Supporting Information

Lone Pair-π vs σ-Hole-π Interactions in Bromine Head Containing Oxacalix[2]arene[2]triazines

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General information

Chemical shifts are reported in ppm versus tetramethylsilane with either tetramethylsilane or the residual solvent resonance used as an internal standard. Melting points are uncorrected. Solvents were dried according to standard procedures prior to use. All other major chemicals were obtained from commercial sources and used without further purification.

Crystallography

Intensity data for the crystals **3**·CH_2Cl_2 was collected on a XcaliburS CCD diffractometer (Oxford Diffraction) using Mo-Ka radiation at 100.

The structure was solved with direct methods using SHELXS-2014/7 or SHELXT [1,2] and refinements were carried out against F^2 by using SHELXL-2014/7 [1,2] or OLEX2 [3] The C–H hydrogen atoms were positioned with idealized geometry and refined using a riding model. All non-hydrogen atoms were refined using anisotropic displacement parameters.

CCDC-1811292 (**3**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

For decimal rounding of numerical parameters and su values the rules of IUCr have been employed [4].

Theoretical Methods

The calculations of the non-covalent interactions were carried out using the TURBOMOLE 7.0 [5] and the M06-2X/def2-TZVP level of theory. To evaluate the interactions in the solid state, the crystallographic coordinates have been used. This procedure and level of theory have been successfully used to evaluate similar interactions [6]. The interaction energies have been computed by calculating the difference between the energies of isolated monomers and their assembly. The interaction energies were calculated with correction for the basis set superposition

error (BSSE) by using the Boys–Bernardi counterpoise technique [7]. The NBO calculations have been performed at the M06-2X/def2-TZVP level of theory by means of the Gaussian09 calculation package[8]. The molecular electrostatic potential surfaces have been computed using the SPARTAN software [9].

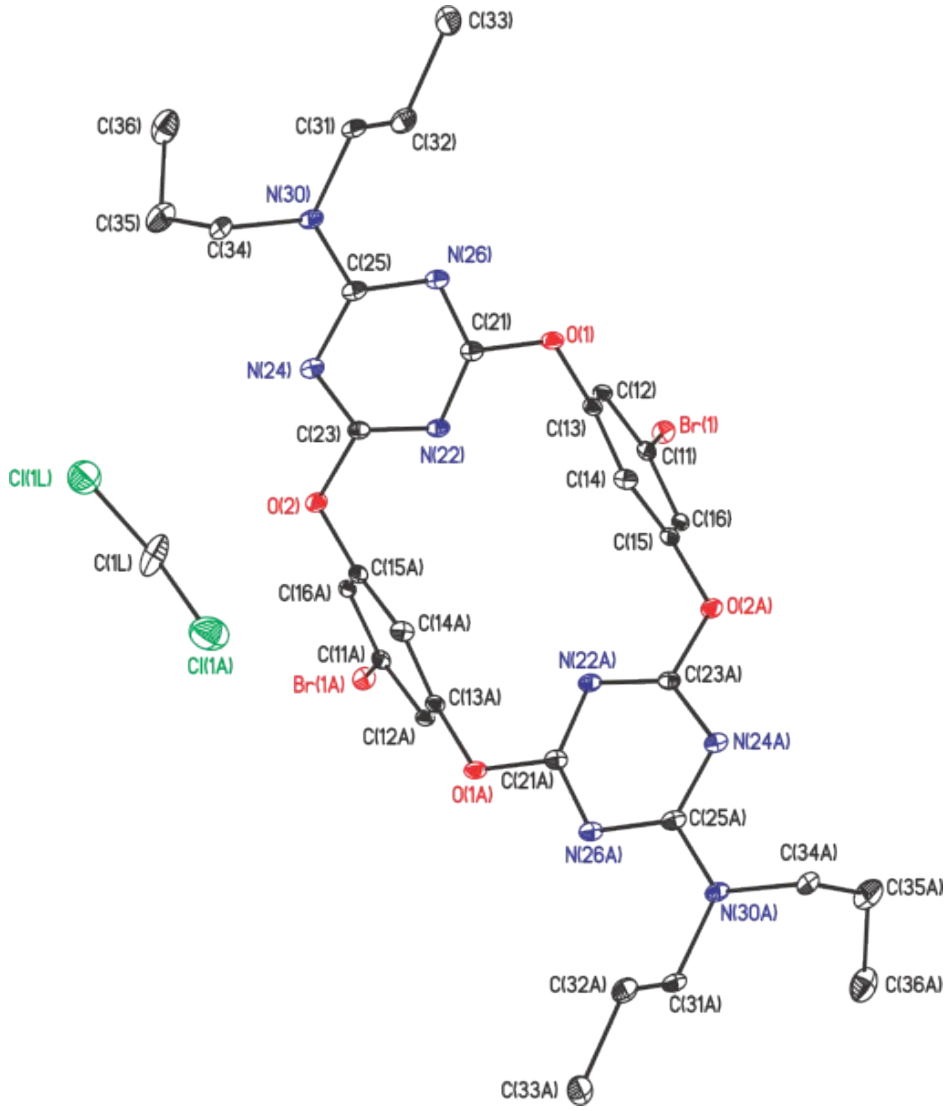


Fig. S1. ORTEP diagram of **3**·CH_2Cl_2: All hydrogen atoms are omitted for clarity. Selected bond lengths (Å): O(1)-C(13) 1.406(3); O(1)-C(21) 1.351(4); O(2)-C(15A) 1.407(3); O(2)-C(23) 1.357(4); C(25)-N(30) 1.338(4); Br(1)-C(11) 1.894(3), Selected interatomic distances (Å): O(1)-O(2) 4.806;

O(1)-O(2A) 4.604; N(22)-N(22A) 4.575; C(25)-C(25A) 9.263; N(30)-N(30A) 11.607, Selected bond angles (°): C(21)-O(1)-C(13) 118.8(2); C(23)-O(2)-C(15A) 119.0(2).

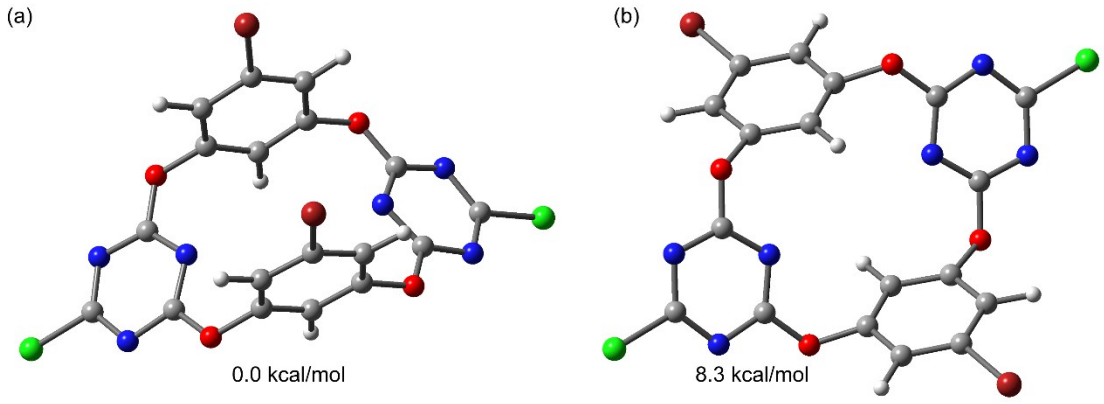
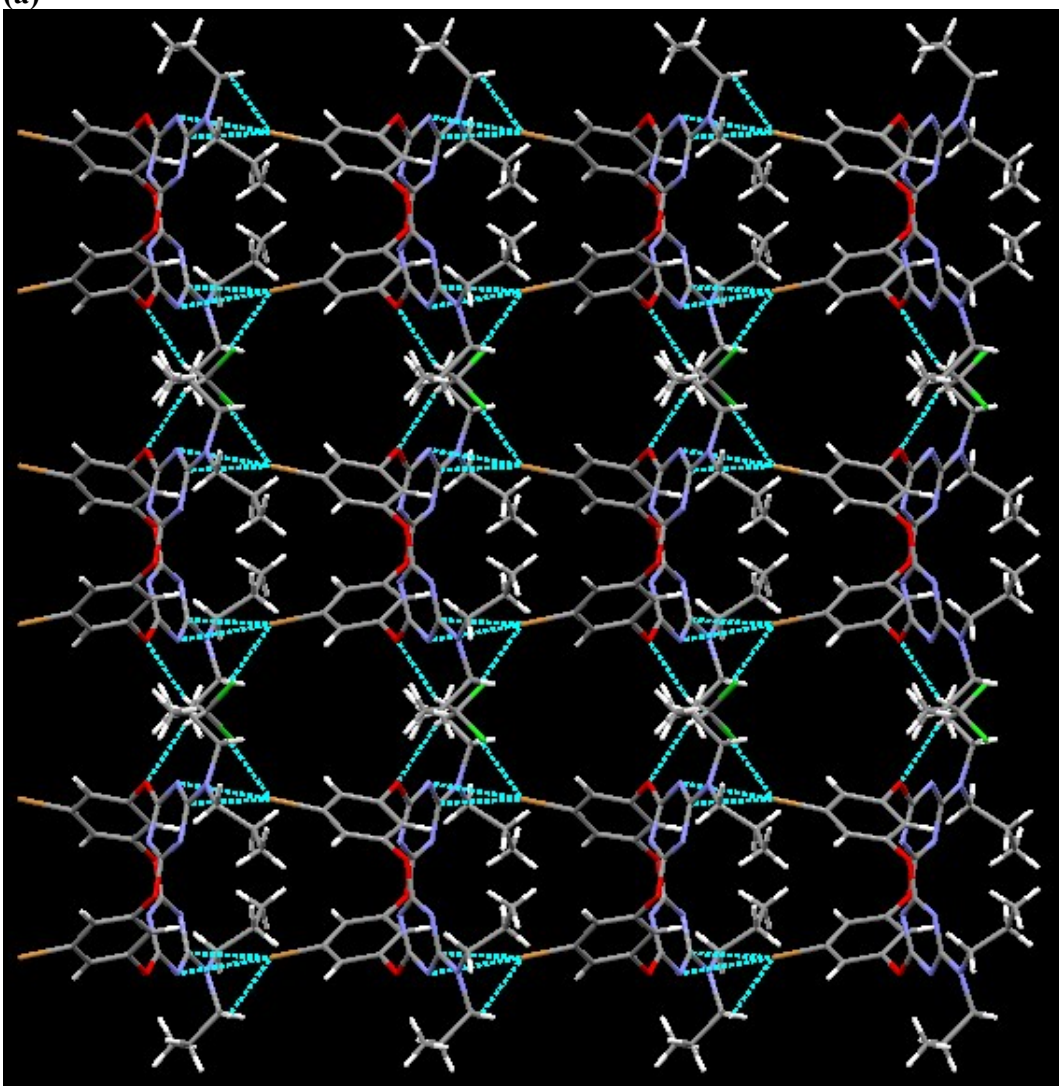
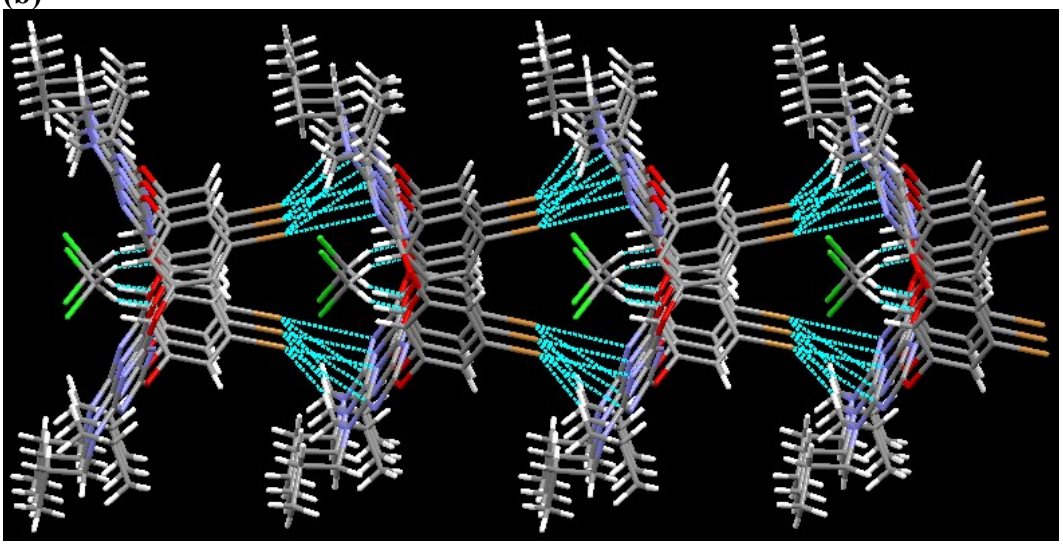


Fig. S2. Two minimum conformers of the chloro-substituted oxacalix[2]arene[2]triazine and their relative energy at the M06-2X/def2-TZVP level of theory

(a)



(b)



(c)

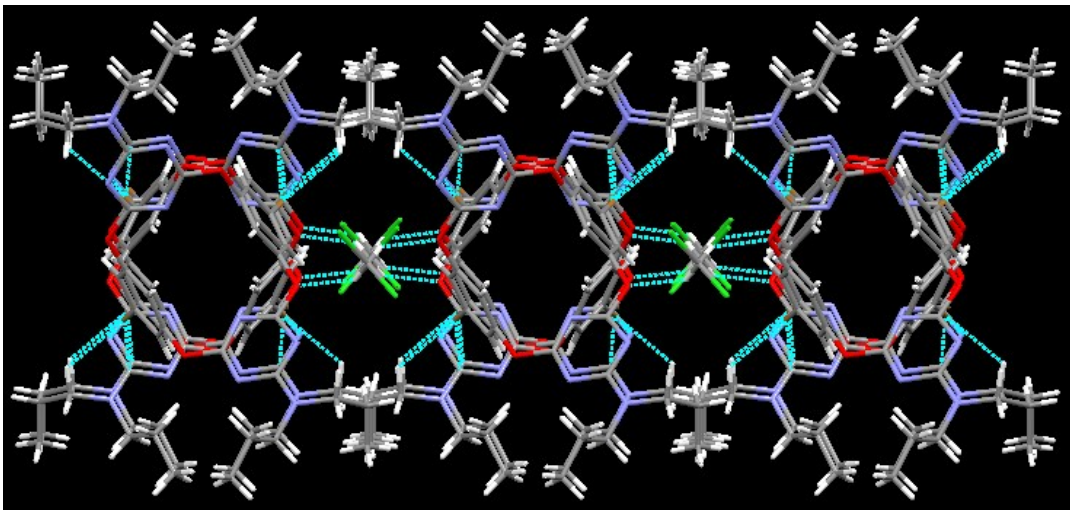


Fig. S3: Showing connection of individual 1D-supramolecular chains with each other by means of CH···O [C(1L)-H(1L)···O(2) 2.419°] interactions, (a) *a*-axis; (b) *b*-axis; (c) *c*-axis

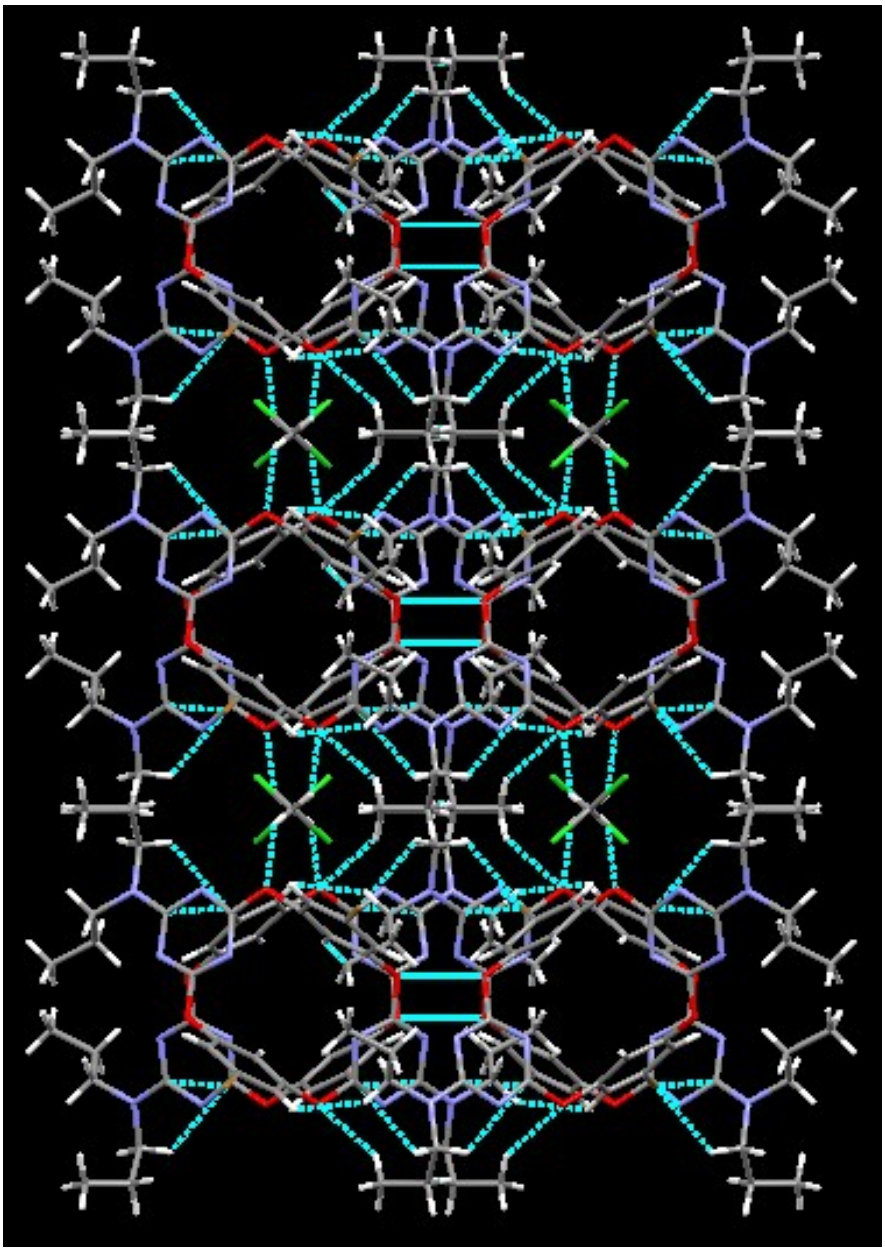


Fig. S4: View of the 3D-crystal packing of **3** along *c*-axis

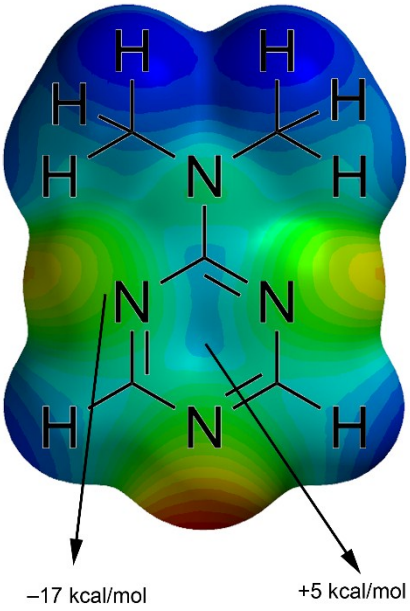


Fig. S5. MEP surface of $–NMe_2$ substituted *s*-triazine plotted onto the van der Waals surface. The energy values at several points of the surface are given.

Table S1. Crystal data and structure refinement for **3**.

Empirical formula	$C_{31}\ H_{36}\ Br_2\ Cl_2\ N_8\ O_4$	
Formula weight	815.40	
Temperature	173 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pcca	
Unit cell dimensions	a = 18.0444(6) Å	α= 90°.
	b = 11.4284(5) Å	β= 90°.
	c = 17.2410(6) Å	γ = 90°.
Volume	3555.4(2) $Å^3$	
Z	4	
Density (calculated)	1.523 Mg/m^3	
Absorption coefficient	2.478 mm^{-1}	
F(000)	1656	
Crystal size	0.266 x 0.165 x 0.148 mm^3	
Theta range for data collection	2.257 to 25.998°.	
Index ranges	-22<=h<=22, -12<=k<=14, -21<=l<=21	
Reflections collected	20133	
Independent reflections	3499 [R(int) = 0.0353]	
Completeness to theta = 25.998°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.81988	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3499 / 0 / 219	
Goodness-of-fit on F^2	1.141	
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.1080	
R indices (all data)	R1 = 0.0455, wR2 = 0.1122	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.108 and -0.941 $e.Å^{-3}$	

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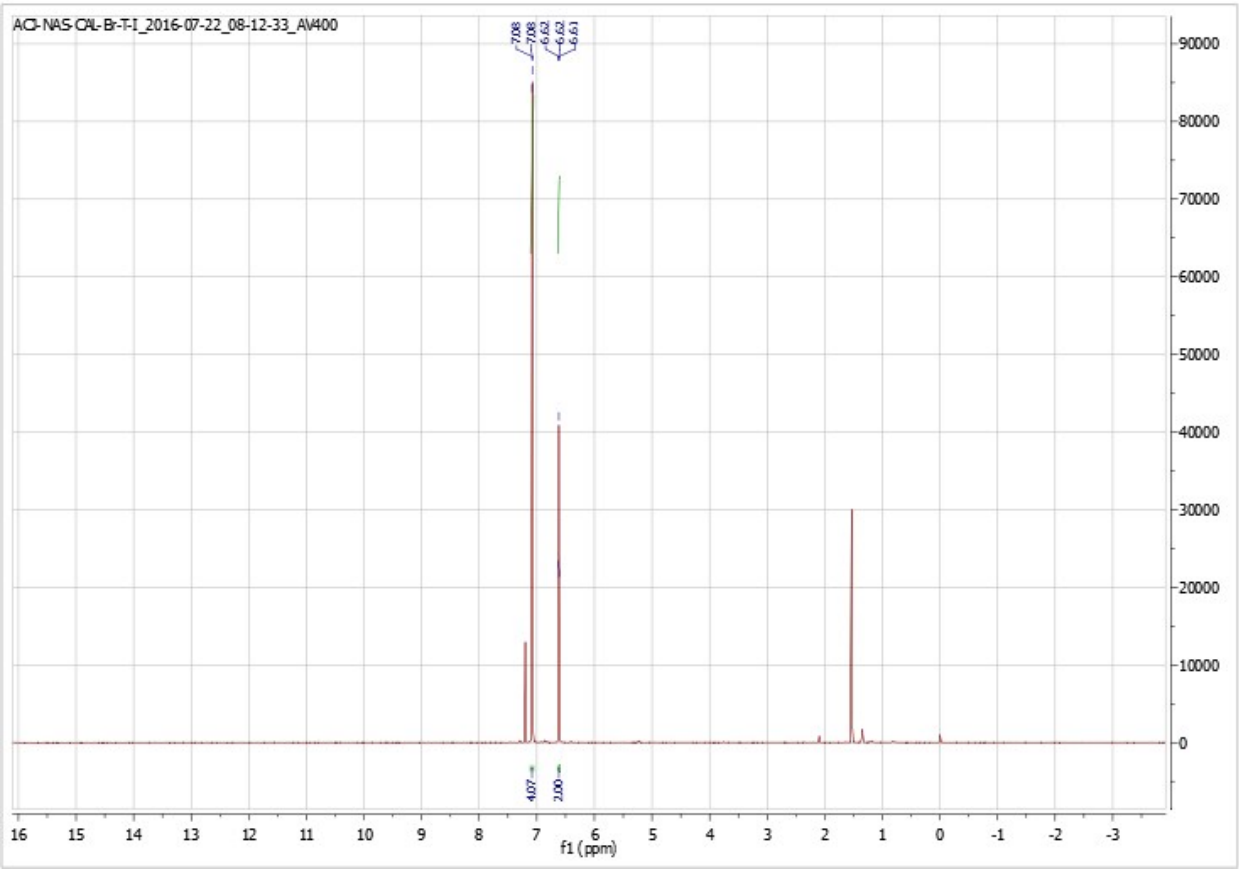
Copies of ^{1}H & ^{13}C NMR

^{1}H NMR of oxacalix[2]arene[2]triazine **2**



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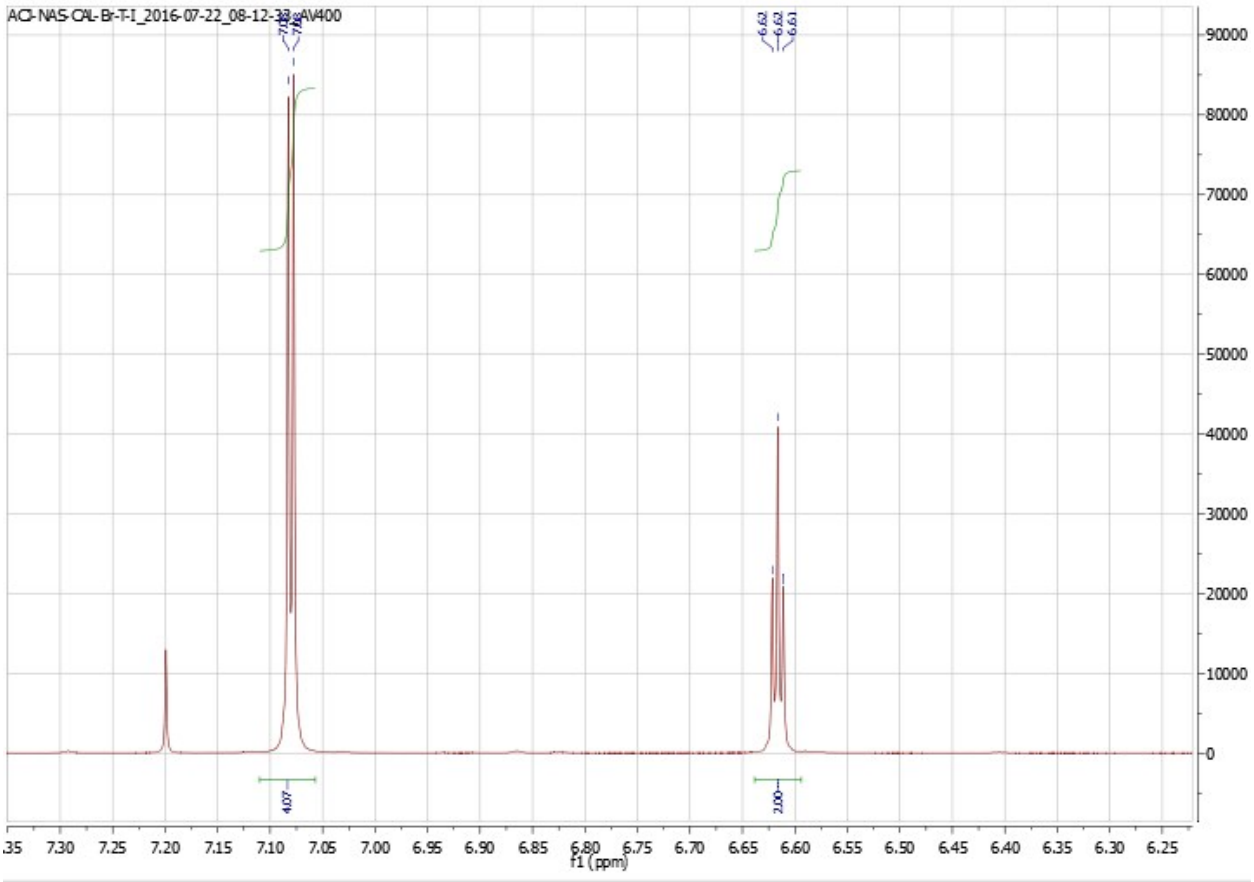

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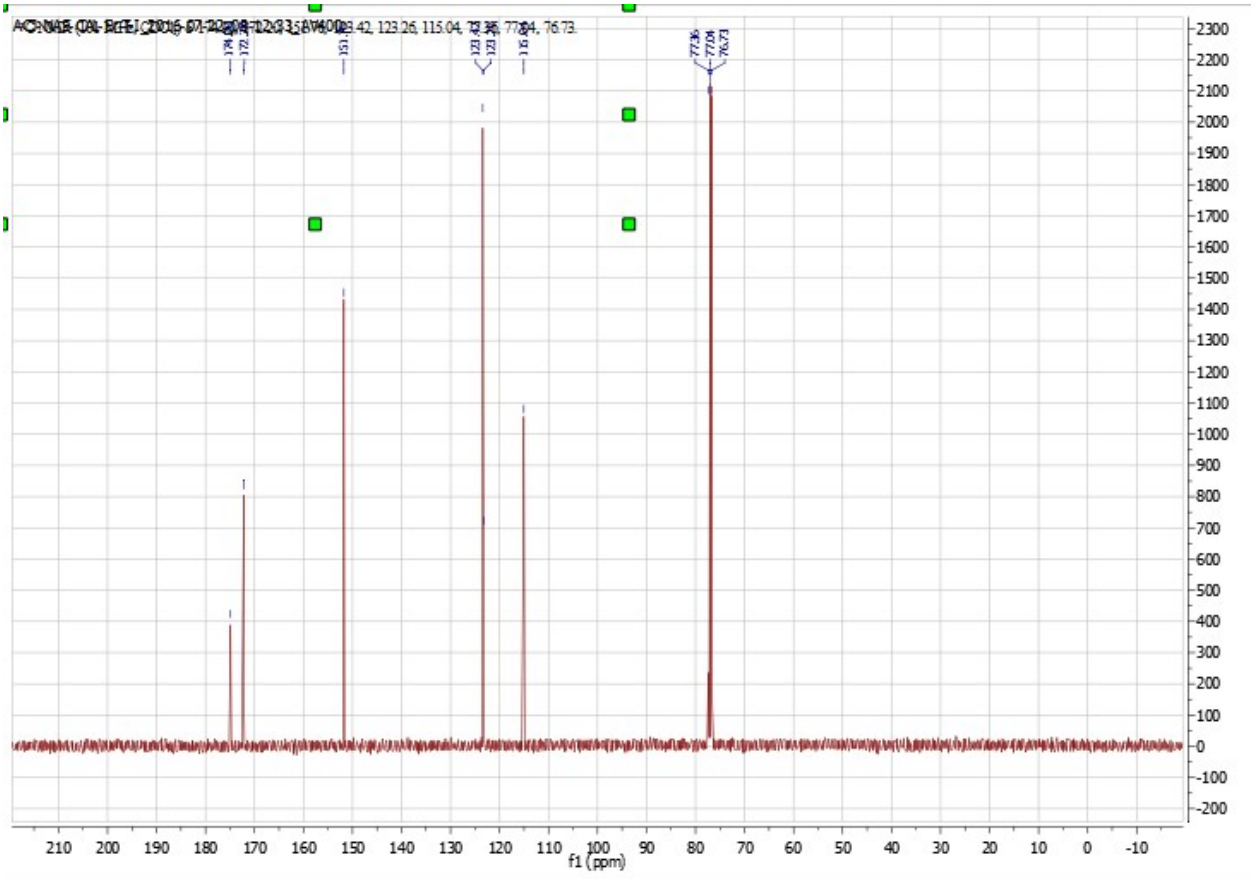

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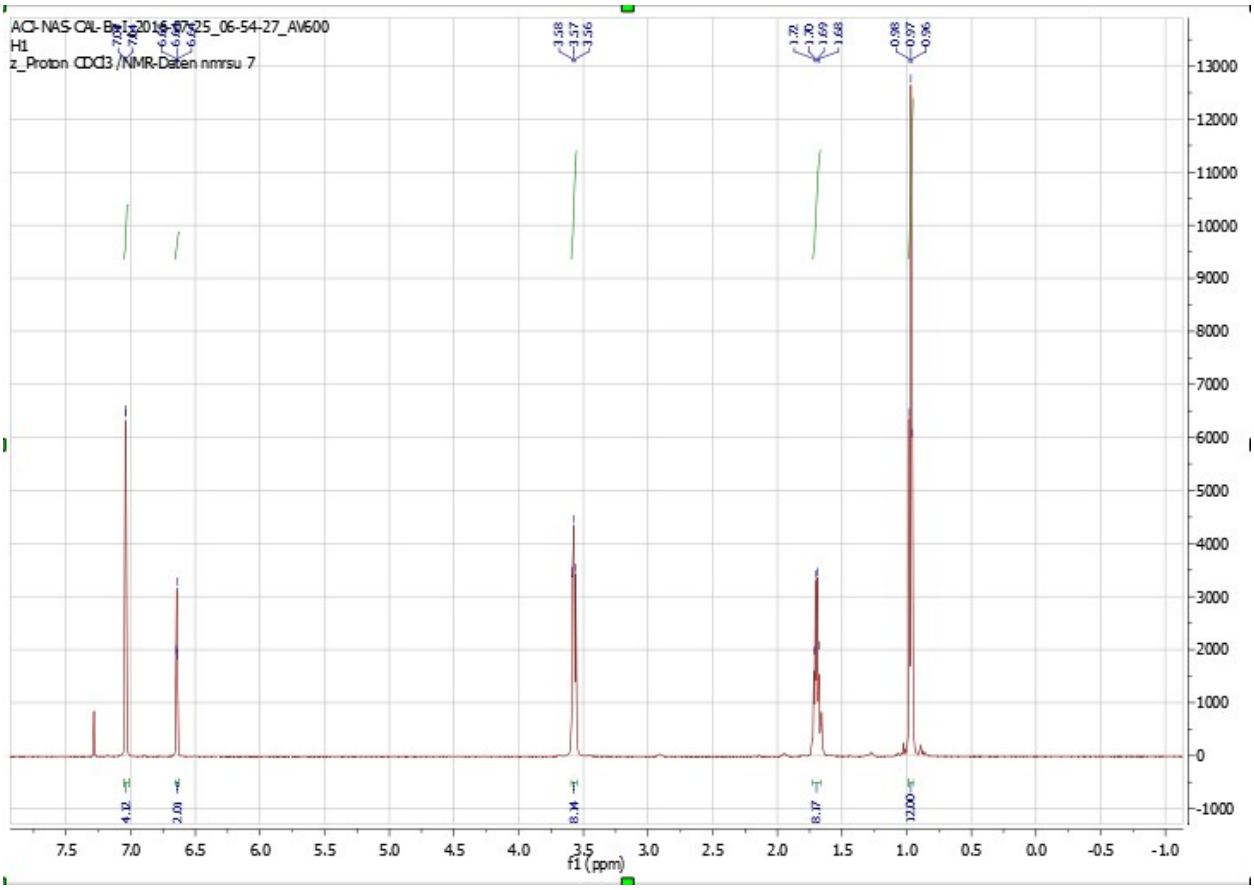

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