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# Hydrogen Bond Energies and Cooperativity in Substituted Calix[*n*]arenes (*n* = 4, 5)

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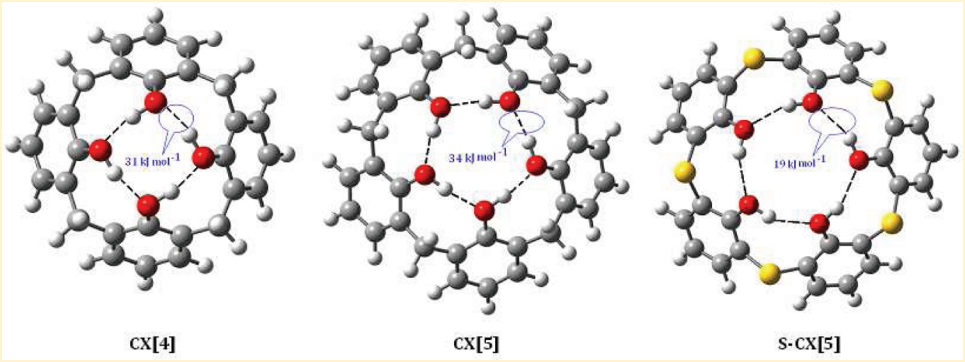
Supporting Information




**ABSTRACT:** Hydrogen-bonded interactions in *para*-substituted calix[*n*]arenes (CX[*n*]) (*n* = 4, 5) and their thia analogues are analyzed using the recently proposed molecular tailoring approach. The cooperative contribution toward the hydrogen-bonding network within the CX[5] host is shown to be nearly 5 times larger than that in its thia analogue. Hydrogen bond strengths in the O−H···O network are enhanced on substitution of an electron-donating group. The cooperativity contributions are reflected in the electron density at the bond critical point in the quantum theory of atoms in molecules.

## INTRODUCTION

The family of cyclodextrins (CDs),[1] and higher generation cucurbituril[2] and calixarene (CX)[3−5] hosts, has attracted significant attention in molecular recognition and supramolecular chemistry owing to their selective and efficient binding toward neutral or cationic guests and macromolecules as well.[5−12] The electronic structure of such novel macrocyclic receptors should prove useful in understanding host-guest interactions at the molecular level.[13−16] Hydrogen bonding and the underlying cooperativity therein govern the energetics of CD or CX conformers.[17,18] With this view intra- and intermolecular hydrogen bond energies (HBEs) are analyzed by $^1$H NMR, vibrational spectroscopy experiments and molecular modeling.[19−22] The varying definitions of an intermolecular hydrogen bond pose certain difficulties for estimation of the corresponding bond energies.[23] Recently, Gadre and co-workers[23−26] proposed a direct method to derive HBEs based on the molecular tailoring approach (MTA) wherein a molecule is scissored into a set of fragments and HBEs are subsequently estimated by appropriate addition or subtraction of the overlapping part from each fragment. Hydrogen-bonded interactions in biological molecules and those in novel hosts considered in the previous studies exhibit cooperativity,[24−26] which links together molecules or parts thereof into three-dimensional arrays. Because of polarizability or charge transfer characteristics of such continuous patterns, the bond energy of a hydrogen-bonded structure is greater than the sum of the bond energies of the individual bonds..[27−29] The cooperative effect was first observed in CDs that possess intermolecular and intramolecular hydrogen bonds from primary and secondary hydroxyl groups.[27,30−32] Recently, the structure and stability of $\alpha$-, $\beta$-, and $\gamma$-CD conformers have been analyzed in terms of HBEs and cooperativity from MTA-based method.[26] HBEs thus obtained vary from 4.6 to 34.7 kJ mol$^{-1}$, and cooperative contributions are shown to be 1.0−11.5 kJ mol$^{-1}$. Interestingly, calixarenes, the third generation of supramolecular hosts, are composed of phenolic units linked via methylene groups that engender bowl-shaped cavities of varying dimensions.[33] Hydroxyl groups facilitating the hydrogen-bonded network in CX[*n*] can further be modified to enhance the selectivity and binding toward a guest.[33−35] It has been shown that thiacalixarenes (S-CX[*n*]) in which bridging $CH_2$ groups are replaced by S atoms can serve as a platform for a variety of applications in catalysis, chromatography, drug delivery machines, and pharmaceutical science.[36,37] Furthermore, the host cavity dimensions and electronic charge

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distribution therein provide insights for host-guest binding.[15,16] Intramolecular hydrogen bonding further governs the cavity-forming process. Thus, hydrogen-bonding sites when properly positioned within the same molecular architecture are responsible for the formation, preorganization, and binding ability of the host.[38] The interconnected network of hydrogen bonds leads to a phenomenon termed "cooperativity",[39,40] which can be gauged indirectly from the geometry, dipole moments, and IR spectral frequencies and band intensities.[40−43] Thus, the structural features and energetics of cooperative H-bonding in CX[$n$] receptors are of primary importance. Hydrogen bonding in CX[$n$] derivatives has been characterized from $^1$H NMR[44] or the OH stretching vibration in IR spectroscopy experiments.[45,46] A series of NMR relaxation measurements in nonpolar solvents were applied for studying the dynamics of the circular hydrogen bond array in CX[4].[29] Subsequently, cooperative intramolecular hydrogen bonding in CX[4] and S-CX[4] and their *t*-Bu derivatives has further been investigated. A substantial frequency red shift in the O−H vibration of the phenol monomer observed in the infrared spectra of CX[4] suggested strong cooperative intramolecular hydrogen bonding, which was inferred from duplication of the number of O−H infrared bands and H-bond enthalpy.[45] Moreover, Fourier transform IR spectroscopic measurements on CX[$n$] ($n$ = 4, 6, 8) have shown that cyclic cooperative intramolecular hydrogen bonding is responsible for a stable conformation which is not affected by the presence of bulky substituents.[47] In a very recent work, Novikov and Shapiro[18] have studied the energetics and cooperative hydrogen bonding in *para*-substituted calix[$n$]arenes and thiacalix[$n$]arenes employing quantum chemical and density functional calculations. Intramolecular HBEs in calixarene hosts were calculated in terms of the energy difference between the monoanion and the neutral system and by further computing the energy of phenol relative to its anion, which enables one to elucidate the mechanism of nucleophilic substitution reactions. The present study focuses on systematic analyses of H-bond interactions in substituted calix[$n$]arene ($n$ = 4, 5) conformers. The energies, cooperativity in particular how they correlate to topographical indices in molecular electron density and vibrational frequency have been investigated in this work.

## COMPUTATIONAL METHOD

Geometry optimizations of different CX[$n$] and S-CX[$n$] ($n$ = 4, 5) conformers were carried out within the framework of density functional theory (DFT) incorporating Becke's three-parameter exchange with the Lee, Yang, and Parr (B3LYP)[47,48] correlation functional employing the 6-311G(d, p) basis set. Calculations were carried out using the Gaussian 09 suite[49] of programs. The optimized geometry of the CX[$n$] monomer is displayed in Figure 1. Stationary point geometries were confirmed to be local minima on the potential energy surface since all the normal vibrational frequencies turned out to be real. The quantum theory of atoms in molecules (QTAIM) proposed by Bader and co-workers[50,51] was used to investigate the molecular electron density (MED) topography, and accordingly, the bond critical point (bcp), characterized as (3, −1) CP, of hydrogen bonds was located. The program UNIVIS developed in our laboratory was used to calculate the density at the bcp ($\rho_{bcp}$) in the corresponding MED topography.[52]

A brief outline of the methodology for estimating HBEs in O−H···O interactions is given below. The CX[$n$] molecule (aromatic rings are chopped off for simplicity) is shown in Figure 2 along with important primary and secondary fragments. Four intramolecular H-bonds labeled as HB1, HB2, HB3, and HB4 are depicted. The primary fragments (fragments 1−4) are generated by replacing each O−H functional group with a H atom. The secondary fragments are the binary overlaps of the primary fragments (excluding dummy H atoms). The single-point energies of primary and all possible secondary, ternary, and quaternary fragments have been utilized in the present MTA model. Details of the MTA method may be found in refs 24 and 25. H-bond energies ($E_{HB}$) of modeled calix[$n$]arene (shown in Figure 2) in the presence of a H-bond network have been obtained by employing the following equations:

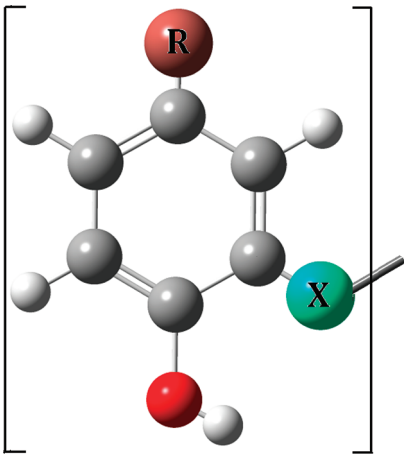


**Figure 1.** Calix[$n$]arene monomer.

$$E_{HB1} = (E_{Frag1} + E_{Frag2} - E_{Frag5}) - E_{modeled\ calix[n]arene}$$

$$E_{HB2} = (E_{Frag2} + E_{Frag3} - E_{Frag6}) - E_{modeled\ calix[n]arene}$$

$$E_{HB3} = (E_{Frag3} + E_{Frag4} - E_{Frag7}) - E_{modeled\ calix[n]arene}$$

$$E_{HB4} = (E_{Frag1} + E_{Frag4} - E_{Frag8}) - E_{modeled\ calix[n]arene}$$

The contribution of the networking effect (cooperativity) toward each individual hydrogen bond has been obtained by isolating the corresponding H-bond from the network.[24] Cooperative contributions are calculated from the difference in energy of a particular hydrogen bond in the presence and absence of a network. For example, $E_{HB1}$ in the absence of a H-bond network can be evaluated by considering fragment 7 as the parent molecule. Here, in fragment 7, HB1 is no longer a part of the H-bond network. The HBE estimated in fragment 7 is referred to as $E_{HB1}$ in the absence of a network. The cooperativity contribution toward HB1 can thus be obtained.

## RESULTS AND DISCUSSION

The CX[$n$] ($n$ = 4, 5) host exhibits exhibits four different conformations, viz., cone, partial cone, 1,2-alternate, and 1,3-


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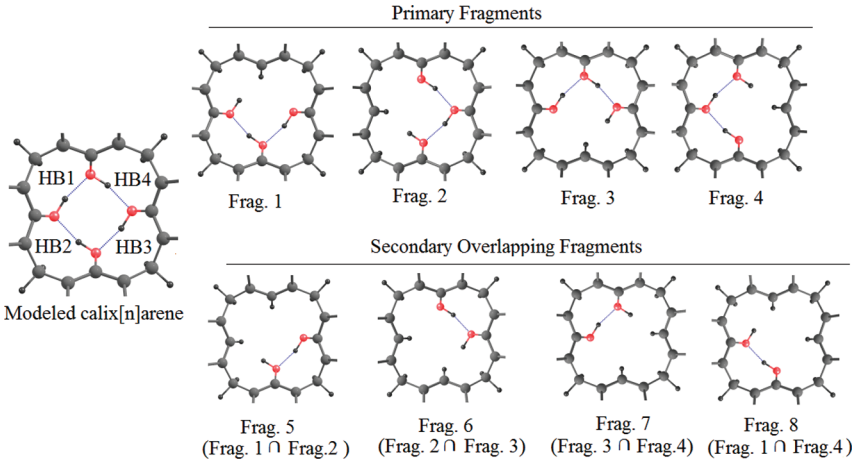


**Figure 2.** MTA method illustrated with CX[4] as a test case.

alternate. It has been shown that in the solid state or in $CCl_4$ solution[4,5,45,53] CX[4] and S-CX[4] exhibit the cone conformation stabilized via an extended hydrogen-bonding network.[38,45,54] Theoretical calculations further support these observations.[55−57] The lowering of energy in this conformer stems from the number and strength of O−H···O and O−H···S interactions. CX[*n*] hosts substituted (at symmetry-equivalent positions) with $NH_2$, *t*-Bu, $CH_2Cl$, $SO_3H$, and $NO_2$ and S-CX[*n*]-R (R = H, *t*-Bu) groups are considered. The self-consistent field (SCF) energies of these conformers from MTA vary within 2 kJ $mol^{-1}$ of the corresponding values from B3LYP theory (cf. Table 1). The HBE values from MTA in different conformers of CX[*n*] and S-CX[*n*] hosts are given in Table 1S of the Supporting Information. It has previously been shown that the estimated error associated with HBEs from MTA turns out to be nearly 2 kJ $mol^{-1}$.[23] As predicted earlier, the energies in CX[4] conformers follow the order cone > partial cone > 1,2-alterrnate > 1,3-alternate, which can also be explained by the number of hydrogen-bonded interactions and cooperativity from the MTA approach. For example, the cone conformer of CX[4] possesses a large number (four) of hydrogen-bonded interactions (which are symmetry related, and hence, only one value is given in Table 1S) and also a relatively large cooperativity contribution. The partial cone and 1,2-alternate conformers reveal the same number (two) of hydrogen-bonded interactions; however, the cooperativity contributions (cf. Table 1S) are relatively large in the former. The 1,3-alternate conformer is void of hydrogen-bonded interactions. Similar inferences can be drawn in the case of CX[5] and S-CX[*n*] hosts. In Table 2 we present the intramolecular HBEs from MTA for cone conformers of CX[*n*] derivatives. As shown, the HBEs in substituted CX[4] hosts are predicted to be nearly 30−33 kJ $mol^{-1}$. It should be remarked here that HBE values in S-CX[4] and S-CX[4]-*t*-Bu due to Novikov and Shapiro[18] are ∼4 times larger owing to bifurcated hydrogen-bonded interactions of phenolate oxygen and charge delocalization subsequent to deprotonation. The CX[4]-*t*-Bu and CX[4]-$NH_2$ hosts reveal strong hydrogen-bonding interactions compared to those in CX[4]-$CH_2Cl$, CX[4]-$NO_2$, and CX[4]-$SO_3H$ or in S-CX[4]. Moreover, HBEs in CX[5] homologues are found to be ∼34 kJ $mol^{-1}$. The hydrogen bond energies of S-CX[4] and S-CX[5] are 25.7 and 19.2 kJ $mol^{-1}$, which are ∼14 and 6 kJ $mol^{-1}$ less than those of their unsubstituted CX[*n*] analogues. The energy rank order of CX[*n*] follows the trend CX[*n*]-*t*-Bu ≈ CX[*n*]-$NH_2$ > CX[*n*]-$CH_2Cl$ > CX[*n*] > CX[*n*]-$SO_3H$ > CX[*n*]-$NO_2$ > S-CX[*n*]-*t*-Bu > S-CX[*n*]. Thus, an increased separation of the O−H···O bond (∼0.1−0.2 Å) in S-CX[*n*] (*n* = 4, 5) led to a small HBE compared to that of CX[*n*]. Katsyuba et al.[45] pointed out that replacement of methylene bridges by sulfide bridges in thia analogues causes elongation of the O−H···O bond (0.1−0.2 Å) with concomitant bond weakening, which emerge with smaller HBE values. It may be remarked here that the electronic effect from the sulfide bridge in addition to the bifurcated O−H···S hydrogen bonds with sulfur as a second proton-acceptor center further leads to bond weakening.

**Table 1. Comparison of SCF Energies (au) in CX[*n*] Derivatives by MTA and B3LYP/6-311G(d,p) Theory**

| molecule | MTA | B3LYP | $\Delta E$ (kJ $mol^{-1}$) |
|---|---|---|---|
| CX[4] | −1382.72405 | −1382.72491 | 2.25 |
| CX[4]-$NH_2$ | −1604.20510 | −1604.20574 | 1.69 |
| CX[4]-*t*-Bu | −2011.90548 | −2200.95034 | 1.63 |
| CX[4]-$CH_2Cl$ | −3378.51967 | −3378.52019 | 1.36 |
| CX[4]-$SO_3H$ | −3878.25385 | −3878.25448 | 1.66 |
| CX[4]-$NO_2$ | −2200.94957 | −2200.95034 | 2.03 |
| S-CX[4] | −2818.26327 | −2818.26340 | 0.33 |
| S-CX[4]-*t*-Bu | −3447.44700 | −3447.44705 | 0.15 |
| CX[5] | −1728.40373 | −1728.40376 | 0.06 |
| CX[5]-$NH_2$ | −2005.25506 | −2005.25497 | −0.23 |
| CX[5]-*t*-Bu | −2514.88101 | −2514.88092 | −0.22 |
| CX[5]-$CH_2Cl$ | −4223.14831 | −4223.14830 | −0.03 |
| CX[5]-$SO_3H$ | −4847.81498 | −4847.81512 | 0.36 |
| CX[5]-$NO_2$ | −2751.18554 | −2751.18562 | 0.19 |
| S-CX[5] | −3522.81232 | −3522.81255 | 0.61 |
| S-CX[5]-*t*-Bu | −4309.29195 | −4309.29197 | 0.07 |

Extended hydrogen-bonded network in CX[5] yield large HBE values compared to those derived for their CX[4] counterparts. The hydrogen bond strength depends on its linearity; deviation from linearity subsequently weakens hydrogen-bonding interactions.[54,58] As may be noted, the hydrogen bond angle in CX[5] hosts turns out to be 170−174° whereas a deviation from linearity of up to ∼20° was found in CX[4] derivatives. Stronger hydrogen-bonded interactions in S-CX[4] than those in S-CX[5] can be explained on parallel lines.

We discuss below how cooperativity in the hydrogen-bonded network influences the strength of the individual H-bonds in O−H···O interactions. As shown in Table 2, the cooperativity


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**Table 2. Hydrogen Bond Distances (Å), Bond Angles (deg), and Hydrogen Bond Energies (kJ mol$^{-1}$) in the Presence and Absence of a Network in CX[4] and CX[5] Derivatives**[a]

| | H-bond distance | bond angle | HBE with network | HBE without network | cooperativity contribution | frequency | $\rho_{bcp}$ |
|---|---|---|---|---|---|---|---|
| CX[4] | 1.704 | 163 | 31.8 | 22.0 | 9.8 | 3290 | 0.0453 |
| CX[4]-$NH_2$ | 1.698 | 165 | 32.5 | 21.8 | 10.6 | 3275 | 0.0462 |
| CX[4]-*t*-Bu | 1.695 | 163 | 32.5 | 21.8 | 10.7 | 3274 | 0.0464 |
| CX[4]-$CH_2Cl$ | 1.702 | 162 | 32.2 | 21.8 | 10.5 | 3288 | 0.0454 |
| CX[4]-$SO_3H$ | 1.708 | 161 | 31.6 | 21.8 | 9.8 | 3303 | 0.0446 |
| CX[4]-$NO_2$ | 1.715 | 160 | 30.9 | 22.1 | 8.8 | 3310 | 0.0439 |
| S-CX[4] | 1.878 | 149 | 25.7 | 20.4 | 5.3 | 3421 | 0.0291 |
| S-CX[4]-*t*-Bu | 1.868 | 150 | 26.2 | 20.5 | 5.7 | 3418 | 0.0298 |
| CX[5] | 1.794 | 173 | 34.1 | 24.9 | 9.3 | 3350 | 0.0353 |
| CX[5]-$NH_2$ | 1.787 | 174 | 34.4 | 24.9 | 9.5 | 3339 | 0.0360 |
| CX[5]-*t*-Bu | 1.788 | 173 | 34.4 | 25.1 | 9.4 | 3345 | 0.0358 |
| CX[5]-$CH_2Cl$ | 1.792 | 172 | 34.0 | 25.1 | 8.9 | 3348 | 0.0353 |
| CX[5]-$SO_3H$ | 1.794 | 171 | 33.4 | 25.1 | 8.3 | 3354 | 0.0351 |
| CX[5]-$NO_2$ | 1.797 | 170 | 33.5 | 25.0 | 8.5 | 3354 | 0.0348 |
| S-CX[5] | 2.169 | 153 | 19.2 | 17.4 | 1.8 | 3490 | 0.0147 |
| S-CX[5]-*t*-Bu | 2.130 | 154 | 20.8 | 18.1 | 2.7 | 3489 | 0.0147 |

[a]The frequency of vibration (cm$^{-1}$) and $\rho_{bcp}$ (au) for the hydrogen bond are also given. See the text for details.

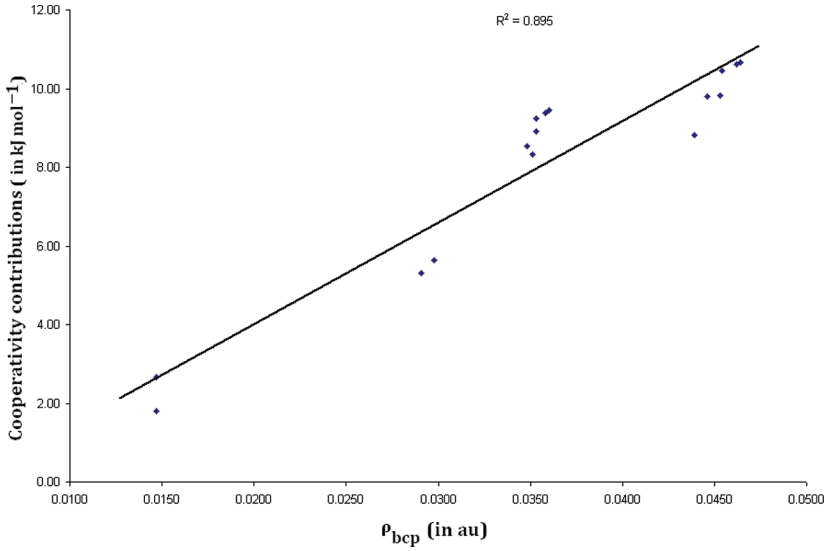


**Figure 3.** Cooperativity contributions as a function of $\rho_{bcp}$.

contribution from individual H-bond strengths in CX[4] derivatives varies from 8.8 to 10.7 kJ mol$^{-1}$, the contribution being larger for CX[*n*] hosts with electron-donating substituents as compared to those with electron-withdrawing substituents. Accordingly, CX[4]-*t*-Bu reveals a large cooperativity contribution compared to that of CX[4]-$NO_2$ (10.7 kJ mol$^{-1}$ versus 8.8 kJ mol$^{-1}$). Cooperativity contributions in CX[4] or CX[4]-*t*-Bu are nearly twice as large as those predicted in their thia analogues. On parallel lines, CX[5] and CX[5]-*t*-Bu show these contributions to be 4−5 times larger than those of their thia counterparts. Theoretical calculations[18] by Novikov and Shapiro on *para*-substituted calix[6]arenes support these inferences.

The hydrogen-bonding interactions in CX[*n*] conformers influence the vibrational frequencies in infrared spectra and result in a frequency downshift (red shift) of O−H stretching compared to the corresponding band arising from a non-interacting hydroxyl group.[45] It has been pointed out earlier that cooperativity is reflected in distinct bands for O−H stretching.[59] A quantitative comparison of cooperative contributions from the MTA approach and the corresponding O−H vibrational frequencies from B3LYP/6-311G(d,p) calculations is shown in Table 2. Thus, CX[*n*] derivatives with electron-donating substituents exhibit a red shift for the O−H vibration compared to that of their unsubstituted analogues.[57] Furthermore, large cooperative contributions in CX[4] derivatives are evident from the lower O−H frequencies (by ∼70 cm$^{-1}$) compared to those in CX[5]. Infrared spectral measurements[60,61] reveal higher O−H stretching frequencies for thia-CX[4] derivatives compared to those of their unsubstituted analogues. A frequency shift in S-CX[*n*] can be explained on parallel lines, which has partly been attributed to electron density transfer from the bridging sulfur to the benzene ring.[60]

The QTAIM method[50,51] has been widely used in the literature to gain deeper insight into hydrogen-bonding interactions. The bcp in the molecular electron density topography suggests the presence of a hydrogen bond and further emerges as its signature. Moreover, the strength of the hydrogen bond can be correlated to $\rho_{bcp}$ values in QTAIM

theory. Table 2 presents $\rho_{bcp}$ data for O−H···O hydrogen-bonded interactions. A plot of cooperativity contributions as a function of $\rho_{bcp}$ shown in Figure 3 turns out to be linear (with correlation coefficient $R^2$ being 0.895). Thus, increasing cooperativity in CX[4] reveals large $\rho_{bcp}$ values in the MED topography. In brief, the present work demonstrates how hydrogen bond strengths and cooperativity in a hydrogen-bonding network can be gauged using the MTA approach. It further brings out a good qualitative correlation with other properties such as the molecular electron density and vibrational frequencies.

## CONCLUSIONS

In the present work we analyze how substitution of an electron-donating or electron-withdrawing functional group directly influences the strength of the intramolecular O−H···O hydrogen bond and cooperativity in CX[$n$] ($n$ = 4, 5) and their thia derivatives using the MTA approach. The HBEs of CX[$n$] derivatives thus obtained vary from 19.2 to 34.5 kJ mol$^{-1}$. Estimated HBEs in CX[$n$] show the following rank order: CX[$n$]-$t$-Bu ≈ CX[$n$]-$NH_2$ > CX[$n$]-$CH_2Cl$ > CX[$n$] > CX[$n$]-$SO_3H$ > CX[$n$]-$NO_2$ > S-CX[$n$]-$t$-Bu > S-CX[$n$].

The HBEs in CX[5] derivatives are seen to be larger than those in CX[4]; a deviation from linearity for the hydrogen bond is noticed in the latter. Large HBE values and cooperative contributions are noticed for CX[$n$] hosts with electron-donating substituents. The O−H stretching frequency and $\rho_{bcp}$ values for hydrogen-bonded interactions are governed by cooperativity contributions from the MTA-based methodology.

## ASSOCIATED CONTENT

### Supporting Information

Hydrogen bond distances and HBEs in cone, partial cone, 1,2-alternate, and 1,3-alternate conformers of CX[4] and CX[5] derivatives and complete ref 49. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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