Macrocyclic Compounds from Benzenedithiols and Triazine: Modification of Tetrathiacalix[4]arene

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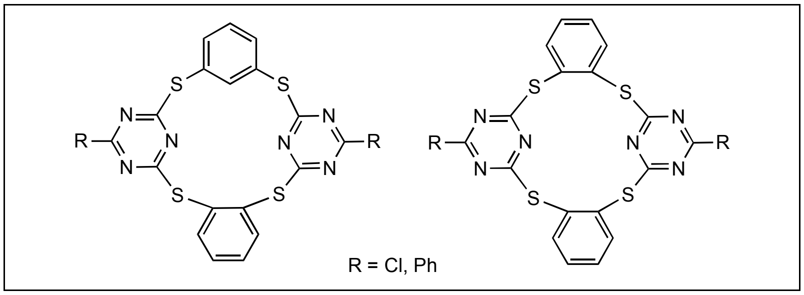

Synthesis of macrocyclic compounds having benzenedithionate and triazine moieties was achieved by an efficient fragment coupling approach. In the solid state, they adopted *1,3*-alternate conformations. Combination of two pairs of electron rich and electron poor units, and *ortho-ortho* and/or *ortho-meta* connections of sulfur atoms with aromatic carbons were novel features of the macrocycles.

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INTRODUCTION

Macrocyclic building blocks have attracted considerable interest in supramolecular chemistry [1]. The methylene bridge of calix[4]arene has been replaced by various heteroatoms such as sulfur, nitrogen, oxygen, boron, silicon, germanium, and phosphorous [2,3].

Some intriguing macrocycles having heterocycles such as calixpyrroles [4], calixpyridines [5], and other heteroaromatics [6] have emerged as powerful tools for binding ions and/or even neutral molecules. Recent results concerning anion recognitions have also shown that triazine is an electron deficient π-aromatic component which can interact with anionic species [7,8]. The triazine [9] skeleton has already been incorporated by many authors for the synthesis of hetroatom-bridged calixarenes the same as pyridine and pyrimidine [10]. Tetrathiacalix[4]arenes have also some unique structural advantages [3,11]. Classical calix[n]arene or [In]metacyclophanes are *meta-meta* connected macrocycles, whereas cyclophanes having *ortho-ortho* or *ortho-meta* connected with methylene or other heteroatoms have not appeared in the literature [12]. Here, 1,2-benzenedithionate seems to decrease the cavity size and simultaneously increase the structural rigidity [13,14].

We report herein, the first synthesis of macrocyclic compounds having benzenedithionate and triazine moieties.

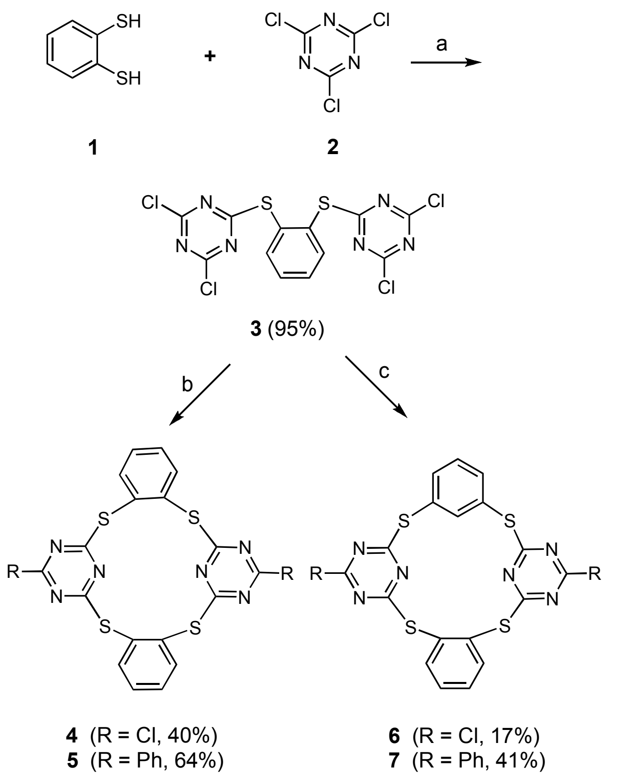
RESULTS AND DISCUSSION

Cyanuric chlorides have high reactivity towards nucleophilic reagents. Therefore, 1,2-benzenedithiol was allowed to react with 2.0 equiv of cyanuric chloride in THF at 0 °C in the presence of diisopropylethylamine (DIPEA) as an acid scavenger (Scheme 1). Linear trimer, 1,2-bis(dichloro-*s*-triazynylthio)benzene (**3**), was generated in slow reactions. The results of controlled experiments are reported in Table 1 (entries 1-6). Isolated yields were surprisingly improved after lengthening of both mixing time of reactants and reaction time under more dilute conditions. The best yield (95%) of linear trimer **3** was observed in the reaction for 45 h.

The macrocyclizative coupling reaction between **1** and **3** was also carried out in acetone at room temperature in dilute condition in the presence of DIPEA as a base. Typical isolated yields of tetrathia[2]arene[2]triazine (**4**) are summarized in Table 1(entries 7-11). The yield of **4** was increased up to 40%. A similar coupling reaction was also carried out between **3** and 1,3-benzenedithiol and *ortho-meta* derivative (**6**) was isolated in 14% yield. Cyclophanes **4** and **6** have each two chloride functional groups and thus open the opportunity to convert them into other derivatives with appropriate nucleophiles.

For instance, chlorine atoms of **4** and **6** were successfully replaced by PhMgBr/THF in THF at 50°C for 10 h. Isolation of corresponding benzo analogues, **5** (64%) and **7** (41%)**,** revealed that the nucleophilic replacement afforded corresponding phenyl derivatives.

Scheme 1



Reagents and conditions: a. THF, DIPEA, 0°C; b. (i) DIPEA, acetone, 1,2-benzenedithiol, rt, (ii) PhMgBr/THF; c. (i) DIPEA, acetone, 1,3-benzenedithiol, rt, (ii) PhMgBr/THF.

The structures of all products were unambiguously characterized by spectroscopic data. In ^{1}H and ^{13}C NMR, the compounds **3**, **4** and **5** showed symmetric signals while unsymmetrical peaks appeared for remaining compounds. Recrystallization of **5** and **7** from hexane/CH_2Cl_2 gave some single crystals suitable for X-ray crystallographic analysis.

Table 1. Synthesis of **3** and **4** by fragment coupling strategy

entry[a]	time[b]	**3**[c]	entry[d]	time[b]	**4**[c]
1	1 + 8 h	3	7	7 + 6 h	24
2	4 + 0 h	30	8	5 + 14 h	30
3	16 + 8 h	78	9	8+ 18 h	24
4	20 + 20 h	91	10	7 + 25 h	40
5	23 + 18 h	82	11	6+ 50 h	21
6	25+ 20 h	95			

[a] A reaction between **1** and **2**, [b] Period of the mixing of reactants + reaction time, [c] Isolated yields in %,[d] A reaction between **3** and **1**.

The compounds adopted the expected *1,3-alternate* conformation in the solid state [15,16]. The pair of central benzene rings framed themselves in a clip-like conformation, while the remaining two triazine rings are

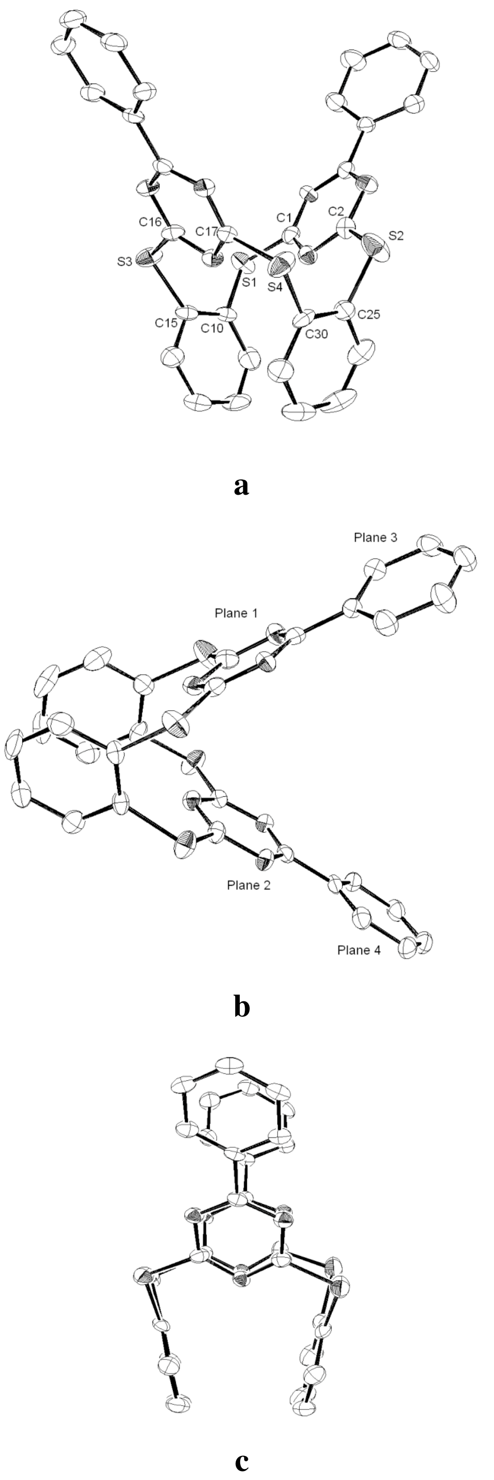


Figure 1. ORTEP structures of compound **5** demonstrating the *1,3-alternate* conformation in the solid state; for clarity all hydrogen atoms are omitted. (a) Top view, where bond lengths Å (sulfur to heteroaromatic carbon) S1-C1 1.745(2), S2-C3 1.731(2), S3-C16 1.7603(19), S4-C17 1.727(2); (sulfur to aromatic carbon) S1-C10 1.769(2), S2-C35 1.7879(19), S3-C15 1.7785(19), S4-C30 1.7919(17) (b) Side view shows π–π stacking where the distance between plane 1 and plane 2 is 4.663 Å and plane 3 and plane 4 is 9.131 Å (c) Side view shows clip like conformation.

roughly coplanar and edge-to-edge oriented and well separated. Conformational structures appeared more clearly due to the attachment of two phenyl groups with the outer *s*-triazine moiety. The four bridging sulfur atoms of both compounds are located nearly at the same plane although they were *ortho-ortho* or *ortho-meta* connected with aromatic units.

For introduction of 1,2-benzodithionate elements in the calixes, the comparative flexibility of the four bridges (sulfur atoms) are reduced while corresponding stresses of the two parallel benzene ring towards the center of cavity are increased. Therefore, π–π stacking interaction of the two central benzene rings, the position of bridging sulfur in the conformational structures and observable cavities were different than *meta-meta* connected tetrathiacalix[4]arene.

The average bond lengths for S-C (heteroaromatic carbon) and S-C (aromatic carbon) are 1.740 and 1.781 Å for **5**, while these values are 1.755 and 1.773 Å for compound **7**. The bond distance from sulfur to the aromatic carbon is larger than that of sulfur to the heteroaromatic carbon (Fig. 1a and 2a). Therefore, the sulfur atom is more conjugated with the triazine units than with the phenyl ring. The same results were also reflected for similar oxa and azacalixerenes [9a].

The dihedral angles between the triazine ring and the outer phenyl ring are 18.839° and 5.406° for compound **5**. Almost the same angles were observed for compound **7**. It seems that the outer phenyl rings and triazines stay in completely different planes due to different electrostatic interactions among various units. The cavity of the macrocycles is an important criterion to hold the various guest species. No solvent molecule was found to bind within cavities, and therefore, the cavities were too small to allow small solvent molecules [11b].

The distances between two triazine rings at the upper rim are 4.663 and 6.292 Å for **5** and **7** respectively (Fig. **1b** and **2b**). The greater separation of the outer phenyl rings of **7** suggests that its comparative cavity size is larger than that of **5**. This result is also expected from bonding arrangements of the sulfur atoms. The cavities are viewed as resulting from a cyclic array of two isolated phenyl rings and triazine units in a *1,3-alternate* fashion. Hence, tuning of the isomeric position of the bridging sulfur can control the cavity size of macrocycle.

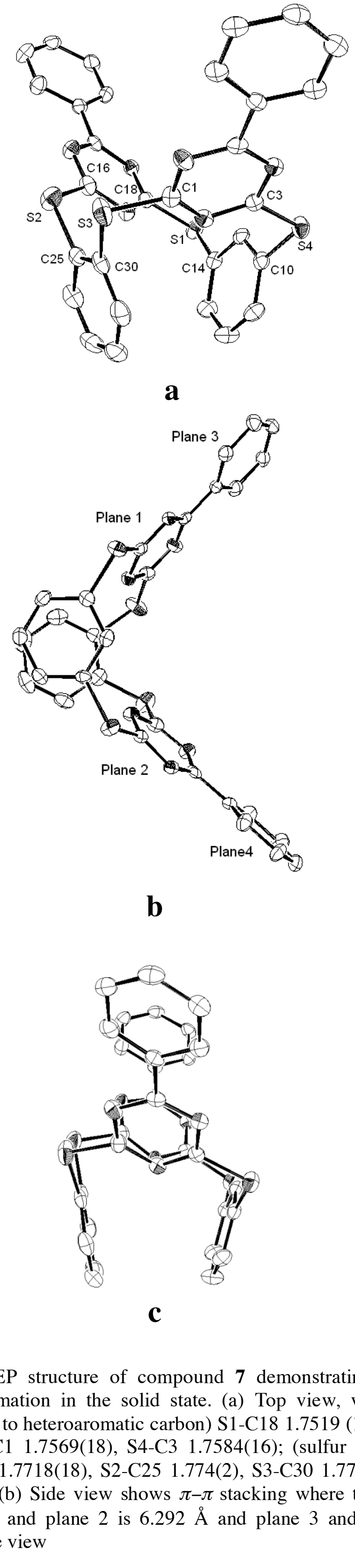


Figure 2. ORTEP structure of compound **7** demonstrating the *1,3-alternate* conformation in the solid state. (a) Top view, where bond lengths Å (sulfur to heteroaromatic carbon) S1-C18 1.7519 (17), S2-C16 1.7532(18), S3-C1 1.7569(18), S4-C3 1.7584(16); (sulfur to aromatic carbon) S1-C14 1.7718(18), S2-C25 1.774(2), S3-C30 1.7748(19), S4-C10 1.7739(18) (b) Side view shows π–π stacking where the distance between plane 1 and plane 2 is 6.292 Å and plane 3 and plane 4 is 12.143 Å (c) Side view

The rings are almost perpendicular to the plane formed by the four bridging sulfur with inclined angles near 90°. The average distances of the face-to-face paralleled phenyl rings are 4.002 and 4.127 Å for compounds **5** and **7**, respectively, suggesting a weak π–π stacking interaction in the solid state. For a similar type of oxacalixarene the average distance of face-to-face the phenyl rings is 4.726 Å [9a]. The parent calixarene has intramolecular hydrogen bonding that forces it into a cone conformation, but macrocycles **5** and **7** lack such bonds. Moreover, to avoid possible steric hindrance from the cone conformation, these molecules adopt a *1,3-alternate* conformation. The crystal structures of these macrocylcles result from the combination of electronic and steric factors of bridging sulfur, triazine as well as phenyl rings.

The same conformation was also observed for azacalix-[2]arene[2]pyridine [9b]· which also adopted a *1,3-alternate* as the most energetically stable conformation. The electron withdrawing nature of triazine is very strong and the steric repulsion between triazinyl and bridging moieties are weak. Therefore, the sulfur atom may favor triazine ring to be conjugated rather than the phenyl ring.

CONCLUSION

Triazine is regarded as a π-deficient aromatic ring with a little positive charge [8], and thus two opposite triazine rings in the macrocycles adopted roughly coplanar and are kept apart from each other. In contrast, however, the two opposite the phenyl rings tend to align in parallel due to weak *π–π* stacking interaction that might bring an extra stabilization to the molecules.

In conclusion, two novel modified tetrathiacalix[4]-arenes have been developed by stepwise fragment coupling approach. The cavity size of the calixarenes was varied for binding positions of sulfur atoms. *Ortho-ortho* and/or *ortho-meta* connections of sulfur atom with aromatic carbon offered some novel structural features in the solid state. Combination of two pairs of electron rich and electron deficient *π*-aromatics indicates a good design for construction of *1,3-alternate* macrocycles. Syntheses of macrocyclic compounds having more structural flexibility by using aromatic dithiols are underway.

EXPERIMENTAL

Melting points were measured with a MEL-TEMP capillary melting point apparatus and are uncorrected. ^{1}H-(400 MHz) and ^{13}C-(101MHz) NMR spectra are recorded on a Bruker AC-400P instrument with $CDCl_3$ as a solvent. ^{1}H NMR chemical shifts are given ppm from internal TMS. ^{13}C NMR chemical shifts are given in relative ppm from internal $CDCl_3$ δ Acetone, CH_2Cl_2 and THF were freshly distilled according to standard laboratory procedures prior to use. 1,2- And 1,3-benzenedithiols were synthesized according to the standard literature methods [17]. Diisopropylethylamine (DIPEA) and cyanuric chloride were purchased from Aldrich and these were used without further purification. FAB MS was measured by using matrix of nitrobenzylalcohol/dithiothreitol (NBA/DTT). C-200 was used for silica gel column chromatography. Elemental analyses were recorded using Yanaco MT-5 apparatus at the elemental analysis division of Iwate University.

1,3-Bis(dichloro-*s*-triazinylthio)benzene (3). In a typical run (run 6, Table 1), a solution of cyanuric chloride (14.75 g, 80 mmol) in THF (200 ml) was taken in a 500 ml three neck reactor under air. Diisopropylethylamine (DIPEA, 4.2 ml, 24 mmol) was poured into the reactor and the mixture was cooled to 0°C. A solution of 1,2-benzenedithiol (2.76 g, 20 mmol) in THF (200 ml) was added dropwise into the reactor over 25 h. The reaction mixture was stirred for 20 h at room temperature. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel using $CHCl_3$/*n*-hexane (1:1) as an eluent to give product **3** (8.30 g, 95%) as a colorless solid. mp 128.0-129.2°C; ir (KBr): 1510, 1478, 1243, 845 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 6.0, 3.2Hz, 2H, ArH), 7.75 (dd, *J* = 6.0, 3.3Hz, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.72, 132.08, 137.59, 170.47, 184.98; FAB MS: m/z = 439 [M+1]$^+$. *Anal* calcd. for $C_{26}H_4N_6S_2$: C 32.90; H 0.92; N 19.18. Found: C 32.90; H 1.08; N 18.85.

Tetrathiacalix[2]*ortho-ortho* arene[2]triazine (4). A solution of DIPEA (0.84 ml, 4.8 mmol) in acetone (140 ml) was stirred under N_2 in a 500 ml three neck flask fitted with two dropping funnels. 1,2-Benzenedithiol (0.28 g, 2 mmol) was dissolved in acetone (60 ml) and the solution was taken in one dropping funnel. In another dropping funnel, a solution of compound **3** (0.87 g, 2 mmol) in acetone (60 ml) was taken at the same time. The two reactants were simultaneously dropped into the DIPEA solution under constant stirring over 7 h at room temperature. The reaction mixture was stirred for 25 h at room temperature. Acetone was evaporated and crude product was separated by column chromatography on silica gel using $CHCl_3$/ *n*-hexane (2:1) as an eluent to yield product **4** (40%) as a colorless solid. mp. >300.0 °C; ir (KBr): 1502, 1460, 1249, 843, 759, 561 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (dd, *J* = 5.5, 3.6 Hz, 4H, ArH), 7.41 (dd, *J* =5.5, 3.6 Hz, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.35, 132.49, 137.77, 168.02, 183.04; FAB MS: m/z = 507 [M+1]$^+$. *Anal* calcd. for $C_{18}H_8N_6S_4Cl_2$: C 42.60; H 1.59; N 16.56. Found: C 42.52; H 1.80; N 16.22.

Compound 5. Macrocycle **4** (0.10 g, 0.2 mmol) was dissolved in THF (20 ml) and the solution was placed in an ice-bath under N_2. PhMgBr in THF (5 equiv.) was added and the reaction mixture was refluxed for 10 h at 50 °C. The reaction mixture was quenched with ice water, acidified with HCl and extracted with CH_2Cl_2. The organic product was dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography by using $CHCl_3$/*n*-hexane (2:1) as an eluent to afford **5** in 64% yield. Colorless solid, mp. >300.0 °C; ir (KBr): 1495, 1442, 1249, 763 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, *J* = 3.4, 6.0 Hz, 4H, ArH), 7.43 (t, *J* = 8.0 Hz, 2H, ArH), 7.46 (dd, *J* =3.4, 6.0Hz, 4H, ArH), 7.52 (t, *J* = 7.2Hz, 4H, ArH), 8.40 (d, *J* = 8.4Hz, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ 128.54, 129.23, 130.62, 132.80, 133.50, 134.32, 137.71, 168.77, 181.79; FAB MS: m/z = 591[M+1]$^+$. *Anal* calcd. for $C_{30}H_{18}N_6S_4$: C 60.99; H 3.07; N 14.23. Found: C 60.90; H 3.15; N 14.23.

Tetrathiacalix[2] *ortho-ortho* and *ortho-para* arene[2]-triazine (6). The experimental procedure for compound **6** was the same as that of compound **4**. In both cases a single macrocyle was isolated. Generation of macrocyles larger than **4** or **6** was not observed at all. Colorless solid, mp. 300.0 °C; ir (KBr): 1493, 1441, 1375, 1315, 1275, 124, 840, 762, 693, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (t, *J* = 8.4 Hz, 1H, ArH), 7.29-7.40 (m, 6H, ArH), 7.43 (t, *J* =1.7 Hz, 1H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ 127.69, 130.49, 131.01, 132.20, 137.30, 137.61, 143.90, 168.04, 182.82, 184.02; FAB MS: m/z = 507 [M+1]$^+$. *Anal* calcd. for $C_{18}H_8N_6S_4Cl_2$: C 42.60; H 1.59; N 16.56. Found: C 42.54; H 1.81; N 16.29.

Compound 7. The experimental procedure for compound **7** was as same as that of compound **5**. Colorless solid, mp. >300.0 °C; ir (KBr): 1492, 1441, 1375, 1316, 1275, 1248, 837, 763, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16-7.20 (m 1H, ArH), 7.26-7.30 (m, 2H, ArH), 7.37-7.39 (m 2H, ArH), 7.42-7.46 (m, 2H, ArH), 7.48-7.51 (m, 5H, ArH), 7.53-7.58 (m, 2H, ArH), 8.43-8.45 (m, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$): δ 127.01, 127.69, 128.00, 129.00, 130.49, 131.01, 132.20, 132.40, 136.53, 137.30, 137.61, 143.90, 168.04, 169.10, 182.82, 184.50; FAB MS: m/z = 591 [M+1]$^+$. *Anal* calcd. for $C_{30}H_{18}N_6S_4$: C 60.99; H 3.07; N 14.23. Found: C 60.70; H 3.35; N 14.20.

Crystallographic information. X-ray crystal data for compounds **5** and **7** have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 640621 and CCDC 640622, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK [fax: 44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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[15] Crystal data for compound **5**: M = 590.74, $C_{30}H_{18}N_6S_4$, monoclinic, space group $P2_1/n$ (#14), a = 9.304(5) Å, b = 20.734(3) Å, c = 14.224 (3) Å, β = 90.6696(16)° V= 2743.6(16)Å^3, Z = 4, D_{calc}= 1.430g cm^{-3}, T = 123 K, Radiation $M_0K\alpha$ (λ=71075 Å). A colorless prism crystal of approximate dimensions of 0.20 x 0.20 x 0.10 mm was used for the measurement. The structure was solved by the direct methods and expanded using Fourier technique (DIRDIF-99). All the calculations were performed using crystal structure 3.5.1 crystal structure analysis package of Rigaku and Rigaku/MSC. The final cycle of full matrix least squares refinement was 0.20 x 0.20 x 0.10 mm was used for the measurement. The structure was solved by the direct methods and expanded using Fourier technique (DIRDIF-99). All the calculations based on 6045 observed reflections (I >2.00σ (I)) and 361 variables parameters with R1= 0.0399 and wR2= 0.0497(all data).

[16] Crystal data for compound **7**: M = 590.74, $C_{30}H_{18}N_6S_4$, orthorhombic, space group $P2_12_12_1/n$ (#19), a = 10.0499(6) Å, b = 14.1979(10) Å, c = 19.0802(14) Å, V= 2722.5(3) Å^3, Z = 4, D_{calc}= 1.441g cm^{-3}, T = 123 K, Radiation $M_0K\alpha$ (λ= 0.7107A). A colorless block crystal of approximate dimensions of 0.40 x 0.20 x 0.20 mm was used for the measurement. The structure was solved by the direct methods and expanded using Fourier technique (DIRDIF-99). All the calculations were performed using crystal structure 3.5.1 crystal structure analysis package of Rigaku and Rigaku/MSC. The final cycle of full matrix least squares refinement was based on 6223 observed reflections (I >2.00σ (I)) and 380 variables parameters with R1= 0.0296 and wR2= 0.0557(all data).

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