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Supramolecular architecture of self-adhesive calix[4]arene thiourea derivative by hydrogen bonding and π−π interactions

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Abstract

Two calix[4]arene thiourea derivative **2** and **3** have been prepared by the reaction of the easily accessible 1,3-distally substituted calix[4]arene amine **1** with the corresponding isothiocyanate in dry CH_2Cl_2 with satisfactory yield. The single crystal of **2** was prepared, and X-ray crystallographic analysis clearly revealed that the interleaving 2D supramolecular architecture formed by synergic hydrogen bonding and π−π interactions.

Keywords: Calix[4]arene thiourea derivative; Supramolecular architecture; Hydrogen bonding; π−π Interaction

1. Introduction

It is well documented that calixarene derivatives can be taken as molecular acceptors to fabricate or self-organize forming supramolecular assembly, which are currently investigated extensively in the fields of chemical, biological, and materials science and technology [1]. One of the most important features of these supramolecular architectures is the simultaneous operation of several cooperative weak forces working between receptor (host) and substrate (guest), such as hydrogen bonding, hydrophobic, π−π, CH−π and metal−ligand interactions [2]. Indeed, various of self-complementary calixarene derivatives involving the pre-organized carboxylic acids, pyridyl, urea functions which form definite dimers [3], capsules [4], vesicles [5], rosettes [6], rodlike [7], tubules [8], through noncovalent interactions have been reported recently. Unfortunately, the assembly of calix[4]arene derivative bearing thiourea groups in the low rim has not yet been reported to the best of our knowledge. In the present paper, we report the synthesis of two calix[4]arene thiourea derivatives **2** and **3** and then the single crystal X-ray structure of **2**, which confirms unambiguous the interleaving 2D supramolecular architecture formed by synergic hydrogen bonding and π−π interactions in the crystalline state. It is another point of special interest to understand the effects of the types and the number of substitutes attached on calixarenes for molecular self-assembly.

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2. Experimental

2.1. Materials and general methods

Starting materials were commercial available unless otherwise noted. 1,3-Distally substituted *p-tert*-butylcalix[4]arene amine **1** was prepared according to the literature procedures [9]. Melting points, measured with an XT-4 apparatus, are uncorrected. ^{1}H-NMR spectra were recorded on a Bruker AC—P200 instrument at 200 MHz in $CDCl_3$ solution, using tetramethylsilane as an internal reference. IR spectra were recorded on a Bio-Rad FTS 135 instrument. Elemental analyses were performed on a Perkin-Elmer 2400C instrument. FAB mass spectra were obtained on a VG ZAB-HS apparatus.

2.2. Syntheses of the compounds

A solution of **1** (0.27 mmol) and the corresponding isothiocyanate (1.08 mmol) in dry CH_2Cl_2 (15 ml) was stirred for 4 h at room temperature. After completion of the reaction, the solution was concentrated at reduced pressure. The remaining solid residue was recrystallized from acetonitrile to obtain **2** in 90% and **3** in 88% yield, respectively. Compound **2**: mp: >280 °C; FAB-MS: *m/z* 1005(M^+); FT-IR (KBr): ν (cm^{-1}) 3305.5, 3218.1, 2959.7, 2905.7, 2869.9, 2092.4, 1593.7, 1541.4, 1485.3, 1460.9, 1420.8, 1391.6, 1362.9, 1314.1, 1240.7, 1196.7, 1124.5, 1080.1, 1043.0, 978.2, 916.8, 871.6, 779.6; ^{1}H-NMR ($CDCl_3$, TMS): δ (ppm) 7.88 (s, 2H, OH), 7.85 (br, 2H, NH) 7.78 (s, 2H, NH), 7.26–7.16 (m, 10H, ArH), 6.93 (s, 4H, ArH), 6.91 (s, 4H, ArH), 4.11 (br, 8H, OCH_2CH_2N), 3.86 (d, 4H, $J = 13.2$ Hz, $ArCH_2Ar$), 3.28 (d, 4H, $J = 13.2$ Hz, $ArCH_2Ar$), 1.26 (s, 18H, $C(CH_3)_3$), 0.90 (s, 18H, $C(CH_3)_3$); Anal. Calcd. for $C_{62}H_{76}N_4O_4S_2$: C, 74.07; H, 7.62; N, 5.57; Found: C, 73.85; H, 7.47; N, 5.60. Compound 3: mp: >280 °C; FAB-MS: *m/z* 1105 (M^+); FT-IR (KBr): ν (cm − 1 3273.9), 3160.9, 3052.2, 2960.9, 2906.2, 2870.9, 2102.3, 1594.6, 1538.8, 1484.8, 1461.7, 1394.4, 1363.3, 1336.7, 1298.4, 1202.4, 1125.0, 1086.1, 1029.0, 916.4, 870.7, 779.4; ^{1}H-NMR (CDCl3, TMS): δ (ppm) 8.04 (s, 2H, NH), 7.96 (s, 2H, NH), 7.84–7.29 (m, 14H, ArH), 6.81 (s, 4H, ArH), 6.78 (s, 2H, OH), 6.71 (s, 4H, ArH), 3.72–3.67 (m, 8H, OCH_2CH_2N), 3.26 (d, 4H, $J = 12.6$ Hz, $ArCH_2Ar$), 2.99 (d, 4H, $J = 12.6$ Hz, $ArCH_2Ar$), 1.23 (s, 18H, $C(CH_3)_3$), 0.99 (s, 18H, $C(CH_3)_3$); Anal. Calcd. for $C_{70}H_{80}N_4O_4S_2$: C, 76.05; H, 7.29; N, 5.07; Found: C, 75.93; H, 7.21; N, 5.12.

2.3. X-ray crystallographic studies of compound 2

A small amount of **2** was dissolved in hot acetonitrile to make a saturated solution, which was then cooled to room temperature. After removing the precipitates by filtration, the resultant solution was kept at 10 °C for a week. The crystal formed was collected along with its mother liquor for X-ray crystallographic analysis. Single crystal X-ray diffraction measurements were carried out at room temperature with a Siemens SMART CCD Area Detector System using a Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were obtained with least-squares refinements. The structure was solved by direct methods and semi-empirical absorption corrections (SADABS) were applied. The final refinement was carried out by full matrix least-squares methods with anisotropic thermal parameters on F^2.

Table 1
Crystal data and structure refinement for calix[4]arene thiourea derivative **2**

Empirical formula	$C_{64}H_{81}N_5O_5S_2$
Formula weight	1064.46
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	$a = 12.082(4)$, $b = 16.478(6)$ and $c = 18.362(6)$ Å $\alpha = 85.147(7)$, $\beta = 72.438(7)$ and $\gamma = 75.758(7)°$
Volume (Å)	3378(2)
Z	2
D_{calcd} (g cm^{-3})	1.047
Absorption coefficient	0.125 mm^{-1}
F(000)	1144
Crystal size (mm^3)	0.40 × 0.25 × 0.08
θ range for data collection	1.85–25.03°
Range of *h*, *k*, *l*	− 14/14, − 19/15, − 17/21
Reflections collected	13973
Independent reflections	11732
Parameters	685
R and R_w [$I > 2\sigma(I)$]	0.1007, 0.2502
Residual electron densities (e $Å^{-3}$)	0.653 to − 0.335
Goodness-of-fit on F^2	0.982

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for calix[4]arene thiourea derivative **2**

Atom	*x*	*y*	*z*	U_{eq}
C(1)	4264(4)	8561(3)	702(3)	38(1)
C(2)	4859(5)	7764(4)	427(3)	48(1)
C(3)	5821(5)	7275(3)	665(3)	49(1)
C(4)	6169(5)	7643(4)	1193(3)	51(1)
C(5)	5618(4)	8441(4)	1470(3)	44(1)
C(6)	5986(5)	8783(4)	2098(3)	51(2)
C(7)	5417(5)	8457(4)	2880(3)	45(1)
C(8)	5996(5)	7723(4)	3162(3)	58(2)
C(9)	5507(5)	7367(4)	3857(4)	56(2)
C(10)	4405(5)	7798(4)	4295(3)	49(1)
C(11)	3772(4)	8538(3)	4042(3)	40(1)
C(12)	2531(4)	8947(3)	4517(3)	43(1)
C(13)	1642(4)	8580(3)	4308(3)	37(1)
C(14)	1495(5)	7784(3)	4578(3)	46(1)
C(15)	807(5)	7367(3)	4355(3)	47(1)
C(16)	215(5)	7775(4)	3831(3)	47(1)
C(17)	307(4)	8572(3)	3547(3)	39(1)
C(18)	−251(4)	8961(4)	2927(3)	46(1)
C(19)	494(4)	8630(3)	2145(3)	43(1)
C(20)	328(5)	7898(4)	1877(3)	50(1)
C(21)	1016(5)	7531(3)	1200(3)	48(1)
C(22)	1899(5)	7922(3)	752(3)	45(1)
C(23)	2117(4)	8636(3)	986(3)	38(1)
C(24)	3143(5)	8990(4)	499(3)	45(1)
C(25)	4686(4)	8902(3)	1201(3)	38(1)
C(26)	1409(4)	8976(3)	1682(3)	38(1)
C(27)	1004(4)	8974(3)	3811(3)	36(1)
C(28)	4296(4)	8862(3)	3334(3)	40(1)
C(29)	6455(6)	6408(4)	338(4)	70(2)
C(30)	6950(17)	5854(7)	948(11)	239(9)
C(31)	7451(13)	6473(7)	−331(8)	253(11)
C(32)	5616(10)	5953(7)	203(11)	238(10)
C(33)	6139(6)	6537(5)	4153(4)	78(2)
C(34)	6196(16)	6644(8)	4929(8)	220(9)
C(35)	7388(11)	6241(10)	3657(10)	247(10)
C(36)	5490(14)	5909(6)	4182(12)	247(10)
C(37)	682(6)	6493(4)	4664(4)	67(2)
C(38)	456(14)	5989(6)	4077(8)	183(6)
C(39)	−394(12)	6571(6)	5326(7)	202(8)
C(40)	1765(12)	6012(7)	4852(11)	242(10)
C(41)	872(6)	6711(4)	960(4)	68(2)
C(42)	1751(12)	5998(6)	1197(8)	169(6)
C(43)	−332(10)	6550(8)	1364(9)	200(7)
C(44)	1103(16)	6687(7)	107(6)	194(7)
C(45)	204(5)	10437(3)	3951(3)	44(1)
C(46)	271(5)	11244(3)	3501(3)	44(1)
C(47)	−1099(5)	11592(3)	2696(3)	44(1)
C(48)	−249(5)	11466(4)	1280(3)	48(1)
C(49)	−445(5)	11076(4)	702(3)	59(2)
C(50)	405(6)	10930(4)	2(4)	71(2)
C(51)	1482(7)	11143(4)	−113(4)	72(2)
C(52)	1691(5)	11528(4)	446(3)	63(2)
C(53)	825(5)	11694(4)	1135(3)	58(2)
C(54)	4625(5)	10365(3)	1060(3)	47(1)
C(55)	4066(5)	11155(4)	1513(3)	48(1)
C(56)	5214(5)	11521(4)	2290(3)	45(1)
C(57)	4453(5)	11400(4)	3727(3)	51(2)
C(58)	3225(5)	11581(4)	3860(3)	56(2)
C(59)	2495(6)	11423(4)	4561(3)	64(2)
C(60)	2956(6)	11126(5)	5147(4)	72(2)
C(61)	4167(7)	10966(5)	5040(4)	71(2)
C(62)	4911(6)	11088(4)	4331(3)	61(2)
C(63)	3319(7)	7236(5)	2495(4)	88(2)
C(64)	3673(11)	6362(8)	2534(6)	128(4)
N(1)	5273(4)	11559(3)	3013(2)	55(1)
N(2)	4393(4)	11136(3)	2205(2)	49(1)
N(3)	−1175(4)	11634(3)	1970(2)	56(1)
N(4)	−25(4)	11242(3)	2792(2)	47(1)
N(5)	3890(16)	5665(9)	2544(9)	252(8)
O(1)	4104(3)	9706(2)	1482(2)	45(1)
O(2)	3685(3)	9591(2)	3073(2)	49(1)
O(3)	1125(3)	9775(2)	3530(2)	43(1)
O(4)	1612(3)	9678(2)	1926(2)	48(1)
S(1)	6131(2)	11924(1)	1567(1)	71(1)
S(2)	−2306(1)	11965(1)	3421(1)	65(1)
O(5)	1876(8)	2889(7)	2481(4)	214(5)

Further details of the structural analyses are given in Table 1. Positional parameters and atomic coordinates are given in Table 2, whereas selected bond distances and angles are listed in Tables 3 and 4.

Table 3
Selected bond lengths (Å) for calix[4]arene thiourea derivative **2**

C(1)–C(2)	1.387(7)	C(29)–C(32)	1.485(12)
C(1)–C(25)	1.388(7)	C(29)–C(30)	1.551(16)
C(1)–C(24)	1.505(7)	C(45)–O(3)	1.434(6)
C(2)–C(3)	1.407(8)	C(45)–C(46)	1.512(7)
C(3)–C(4)	1.398(8)	C(46)–N(4)	1.451(6)
C(3)–C(29)	1.523(8)	C(47)–N(4)	1.342(7)
C(4)–C(5)	1.382(8)	C(47)–N(3)	1.359(6)
C(5)–C(25)	1.393(7)	C(47)–S(2)	1.673(6)
C(5)–C(6)	1.545(7)	C(48)–C(53)	1.382(8)
C(6)–C(7)	1.510(7)	C(48)–C(49)	1.393(8)
C(23)–C(24)	1.509(7)	C(48)–N(3)	1.409(7)
C(25)–O(1)	1.397(6)	C(49)–C(50)	1.378(8)
C(26)–O(4)	1.377(6)	C(50)–C(51)	1.381(9)
C(27)–O(3)	1.401(6)	C(51)–C(52)	1.366(9)
C(28)–O(2)	1.377(6)	C(52)–C(53)	1.375(8)
C(29)–C(31)	1.456(12)	C(54)–O(1)	1.441(6)

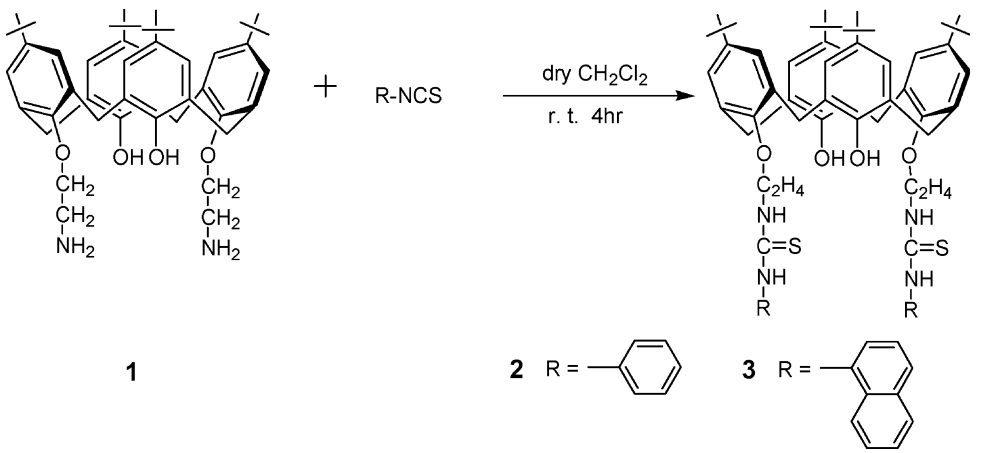
Table 4
Selected bond angles (deg) for calix[4]arene thiourea derivative **2**

C(2)–C(1)–C(25)	118.1(5)	O(2)–C(28)–C(7)	119.6(5)
C(2)–C(1)–C(24)	119.1(5)	C(11)–C(28)–C(7)	121.3(5)
C(25)–C(1)–C(24)	122.7(5)	C(31)–C(29)–C(32)	114.1(11)
C(1)–C(2)–C(3)	122.8(5)	C(31)–C(29)–C(3)	109.6(6)
C(4)–C(3)–C(2)	116.1(5)	C(32)–C(29)–C(3)	112.2(6)
C(4)–C(3)–C(29)	123.0(5)	C(31)–C(29)–C(30)	108.6(11)
C(2)–C(3)–C(29)	120.8(5)	C(32)–C(29)–C(30)	103.2(11)
C(5)–C(4)–C(3)	123.0(5)	C(3)–C(29)–C(30)	109.0(7)
C(4)–C(5)–C(25)	118.2(5)	O(3)–C(45)–C(46)	108.5(4)
C(4)–C(5)–C(6)	120.2(5)	N(4)–C(46)–C(45)	112.4(4)
C(25)–C(5)–C(6)	121.5(5)	N(4)–C(47)–N(3)	116.7(5)
C(7)–C(6)–C(5)	111.7(4)	N(4)–C(47)–S(2)	123.0(4)
C(8)–C(7)–C(6)	120.2(5)	N(3)–C(47)–S(2)	120.3(4)
C(28)–C(7)–C(6)	122.1(5)	C(53)–C(48)–C(49)	118.2(5)
C(1)–C(24)–C(23)	109.5(4)	C(53)–C(48)–N(3)	123.7(5)
C(1)–C(25)–C(5)	121.6(5)	C(49)–C(48)–N(3)	118.1(5)
C(1)–C(25)–O(1)	119.0(4)	C(50)–C(49)–C(48)	120.8(6)
C(5)–C(25)–O(1)	119.3(4)	C(51)–C(50)–C(49)	119.3(6)
C(23)–C(26)–O(4)	119.2(4)	C(52)–C(51)–C(50)	120.8(6)
C(23)–C(26)–C(19)	121.9(5)	C(51)–C(52)–C(53)	119.6(6)
O(4)–C(26)–C(19)	118.8(4)	C(52)–C(53)–C(48)	121.3(6)
C(13)–C(27)–C(17)	121.7(5)	C(47)–N(3)–C(48)	128.8(5)
C(13)–C(27)–O(3)	118.9(5)	C(47)–N(4)–C(46)	124.6(4)
C(17)–C(27)–O(3)	119.2(4)	C(25)–O(1)–C(54)	114.5(4)
O(2)–C(28)–C(11)	119.2(4)	C(27)–O(3)–C(45)	113.5(4)

3. Results and discussion

The synthesis of calix[4]arene thiourea derivative **2** has been reported previously in Ref. [10]. But we improved slightly the procedure without adding triethylamine. As shown in Scheme 1, a facile strategy has been developed for the syntheses calix[4]arene thiourea derivative **2** and **3** by the reaction of the easily accessible 1,3-distally substituted calix[4]arene amine **1** with the corresponding isothiocyanate in dry CH_2Cl_2 with satisfactory yield. The constitutions of **2** and **3** were proved by FAB-MS, FT-IR spectra and elemental analyses. The ^{1}H NMR spectra of **2** and **3** show a pair of doublet arising from the methylene protons, which demonstrate that both are distal isomers with cone conformation.

As can been seen in Fig. 1, the crystal structure of **2** displays a flattened, approximate two-fold symmetry cone conformation. The two phenyl rings which bear the urea moieties form with the least square plane defined by methylene bridge dihedral angles of 66.8 and 67.8°, respectively. As a consequence, the other two phenyl rings are pushed towards the exterior of the cavity mentioned above ($\delta = 56.8$ and 57.4°). The dihedral angles between opposite rings are 45.4 and 66.0°, respectively. Thus the opening of the cavity becomes elliptical accompanying with the *tert*-butyl groups pitched slightly away from the cavity. The two stronger intramolecular O–H···O hydrogen bonding between the phenolic oxygens and the proximal ethereal oxygens [d(O2···O1) = 2.808 Å, ∠O2–H2···O1 = 172.0°; d(O4–H4···O3) = 2.833 Å, ∠O4–H4···O3 = 172.5°] and two weaker transannular hydrogen bonding interactions of N2–H2···O2 [d(N2···O2) = 3.052 Å; ∠N2–H2···O2 = 147.0°] and N4–H4···O4 [d(N4···O4) = 3.060 Å; ∠N4–H4···O4 = 142.2°] are jointly responsible for such



Scheme 1. Strategy for the synthesis of calix[4]arene thiourea derivative **2** and **3**.

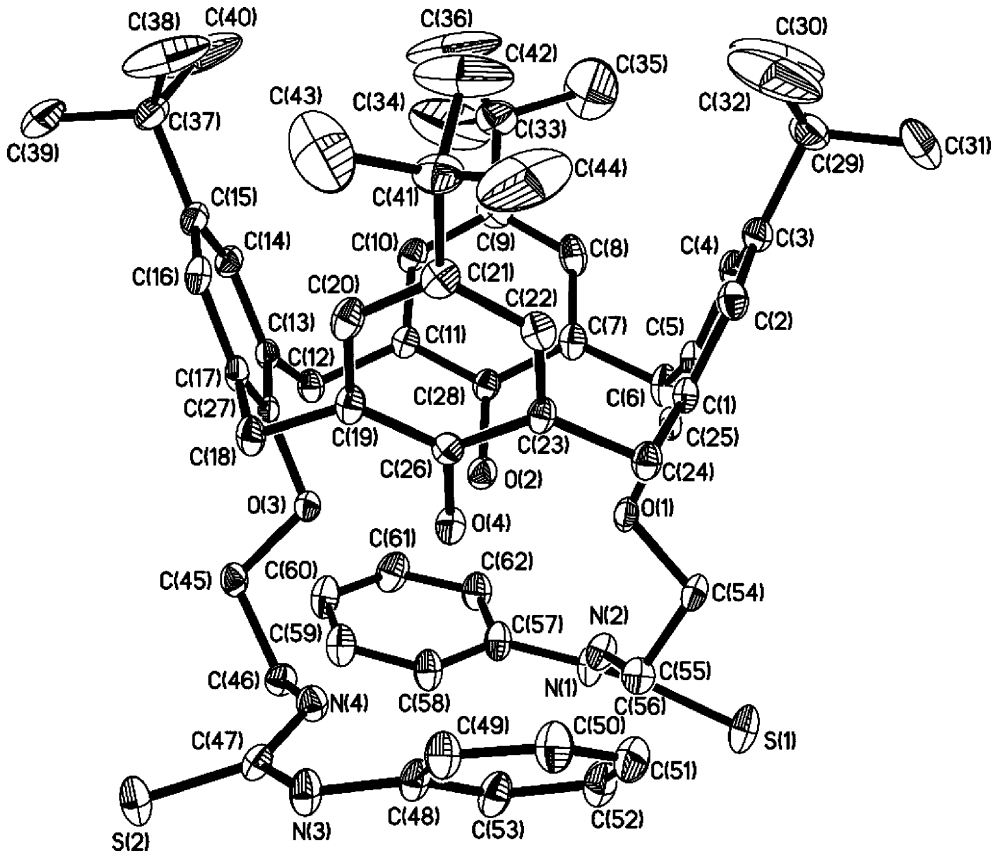


Fig. 1. ORTEP drawing of crystal structure of **2** (hydrogen atoms and a acetonitrile molecule are omitted for clarity).

an open conformation features. Interestingly, the other two phenyl rings of **2** are tilted with respect to the least-squares plane defined by the methylene groups with the dihedral angles of 19.4 and 28.2°, respectively. Meanwhile, The structure of **2**-acetonitrile complex shows that the acetonitrile lies on the pseudo crystallographic four-fold axis with the nitrogen atom directed *exo* and the methyl pointing *inside* the intramolecular cavity, which is attributed to the specific CH−π interaction between the acetonitrile CH_3 group and the aromatic nuclei of **2**. These structural characteristics promote the possibility of the self-assembly of **2** by the cooperative hydrogen bonding and π−π interactions in the solid state.

As can be readily seen from Fig. 2, both thiourea groups attached to lower rim of **2** are connected with the others in adjacent **2** along the *a* axis through specific N−H···S hydrogen bonding between adjacent thiourea group. The distances and angles of two N−H···S hydrogen bonding are 3.455, 3.463 Å, and 168.3, 165.9°, respectively, which indicate that both hydrogen bonding are same in strength. The uniform hand-in-hand pattern results in the 1D chainlike structure formation of **2**.

A more intriguing feature of this architecture is the mutual penetration of 1D chainlike by the intermolecular π−π interactions to fabricate 2D supramolecular assembly. As can be seen from Fig. 3, each of phenyls bearing thiourea group is offset-stacked to one of the phenyl of a neighboring **2**, and simultaneously interacts with the two 'tilted-down' phenyls of the neighboring identical **2** in the edge-to-face mode. The centroid separation of the offset stacking is 5.231 Å, while the centroid separations and dihedral angles of the edge-to-face interaction are 4.688 Å and

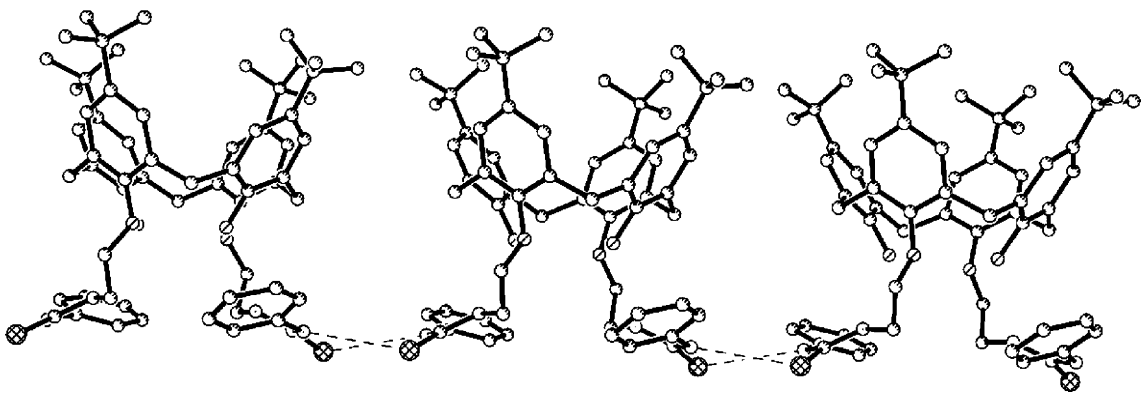


Fig. 2. 1D chainlike structure of **2** formed by hydrogen bonding along *a* axis.

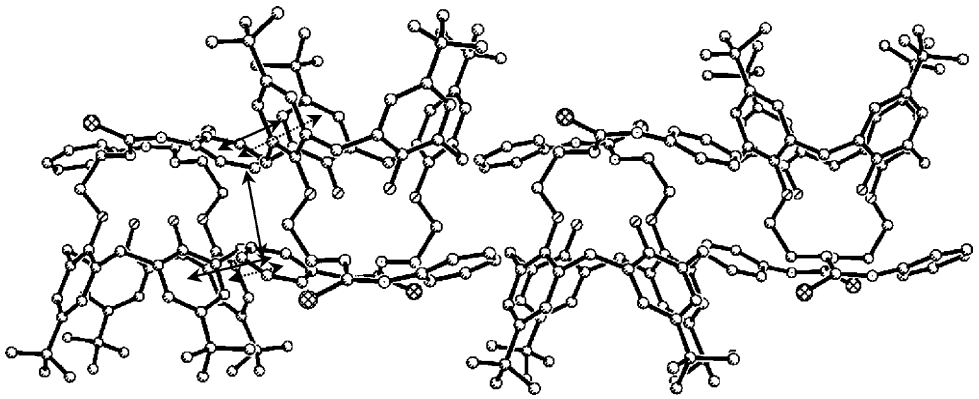


Fig. 3. 1D zig–zag structure formed by π–π interactions along *b* axis. (Double-headed arrows represent the π–π interacting inter-phenyl plane).

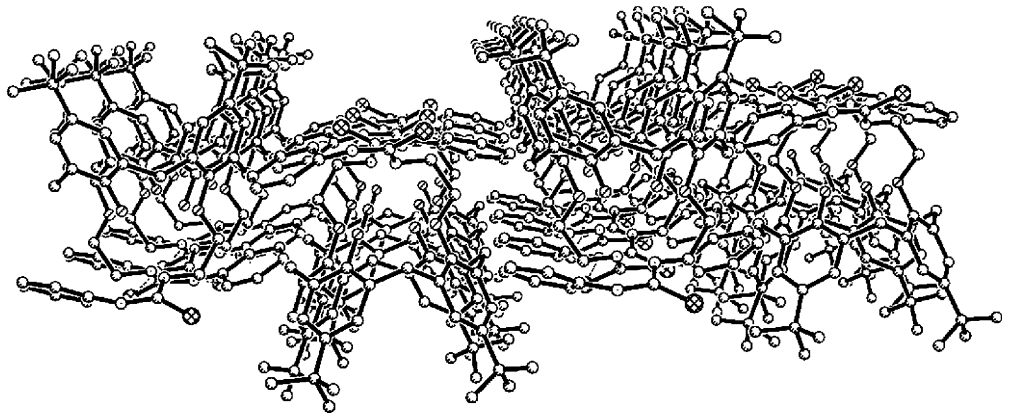


Fig. 4. Higher-order 2D supramolecular architecture of **2** formed by synergic hydrogen bonding and π–π interactions.

39.2°, 4.746 Å and 74.7°, respectively. These values are quite reasonable in view of the π−π interaction theory [11–14] and therefore such interactions contribute greatly to the stabilization of the neatly supramolecular cross-bedded self-adhesive structure shown in Fig. 4, which is distinguished from the assemblies of calixarene urea derivatives reported by Böhmer [15].

4. Conclusions

In conclusion, we have presented two novel calix[4]arene thiourea derivative **2** and **3** and the direct evidence for the formation and structural details of a unique 2D supramolecular architecture of crystalline **2** possessing thiourea functions at the lower rims. The rigid linear strand structure was ascribed to the hydrogen bonding interaction of two thiourea units between two adjacent **2**. The zig−zag are mediated by the synergetic offset stacking and edge-to-face π−π interactions. Further the cross-bedded network ultimately weaves the higher-order 2D architecture. The structural hierarchy and sophisticated modes of intermolecular interactions revealed in the present study may be compared to the highly ordered biological supramolecular systems such as globular proteins [16] and cysteine proteinases [17], and thrown lights on the design of relevant organic supramolecular assemblies based on the noncovalent interactions.

5. Supplementary materials

Crystallographic data for calix[4]arene thiourea derivative **2** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary materials (No. CCDC-161205). Copies of available material can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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