Electronic Supporting Information for

H-bonded anion-anion complex trapped in a squaramido-based receptor

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1. Table S1

Table 1. Crystal data and structure refinement for **1**.

Identification code	1
Empirical formula	C33 H62 N8 O16
Formula weight	826.90
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	
a (Å)	6.196(8)
b (Å)	13.132(11)
c (Å)	13.815(13)
α (°)	73.83(5)
β (°)	83.92(6)
γ (°)	78.69(6)
Volume	1057.1(19) $Å^3$
Z	1
Density (calculated)	1.299 Mg/m^3
Absorption coefficient	0.104 mm^{-1}
F(000)	444
Crystal size	0.2 x 0.1 x 0.1 mm^3
Theta range for data collection	1.929 to 32.521°
Index ranges	-9<=h<=9, -18<=k<=19, 0<=l<=20
Reflections collected	6197
Independent reflections	6189 [R(int) = 0.0411]
Completeness to theta = 25.003°	92.9 %
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	6189 / 16 / 279
Goodness-of-fit on F^2	0.885
Final R indices [I>2sigma(I)]	R1 = 0.0826, wR2 = 0.2102
R indices (all data)	R1 = 0.1770, wR2 = 0.2466
Largest diff. peak and hole	0.574 and -0.457 $e.Å^{-3}$

2. Experimental details

Synthesis of 3,4-Bis(2-dimethylamino-ethylamino)-cyclobut-3-ene-1,2-dione

2-N,N-ethylendiamine (3.09 mL, 28.29 mmol) was added to a solution of diethyl-squarate (1.60 g, 9.43 mmol) in absolute ethanol (66 mL) at r.t. under vigorous stirring and argon atmosphere. After 24 hours, the resulting white solid was filtered and washed with cold absolute ethanol (2 x 10 mL). The solid was dried under vacuum to yield 84% (2.01 g).

^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 7.45 (s, 2H); 3.59 (m, J = 4 Hz, 4H); 2.37 (t, J = 4 Hz, 4H); 2.15 (s, 6H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 184.2, 169.7, 58.5, 43.1, 38.4 ppm. MS (ESI) m/z (%): 255.3 (M+H+, 100).

Preparation of crystals of 1

A solution of 3,4-Bis(2-dimethylamino-ethylamino)-cyclobut-3-ene-1,2-dione (50.2 mg, 0.20 mmol) and fumaric acid (22.8 mg, 0.20 mmol) in etanol (6 mL) was prepared. Since the solid did not completely dissolve, DMSO (8 mL) and water (1mL) were added at 40 ºC until a total dissolution. An aliquot was placed at r.t. in a thin vial and it was sealed with a septum and a needle, through which methanol was allowed to diffuse into the solution. After one month thin needles of **1** crystallized.

X-ray data collection details

A colorless prism-like specimen of $C_{33}H_{62}N_8O_{16}$, approximate dimensions 0.100 mm x 0.100 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a MAR345 system equipped with a graphite monochromator and a Mo fine-focus sealed tube (λ = 0.71073 Å).

The frames were integrated with the MARSCALE (Claudio Klein, 2007) using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 6197 reflections to a maximum θ angle of 32.52° (0.66 Å resolution), of which 6189 were independent (average redundancy 1.001, completeness = 80.7%, R_{sig} = 20.91%) and 2144 (34.64%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 6.196(8) Å, $\underline{b}$ = 13.132(11) Å, $\underline{c}$ = 13.815(13) Å, α = 73.83(5)°, β = 83.92(6)°, γ = 78.69(6)°, volume = 1057.1(19) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I).

The structure was solved and refined using the 'SHELXL-97 (Sheldrick, 1997), using the space group P -1, with Z = 1 for the formula unit, $C_{33}H_{62}N_8O_{16}$. The final anisotropic full-matrix least-squares refinement on F^2 with 279 variables converged at R1 = 8.26%, for the observed data and wR2 = 24.66% for all data. The goodness-of-fit was 0.885. The largest peak in the final difference electron density synthesis was 0.574 e$^-$/Å^3 and the largest hole was -0.457 e$^-$/Å^3 with an RMS deviation of 0.060 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.299 g/cm^{3}and F(000), 444 e$^-$.

3. Theoretical methods

The energies of the anion···anion complexes included in this study were computed using the RI-MP2/aug-cc-pVTZ level of theory by means of the program

TURBOMOLE version 7.0.[1] The minimum nature of the complexes have been verified by performing frequency calculations. To evaluate the interactions in the solid state, we have used the crystallographic coordinates at the RI-MP2/def2-TZVP level of theory. The Bader's "Atoms in molecules" theory has been used to study the interactions discussed herein by means of the AIMall calculation package.[2]

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[1] R. Ahlrichs, M. Bär, M. Hacer, H. Horn and C. Kömel, *Chem. Phys. Lett.*, 1989, **162**, 165.
[2] AIMAll (Version 13.05.06), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, 2013.