absent in DEPT-135 but appear in a normal ^{13}C NMR spectrum. 5-Nitrobenzimidazol-2(1*H*)-one and 5,6-dinitrobenzimidazol-2(1*H*)-one were prepared according to the reported procedures.[9]

Synthesis of the diones 3a,b, 5a and 22. General procedure

A solution of isophthaloyl dichloride **2a** (10.0 g, 0.05 mol) in chloroform (200 ml) containing suspended $AlCl_3$ (anhyd.)

(13.5 g, 0.11 mol) was stirred for 2 h. The solution of 2-methylanisole **1a** (18.3 g, 0.15 mol) in chloroform (20 ml) was added dropwise during 30 min. The mixture was stirred for 48 h and then refluxed for 15 min to ensure the completion of the reaction. After cooling in an ice-bath, the reaction mixture was quenched with methanol (30 ml) and washed with water. The organic layer was dried over Na_2SO_4 (anhyd.). The chloroform layer was distilled and the residue was crystallized from methanol–dichloromethane mixture to give the pure dione **3a**. Similarly, the reaction of the pyridinedicarbonyl dichloride **2b** with 2-methylanisole **1a** gave the dione **3b**. Similar reactions of 4-methylanisole **20** and 2-methylphenyl octyl ether **1b** with isophthaloyl dichloride provided a mixture of mono ketone **21** and dione **22**, and **5a**, respectively, which were purified by column chromatography.

3a: (65%); mp 136 °C (from CH_2Cl_2 + MeOH); *m*/*z* 374 (M^+); $\delta_H(CDCl_3)$, 2.26 (6H, s, 2 × CH_3), 3.91 (6H, s, 2 × OCH_3), 6.87 (2 H, d, *J* 8.4 Hz, ArH), 7.57–7.70 (5H, m, ArH), 7.96 (2H, d, *J* 8.4 Hz, ArH), 8.06 (1H, s, ArH); $\delta_C(CDCl_3)$ (normal/DEPT-135) 16.26 (+ve, CH_3), 55.49 (+ve, OCH_3), 109.04 (+ve, ArCH), 126.92 (ab, ArC), 128.26 (+ve, ArCH), 129.18 (ab, ArC), 130.67 (+ve, ArCH), 132.60 (+ve, ArCH), 138.47 (ab, ArC), 161.74 (ab, ArC), 194.90 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1600, (C=O), 1650 (C=O), 1670 (C=O) (Found: C, 77.2; H, 6.4. $C_{24}H_{22}O_4$ requires C, 77.01; H, 5.88%).

3b: (60%); mp 155 °C (from $CHCl_3$); *m*/*z* 375 (M^+); $\delta_H(CDCl_3)$ 2.16 (6H, s, 2 × CH_3), 3.89 (6H, s, 2 × OCH_3), 6.79 (2H, d, *J* 8.4 Hz, ArH), 8.02–8.21 (7H, m, ArH); $\delta_C(CDCl_3)$ (normal/DEPT-135) 16.17 (+ve, CH_3), 55.51 (+ve, OCH_3), 108.96 (+ve, CH), 126.32 (+ve, CH), 128.34 (ab, C), 131.93 (+ve, CH), 133.73 (+ve, CH), 138.00 (+ve, CH), 154.59 (ab, C), 161.97 (ab, C), 191.30 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1655 (C=O), 1650 (C=O), 1599 (C=O) (Found: C, 73.7; H, 5.4; N, 3.9. $C_{23}H_{21}N_1O_4$ requires C, 73.60; H, 5.60; N, 3.73%).

5a: (70%); mp 58 °C (from EtOH); *m*/*z* 570 (M^+); $\delta_H(CDCl_3)$ 0.88 (6H, t, *J* 6.4 Hz, 2 × CH_3), 1.16–1.47 (20H, m, 10 × CH_2), 1.83 (4H, q, *J* 6.4 Hz, 2 × CH_2), 2.25 (6H, s, 2 × CH_3), 4.02 (4H, t, *J* 6.4 Hz, 2 × OCH_2), 6.81 (2H, d, *J* 6.8 Hz, 2 × ArH), 7.54–7.67 (5H, m, 5 × ArH), 7.93 (2H, d, *J* 6.8 Hz, 2 × ArH), 8.03 (1H, s, ArH); $\delta_C(CDCl_3)$ (normal/DEPT-135) 14.03 (+ve, CH_3), 16.22 (+ve, CH_3), 22.58 (−ve, CH_2), 26.04 (−ve, CH_2), 29.16 (−ve, CH_2), 29.25 (−ve, CH_2), 31.73 (−ve, CH_2), 68.06 (−ve, OCH_2), 109.88 (+ve, ArCH), 126.81 (+ve, ArCH), 128.04 (ab, C), 128.94 (ab, C), 130.49 (+ve, ArCH), 132.36 (ab, C), 132.55 (ab, C), 138.48 (ab, C), 161.15 (ab, C), 194.27 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1605 (C=O), 1652 (C=O), 1676 (C=O).

21: (17%); thick liquid; *m*/*z* 286 (M^+, 100%); $\delta_H(CDCl_3)$ 2.34 (3H, s, CH_3), 3.66 (3H, s, OCH_3), 3.92 (3H, s, CO_2CH_3), 6.87 (1H, d, *J* 8.4 Hz, ArH), 7.20 (1H, s, ArH), 7.27 (1H, d, *J* 7.8 Hz, ArH), 7.50 (1H, t, *J* 7.8 Hz, ArH), 7.98 (1H, d, *J* 7.8 Hz, ArH), 8.20 (1H, d, *J* 7.8 Hz, ArH), 8.39 (1H, s, ArH); δ_C ($CDCl_3$) 20.40 (+ve, CH_3), 52.16 (+ve, OCH_3), 55.55 (+ve, OCH_3), 111.54 (+ve, ArCH), 118.45 (+ve, ArCH), 127.65 (ab, ArC), 128.24 (+ve, ArCH), 130.19 (+ve, ArCh), 130.29 (+ve, ArCh), 132.45 (+ve, ArCH), 133.56 (ab, ArC), 137.49 (+ve, ArCH), 137.62 (ab, ArC), 155.48 (ab, ArC), 161.48 (ab, ArC), 166.23 (ab, C=O), 195.27 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1640, (C=O), 1670 (C=O).

22: (28%); mp 80 °C (from ethyl acetate); *m*/*z* 374 (M^+); $\delta_H(CDCl_3)$ 2.33 (6H, s, 2 × CH_3), 3.65 (6H, s, 2 × OCH_3), 6.84 (2H, d, *J* 8.2 Hz, ArH), 7.17 (2H, s, ArH), 7.23 (2H, d, *J* 8.2 Hz, ArH), 7.47 (1H, t, *J* 7.6 Hz, ArH), 7.94 (2H, d, *J* 7.6 Hz, ArH), 8.17 (1H, s, ArH); $\delta_C(CDCl_3)$ (normal/DEPT-135) 20.42 (+ve, Me), 55.60 (+ve, OMe), 111.62 (+ve, ArH), 127.99 (+ve, ArCH), 128.35 (ab, ArC), 130.04 (ab, ArC), 130.19 (+ve, ArCH), 130.90 (+ve, ArCH), 132.68 (+ve, ArCH), 133.48 (+ve, ArCH), 138.24 (ab, ArC), 155.45 (ab, ArC), 195.39 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1650 (C=O), 1672 (C=O) (Found: C, 77.5; H, 5.5. $C_{24}H_{22}O_4$ requires C, 77.01; H, 5.88%).

Synthesis of dibromides 4a,b, 5b and 23. General procedure

A solution of dione **3a** (4.0 g, 0.011 mol) in CCl_4 (200 ml) containing suspended NBS (4.09 g, 0.023 mol) and benzoyl peroxide (50 mg) was refluxed for 2 h. The solid that separated was filtered off, the filtrate was distilled under vacuum, and the residue was crystallized from methanol to give pure dibromide **4a**. Similarly, bromination of diones **3b**, **5a** and **22** provided the dibromides **4b**, **5b** and **23**.

4a: (80%); mp 120 °C; *m*/*z* 530, 532, 534 (M^+, 1:2:1), 451, 453, 455 (M^+ − Br); $\delta_H(CDCl_3)$ 3.98 (6H, s, 2 × OCH_3), 4.51 (4H, s, 2 × CH_2), 6.93 (2 H, d, *J* 8.6 Hz, H^f), 7.62 (1H, t, *J* 7.6 Hz, H^c), 7.78 (2H, d, *J* 8.6 Hz, H^e), 7.86 (2H, s, H^d), 7.94 (2H, d, *J* 7.6 Hz, H^B), 8.05 (1H, s, H^a); $\delta_C(CDCl_3)$ (normal/DEPT-135) 27.62 (−ve, CH_2), 55.43 (+ve, OCH_3), 109.72 (+ve, ArCH), 125.33 (ab, C), 126.08 (+ve, CH), 127.99 (ab, C), 133.55 (+ve, CH), 133.81 (+ve, CH), 137.88 (+ve, CH), 153.29 (ab, C), 160.74 (ab, C), 189.54 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1602 (C=O), 1647 (C=O) (Found: C, 53.8; H, 4.1. $C_{24}H_{20}Br_2O_4$ requires C, 54.13; H, 3.76%).

4b: (60%); mp 141 °C (from $CHCl_3$); *m*/*z* M^+ (absent), 454, 452 (M^+ − Br); $\delta_H(CDCl_3)$ 3.98 (6H, s, 2 × OCH_3), 4.40 (4H, s, 2 × CH_2), 6.91 (2H, d, *J* 8.6 Hz, H^f), 8.10–8.30 (7H, m, ArH); $\delta_C(CDCl_3$ + DMSO) (normal/DEPT-135) 27.62 (−ve, CH_2), 55.43 (+ve, OCH_3), 109.72 (+ve, ArCH), 125.33 (ab, ArC), 126.08 (+ve, ArCH), 127.99 (ab, ArC), 133.55 (+ve, ArCH), 133.81 (+ve, ArCH), 137.88 (+ve, ArCH), 153.29 (ab, ArC), 160.73 (abt, C), 189.54 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1601 (C=O), 1650 (C=O) (Found; C, 51.9; H, 3.9; N, 2.9. $C_{23}H_{19}Br_2NO_4$ requires C, 51.78; H, 3.56; N, 2.62%).

5b: (50%); mp 60 °C; *m*/*z* 647, 649 (M^+ − Br); $\delta_H(CDCl_3)$ 0.90 (6H, t, *J* 6.4 Hz, 2 × CH_3), 1.17–1.54 (20H, m, 10 × CH_2), 1.89 (4H, p, *J* 6.4 Hz, 2 × CH_2), 4.09 (4H, t, *J* 6.4 Hz, 2 × OCH_2), 4.54 (4H, s, 2 × $BrCH_2$), 6.92 (2H, d, *J* 8.0 Hz, 2 × H^f), 7.60 (1H, t, *J* 7.6 Hz, H^c), 7.78 (2H, d, *J* 8.0 Hz, 2 × H^e), 7.87 (2H, s, H^d), 7.95 (2H, d, *J* 7.6 Hz, 2 × H^b), 8.06 (1H, s, H^c); $\delta_C(CDCl_3)$ (normal/DEPT-135) 14.03 (+ve, CH_3), 22.62 (−ve, CH_2), 26.12 (−ve, CH_2), 26.22 (−ve, CH_2), 29.18 (−ve, CH_2), 29.32 (−ve, CH_2), 31.76 (−ve, CH_2), 68.02 (−ve, OCH_2), 109.93 (+ve, ArCH), 126.79 (+ve, ArCH), 128.14 (ab, C), 128.88 (ab, C), 130.52 (+ve, ArCH), 132.46 (ab, C), 132.56 (ab, C), 138.48 (ab, C), 161.22 (ab, C), 193.67 (ab, C=O); ν_{max}-(KBr)/cm^{-1} 1603 (C=O), 1676 (C=O).

23: (79%); mp 40 °C (from methanol); *m*/*z* 530, 532, 534 (1:2:1); $\delta_H(CDCl_3)$; 4.01 (6H, s, 2 × OCH_3), 4.54 (4H, s, 2 × CH_2), 6.93 (2H, d, *J* 8.4 Hz, H^f), 7.42 (2H, s, H^d), 7.51 (2H, d, *J* 8.4 Hz, H^e), 7.53 (1H, t, *J* 7.6 Hz, H^c), 8.00 (2H, d, *J* 7.6 Hz, H^b), 8.14 (1H, s, H^a); $\delta_C(CDCl_3)$ (normal/DEPT-135) 32.64 (−ve, CH_2), 55.63 (+ve, OMe), 111.80 (+ve, ArCH), 127.89 (ab, ArC), 128.27 (+ve, ArCH), 130.03 (+ve, ArCH), 130.77 (ab, ArC), 131.02 (+ve, ArCH), 133.05 (+ve, ArCH), 134.59 (+ve, ArCH), 137.63 (ab, ArC), 157.18 (ab, ArC), 194.59 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1601 (C=O), 1707 (CO) (Found: C, 53.8; H, 3.5. $C_{24}H_{20}Br_2O_4$ requires C, 54.13; H, 3.76%).

Synthesis of heterocalix[4]arenes 11–19, 24, 25. General procedure

A suspension of **4a** (2.66 g, 0.005 mol) in acetonitrile (800 ml) containing benzimidazol-2(1*H*)-one (0.67 g, 0.005 mol), K_2CO_3 (10 g) and $TBAHSO_4$ (50 mg) was heated to reflux and progress of reaction was monitored by TLC. After completion of reaction, K_2CO_3 was filtered off and washed with acetonitrile. The filtrate and washings were combined, the solvent was distilled off, and the residue was subjected to column chromatography by using ethyl acetate–chloroform (20:80) as eluent to isolate product **11**. Similarly, reactions of **4a** with 5-nitrobenzimidazol-2(1*H*)-one **7**, 5,6-dinitrobenzimidazol-2(1*H*)-one **8**, uracil **9** and quinazole-2,4(1*H*,3*H*)-dione **10** provided the respective heterocalix[4]arenes **13**, **14**, **16** and **18**, respectively. The reactions of **4b** with heterocycles **6**, **9** and **10** provided heterocalix-

arenes **12**, **17** and **19**; **5a** with **8** gave **15**; and **23** with **6** and **9** gave **24** and **25**, respectively.

11: (70%) (30 h); mp 352–354 °C (from $CHCl_3$ + C_6H_6); *m/z* 504 (M^+); δ_H($CDCl_3$) 4.05 (6H, s, 2 × OCH_3), 5.10 (4H, br s, 2 × NCH_2), 7.02–7.08 (6H, m, 2 × H^f, 2 × H^g, 2 × H^h), 7.29 (1H, br s, H^a), 7.54 (1H, t, *J* 7.6 Hz, H^c), 7.75 (2H, br s, 2 × H^d), 7.77 (2H, d, *J* 7.6 Hz, H^b), 8.03 (2H, dd, J_1 8.6, J_2 2.0 Hz, 2 × H^e); δ_C($CDCl_3$) (normal/DEPT-135) 37.28 (−ve, NCH_2), 55.98 (+ve, OCH_3), 108.22 (+ve, ArCH), 111.36 (+ve, ArCH), 121.44 (+ve, ArCH), 124.89 (ab, ArC), 125.27 (+ve, ArCH), 128.91 (ab, ArC), 129.56 (ab, ArC), 130.41 (+ve, ArCH), 131.17 (+ve, ArCH), 131.77 (+ve, ArCH), 132.73 (+ve, ArCH), 139.21 (ab, ArC), 160.54 (ab, C=O), 195.78 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1699 (C=O), 1648 (C=O) (Found: C, 73.8; H, 4.5; N, 5.7%. $C_{31}H_{24}N_2O_5$ requires C, 73.81; H, 4.76; N, 5.56%).

12: (45%) (30 h); mp 299 °C (from $CHCl_3$); *m/z* 505 (M^+, 10%); δ_H($CDCl_3$) 4.05 (6H, s, 2 × OCH_3), 4.95 and 5.27 (4H, AB quartet, *J* 16.0 Hz, 2 × NCH_2), 6.96 (4H, s, 2 × H^g, 2 × H^h), 7.05 (2H, d, *J* 8.6 Hz, 2 × H^f), 7.41 (2H, d, *J* 2.1 Hz, 2 × H^d), 7.53 (2H, d, *J* 7.6 Hz, 2 × H^b), 7.87 (1H, t, *J* 7.6 Hz, H^c), 8.11 (2H, dd, J_1 8.6, J_2 2.1 Hz, 2 × H^e); δ_C($CDCl_3$) (normal/DEPT-135) 37.12 (−ve, NCH_2), 55.96 (+ve, OCH_3), 108.00 (+ve, ArCH), 111.14 (+ve, ArCH), 121.40 (+ve, ArCH), 123.50 (+ve, ArCH), 124.63 (ab, ArC), 128.71 (ab, ArC), 129.12 (ab, ArC), 130.84 (+ve, ArCH), 133.01 (+ve, ArCH), 137.52 (+ve, ArCH), 154.30 (ab, ArC), 156.93 (absent, ArC), 160.88 (ab, C=O), 193.99 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1709 (C=O), 1666 (C=O), 1601 (C=O) (Found: C, 7.16; H, 4.3; N, 8.5. $C_{30}H_{23}N_3O_5$ requires C, 71.29; H, 4.55; N, 8.31%).

13: (35%) (30 h); mp >355 °C (from $CHCl_3$ + C_6H_6); *m/z* 549 (M^+); δ_H($CDCl_3$ + TFA) 4.13 (3H, s, OCH_3), 4.18 (3H, s, OCH_3), 5.28 (4H, s, 2 × NCH_2), 7.15 (2H, d, *J* 9.0 Hz, H^f, $H^{f'}$), 7.31 (1H, s, H^a), 7.42 (1H, d, *J* 8.8 Hz, H^i), 7.74 (1H, t, *J* 7.8 Hz, H^c), 7.82 (2H, br s, H^d, $H^{d'}$), 7.96–8.10 (4H, m, H^b, $H^{b'}$, H^e and $H^{e'}$), 8.20 (1H, d, *J* 8.8 Hz, H^h), 8.36 (1H, s, H^g); δ_C($CDCl_3$ + TFA) (normal/DEPT-135) 38.40 (−ve, NCH_2), 56.33 (+ve, OCH_3), 106.48 (+ve, ArCH), 109.72 (+ve, ArCH), 112.70 (+ve, ArCH), 120.24 (absent, C), 124.31 (ab, C), 127.25 (+ve, ArCH), 128.82 (ab, C), 129.44 (ab, C), 129.53 (ab, C), 130.75 (+ve, ArCH), 133.35 (+ve, ArCH), 133.54 (+ve, ArCH), 134.28 (ab, C), 138.37 (ab, C), 138.46 (ab, C), 143.50 (ab, C), 162.68 (ab, C), 162.79 (ab, C), 201.12 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1650 (C=O), 1726 (C=O) (Found: C, 67.1; H, 4.3; N, 7.5. $C_{31}H_{23}N_3O_7$ requires C, 67.76; H, 4.19; N, 7.65%).

14: (45%) (30 h); mp >355 °C (from $CHCl_3$ + C_6H_6); *m/z* 594 (M^+); ($CDCl_3$ + TFA) 4.14 (6H, s, 2 × OCH_3), 5.30 (4H, s, 2 × NCH_2), 7.17 (2H, d, *J* 8.8 Hz, 2 × ArH), 7.81 (1H, t, *J* 7.8 Hz, ArH), 7.98–8.10 (9H, m, 9 × ArCH); δ_C($CDCl_3$ + TFA) (normal/DEPT-135) 36.22 (−ve, NCH_2), 58.31 (+ve, OCH_3), 106.73 (+ve, ARCH), 112.49 (+ve, ArCH), 123.40 (ab, C), 127.48 (+ve, ArCH), 129.84 (ab, C), 130.85 (+ve, ArCH), 133.27 (+ve, ArCH), 134.00 (+ve, ArCH), 134.40 (+ve, ArCH), 138.05 (ab, C), 139.01 (ab, C), 155.73 (ab, C), 161.46 (ab, C=O), 199.63 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1652 (C=O), 1725 (C=O) (Found: C, 62.7; H, 3.5; N, 9.1. $C_{31}H_{22}N_4O_9$ requires C, 62.62; H, 3.70; N, 9.42%).

15: (12%) (30 h); mp 319–320 °C (from $CHCl_3$ + MeOH); 791 (M^+ + 1); *m/z* (ES) δ_H($CDCl_3$) 0.90 (6h, t, *J* 6.6 Hz, 2 × CH_3), 1.26–1.60 (20H, m, 10 × CH_2), 2.03 (4H, q, *J* 7.0 Hz, 2 × CH_2), 4.21 (4H, br s, 2 × OCH_2), 5.20 (4H, s, 2 × NCH_2), 7.06 (2H, d, *J* 8.6 Hz, 2 × ArH), 7.28 (1H, s, ArCH), 7.75 (1H, t, *J* 7.6 Hz, ArH), 7.88 (2H, s, 2 × ArCH), 7.95–8.01 (6H, m, 6 × ArCH); δ_C($CDCl_3$) (normal/DEPT-135) 14.05 (+ve, CH_3), 22.63 (−ve, CH_2), 26.04 (−ve, CH_2), 29.16 (−ve, CH_2), 29.34 (−ve, CH_2), 31.78 (−ve, CH_2), 37.73 (−ve, NCH_2), 69.53 (−ve, OCH_2), 105.32 (+ve, ArCH), 112.75 (+ve, ArCH), 123.20 (ab, C), 126.14 (+ve, ArCH), 130.09 (+ve, ArCH), 130.85 (ab, C), 130.94 (ab, C), 132.42 (+ve, ArCH), 133.09 (+ve, ArCH), 133.47 (+ve, ArCH), 138.68 (ab, C), 138.88 (ab, C), 155.07 (ab, C), 159.67 (ab, C=O), 195.25 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1699 (C=O), 1648 (C=O) (Found: C, 68.7; H, 6.3; N, 7.5. $C_{45}H_{50}N_4O_9$ requires C, 68.35; H, 6.33; N, 7.09%).

16: (60%) (30 h); mp 333–335 °C (from $CHCl_3$ + C_6H_6); *m/z* 482 (M^+, 8.4%); δ_H($CDCl_3$ + TFA) 3.98 (3H, s, OCH_3), 4.01 (3H, s, OCH_3), 4.52 (1H, br s, NCH_2), 5.05 (1H, br s, NCH_2), 5.42 (2H, br s, 2 × NCH_2), 6.15 (1H, d, *J* 7.0 Hz, H^g), 7.09 (1H, d, *J* 8.4 Hz, $H^{f/f'}$), 7.13 (1H, d, *J* 8.4 Hz, $H^{f'/f}$), 7.41 (2H, br s, $H^{d'}$), 7.46 (1H, s, H^a), 7.59 (1H, d, *J* 7.0 Hz, H^h), 7.78 (1H, t, *J* 6.4 Hz, H^c), 8.01–8.10 (4H, m, H^b, $H^{b'}$, H^e and $H^{e'}$); δ_C($CDCl_3$ + TFA) (normal/DEPT-135) 40.20 (−ve, NCH_2), 48.89 (−ve, NCH_2), 56.04 (+ve, OCH_3), 56.22 (+ve, OCH_3), 101.69 (+ve, UC-5), 112.05 (+ve, ArCH), 112.10 (+ve, ArCH), 128.48 (+ve, ArCH), 129.12 (ab, ArC), 130.84 (+ve, ArCH), 132.86 (+ve, ArCH), 133.24 (+ve, ArCH), 134.30 (+ve, ArCH), 134.70 (+ve, ArCH), 137.63 (ab, ArC), 138.14 (ab, ArC), 145.96 (+ve, UC-6), 151.78 (ab, C=O), 166.45 (ab, C=O), 200.57 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1715 (C=O), 1670 (C=O) (Found: C, 70.0; H, 4.5, N, 5.4. $C_{28}H_{22}N_2O_6$ requires C, 69.71; H, 4.56; N, 5.81%).

17: (40%) (30 h); mp 335 °C (from $CHCl_3$ + CH_3OH); *m/z* 483 (M^+); δ_H($CDCl_3$ + TFA) 3.98 (3H, s, OCH_3), 4.02 (3H, s, OCH_3), 4.69, 5.34 (2H, AB quartet, *J* 14.0 Hz, NCH_2), 4.94 and 5.49 (2H, AB quartet, *J* 14.0 Hz, NCH_2), 6.07 (1H, d, *J* 7.8 Hz, H^g), 7.10 (1H, d, *J* 7.8 Hz, $H^{f/f'}$), 7.12 (1H, d, *J* 7.8 Hz, $H^{f'/f}$), 7.41 (1H, br s, $H^{d/d'}$), 7.48 (1H, br s, $H^{d'/d}$), 7.58 (1H, d, *J* 7.8 Hz, H^h), 8.11–8.17 (4H, m, H^b, $H^{b'}$, H^e, $H^{e'}$), 8.54 (1H, m, H^c); δ_C($CDCl_3$ + TFA) (normal/DEPT-135) 33.22 (−ve, NCH_2), 42.27 (−ve, NCH_2), 55.99 (+ve, OCH_3), 56.10 (+ve, OCH_3), 101.17 (+ve, UC-5), 111.54 (+ve, ArCH), 123.18 (ab, ArC), 125.14 (+ve, ArCH), 125.42 (+ve, ArCH), 127.69 (ab, ArC), 128.45 (ab, ArC), 130.44 (+ve, ArCH), 130.70 (+ve, ArCH), 131.37 (+ve, ArCH), 132.00 (+ve, ArCH), 139.44 (+ve, ArCH), 144.40 (+ve, UC-6), 151.15 (ab, ArC), 155.30 (ab, ArC), 156.00 (ab, ArC), 161.51 (ab, C), 162.42 (ab, C=O), 164.92 (ab, C=O), 193.92 (ab, C=O), 194.10 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1717 (C=O), 1668 (C=O), 1602 (C=O) (Found: C, 67.2; H, 4.1; N, 8.9. $C_{27}H_{21}N_3O_6$ requires C, 67.08; H, 4.35; N, 8.70%).

18: (65%) (30 h); mp 337–339 °C (from $CHCl_3$ + CH_3OH); *m/z* 532 (M^+, 15.8%); δ_H($CDCl_3$ + TFA) 4.05 (3H, s, OCH_3), 4.09 (3H, s, OCH_3), 5.00 and 5.85 (2H, AB quartet, *J* 1.82 Hz, NCH_2), 5.26 and 5.55 (2H, AB quartet, *J* 18.0 Hz, NCH_2), 6.93 (1H, d, *J* 1.3 Hz, $H^{d/d'}$), 7.01 (1H, d, *J* 1.3 Hz, $H^{d'/d'}$), 7.12–7.22 (3H, m, H^f, $H^{f'}$ and H^j), 7.40 (1H, t, *J* 7.4 Hz, H^i), 7.49 (1H, s, H^a), 7.58 (1H, t, *J* 7.6 Hz, H^c), 7.74 (1H, t, *J* 7.4 Hz, H^h), 7.83–7.87 (2H, m, H^b and $H^{b'}$), 8.11–8.24 (3H, m, H^e, $H^{e'}$ and H^g); δ_C($CDCl_3$ + TFA) (normal/DEPT-135) 40.79 (−ve, NCH_2), 43.56 (−ve, NCH_2), 56.17 (+ve, OCH_3), 56.76 (+ve, OCH_3), 111.89 (+ve, CH), 111.98 (+ve, CH), 114.48 (ab, C), 114.75 (+ve, CH), 122.29 (ab, C), 123.60 (ab, C), 125.50 (+ve, CH), 127.54 (+ve, CH), 127.68 (+ve, CH), 127.94 (+ve, CH), 128.30 (ab, C), 128.43 (ab, C), 129.63 (+ve, CH), 130.45 (+ve, CH), 132.41 (+ve, CH), 132.96 (+ve, CH), 133.61 (+ve, CH), 133.87 (+ve, CH), 137.11 (ab, C), 137.65 (+ve, CH), 138.10 (ab, C), 139.72 (ab, C), 151.15 (ab, C), 162.63 (ab, C), 162.83 (ab, C), 164.10 (ab, C), 199.50 (ab, C=O), 200.28 (ab, C=O); ν_{max}(KBr/cm^{-1} 1705 (C=O), 1650 (C=O) (Found: C, 72.1; H, 4.1. $C_{32}H_{24}N_2O_6$ requires C, 72.18; H, 4.51%).

19: (45%); mp 320 °C (from $CHCl_3$ + CH_3OH); *m/z* 533 (M^+); δ_H($CDCl_3$ + TFA) 4.07 (3H, s, OCH_3), 4.10 (3H, s, OCH_3), 5.02 and 5.77 (2H, AB quartet, *J* 18.0 Hz, NCH_2), 5.19 and 5.56 (2H, AB quartet, *J* 16.6 Hz, NCH_2), 6.88 (2H, d, *J* 10.8 Hz, 2 × ArH), 7.08–7.24 (3H, m, 3 × ArH), 7.38 (1H, t, *J* 7.6 Hz, ArH), 7.71 (1H, t, *J* 7.4 Hz, ArH), 7.88 (2H, d, *J* 7.8 Hz, 2 × ArH), 8.15–8.32 (4H, m, 4 × ArH); δ_C($CDCl_3$ + TFA) (normal/DEPT-135) 40.31 (−ve, NCH_2), 42.60 (−ve, NCH_2), 56.15 (+ve, OCH_3), 111.71 (+ve, CH), 114.37 (ab, C), 114.53 (+ve, CH), 122.25 (ab, C), 123.72 (ab, C), 124.37 (+ve, CH), 124.94 (+ve, CH), 125.00 (ab, C), 127.16 (ab, C), 127.55 (ab, C), 128.08 (+ve, CH), 128.79 (+ve, CH), 129.15 (+ve, CH), 131.16

(+ve, CH), 131.77 (+ve, CH), 136.56 (+ve, CH), 139.26 (ab, C), 140.02 (+ve, CH), 150.55 (ab, C), 154.44 (ab, C), 155.14 (ab, C), 162.31 (ab, C=O), 162.68 (ab, C=O), 192.82 (ab, C=O), 193.40 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1707 (C=O), 1665 (C=O), 1601 (C=O) (Found: C, 69.9; H, 3.8; N, 7.5. $C_{31}H_{23}N_3O_6$ requires C, 69.79; H, 4.32; N, 7.88%).

24: (33%); mp 240 °C (from AcOH); *m/z* 504 (M^+); δ_H(TFA + $CDCl_3$) 3.75 (6H, s, 2 × OCH_3), 5.06 (4H, br s, 2 × CH_2), 6.94 (2H, d, *J* 8 Hz, H^f), 7.08 (2H, s, H^d), 7.27–7.30 (4H, m, benzimid.-H), 7.45 (1H, s, H^a), 7.57 (2H, d, *J* 8.0 Hz, H^e), 7.73 (1H, t, *J* 7.6 Hz, H^c), 8.32 (2H, d, *J* 7.6 Hz, H^b); δ_C(TFA + $CDCl_3$) (normal/DEPT-135) 44.71 (−ve, CH_2), 55.58 (+ve, OCH_3), 109.79 (+ve, CH), 112.07 (+ve, CH), 112.62 (+ve, CH), 124.55 (+ve, CH), 126.79 (ab, C), 128.16 (+ve, ArCH), 129.09 (ab, C), 129.49 (ab, C), 132.56 (ab, C), 134.62 (+ve, ArCH), 135.36 (+ve, CH), 136.55 (+ve, CH), 137.37 (ab, C), 159.57 (ab, C), 208.92 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1700 (C=O), 1665 (C=O) (Found: C, 73.5; H, 4.5; N, 5.3. $C_{31}H_{24}N_2O_5$ requires C, 73.81; H, 4.76; N, 5.56%).

25: (10%); mp 280 °C (from chloroform + ethanol); *m/z* 482 (M^+); δ_H($CDCl_3$) 3.75 (6H, s, 2 × OCH_3), 4.69 (2H, s, NCH_2), 4.97 (2H, s, NCH_2), 5.80 (1H, d, *J* 7.8 Hz, U5-H), 6.86 (1H, d, *J* 8.2 Hz, $H^{f/f'}$), 6.89 (1H, d, *J* 8.2 Hz, $H^{f'/f}$), 7.26 (1H, d, *J* 8.2 Hz, $H^{e'/e}$), 7.35 (1H, d, *J* 7.8 Hz, U6-H), 7.44 (3H, s, H^a, H^d, $H^{d'}$), 7.69 (1H, d, *J* 8.2 Hz, $H^{e/e'}$), 7.74 (1H, t, *J* 7.8 Hz, H^c), 8.42 (2H, d, *J* 7.8 Hz, $H^{b/b'}$); δ_C($CDCl_3$) (normal/DEPT-135) 42.80 (−ve, CH_2), 53.62 (−ve, CH_2), 101.67 (+ve, UC-5), 111.90 (+ve, ArH), 112.06 (ab, ArC), 126.34 (ab, ArC), 127.04 (ab, ArC), 127.97 (ab, ArC), 128.16 (ab, ArC), 129.45 (ab, ArC), 130.37 (+ve, ArCH), 130.80 (+ve, ArCH), 131.80 (+ve, ArCH), 133.91 (+ve, ArCH), 134.61 (+ve, ArCH), 134.64 (+ve, ArCH), 137.34 (ab, ArC), 137.83 (ab, ArC), 141.95 (+ve, UC-6), 150.27 (ab, ArC), 157.61 (ab, ArC), 162.74 (ab, ArC), 175.92 (ab, C=O), 194.06 (ab, C=O), 205.35 (ab, C=O), 216.80 (ab, C=O); ν_{max}(KBr)/cm^{-1} 1675, 1660, 1708 (C=O) (Found: C, 70.1; H, 4.4; N, 5.7. $C_{28}H_{22}N_2O_6$ requires C, 69.71; H, 4.56; N, 5.81%).

X-Ray structure analysis of 11–benzene complex †

Crystals of **11**–benzene were obtained by slow evaporation from chloroform–benzene (1 : 1 *v*/*v*) mixture. All intensity-data measurements were carried out at room temperature on a Siemens P4 four-circle diffractometer with graphite-monochromatized MoKα radiation (λ = 0.7169 Å). The crystals with molecular formula $C_{37}H_{30}N_2O_5$ and relative molecular mass 582.63 belonged to the monoclinic septum, *C*2/*c* space group with *a* = 35.636(4), *b* = 9.226(1), *c* = 17.779(2) Å, *V* = 5839.1 (11) Å^3 *Z* = 8. A total of 3885 reflections were collected, out of which 3814 were independent (R_{int} = 0.0239) and 2245 were observed [$I > 2\sigma(I)$]. The data were corrected for Lorentz and polarization effects. No absorption correction was applied.

The structure was solved by direct methods using SHELXTL-PC.[10] A full matrix least-squares refinement on F^2, with anisotropic thermal parameters for all the non-hydrogen atoms, showed disorder in the benzene molecule, as inferred from the short C–C distances and high thermal parameters of three carbons [C(35) to C(37)]. In the initial stages of refinement the benzene molecule [C(32)–C(37)] was refined as a rigid group. At final stages of the refinement it was made free but C–C distances were fixed at 1.390(3) Å. No attempt was made to resolve the disordered atoms. All the hydrogens were fixed geometrically and made to ride on their respective atoms.

† CCDC reference number 207/395. See http://www.rsc.org/suppdata/p1/a9/a906883/ for crystallographic files in .cif format.

The weighting scheme used was

$$w = \frac{1}{[\sigma^2 F_o^2 + (0.1414P)^2 + 4.63P]}$$

where $P = [F_o^2 + 2F_c^2]/3$

A final refinement[11] of 397 parameters with six restraints gave $R = 0.0717$, $wR = 0.1967$ for observed reflections and $R = 0.1286$, $wR = 0.2484$ for all reflections.

Acknowledgements

We thank UGC and DST, New Delhi for financial assistance.

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Paper a906883j