Electronic Supplementary Information

Geometries, interaction energies and complexation free energies of 18-crown-6 with neutral molecules

Ming W. Shi,[a] Li-Juan Yu,[a] Sajesh P. Thomas,[a] Amir Karton[a] and Mark A. Spackman*[a]

School of Chemistry and Biochemistry, University of Western Australia,

Perth, Australia 6009

mark.spackman@uwa.edu.au

Table S1. B3LYP-D3BJ/6-31+G(2df, p) rearrangement energies of crown and guest molecules, and the total rearrangement energy for the 18C6:guest complex (kJ mol^{-1}).

	Crown	Guest	Total
CO	0.5	0.1	0.6
CF_4	0.2	2.0	2.2
Methylcyclopentane	1.1	0.8	1.9
SiH_4	0.2	2.0	2.2
C_3H_8	1.1	0.4	1.5
Methylcyclobutane	1.3	0.5	1.8
C_2H_6	0.7	0.2	0.9
CH_4	0.1	0.2	0.3
PH_3	0.2	0.3	0.5
C_2H_4	0.6	0.1	0.7
CH_3COCH_3	1.4	1.3	2.7
CH_3OCH_3	1.2	0.5	1.7
Methylcyclohexane	0.8	0.7	1.5
NH_3	0.2	0.9	1.1
CH_3CHO	1.9	0.8	2.7
NH_2CH_3	0.7	0.3	1.0
H_2S	0.8	0.0	0.8
$NH_2CH_2CH_3$	0.8	0.4	1.2
CO_2	0.3	0.0	0.3
CH_3COOH	2.3	23.7	26.0
Toluene	0.5	0.4	0.9
C_2H_2	0.8	0	0.8
CCl_4	0.6	0.9	1.5
CH_3Cl	0.9	0.4	1.3
CS_2	1.6	0.7	2.3
HCHO	1.1	0.4	1.5
CH_3CH_2OH	1.0	1.6	2.6
CH_3OH	0.7	0.3	1.0
HCl	1.5	0.1	1.6
$CHCl_3$	1.1	0.8	1.9
CH_2F_2	1.1	1.0	2.1
H_2O	1.0	0.2	1.2

Benzene	2.6	0.3	2.9
HF	1.3	2.9	4.2
CH_3CN	1.5	0.2	1.7
CH_2Cl_2	3.1	0.8	3.9
Aniline	2.4	1.0	3.4
Dimethylsulfone	2.4	2.1	4.5
HCOOH	2.1	19.0	21.1
Phenol	5.9	0.6	6.5
Benzoic acid	3.0	4.3	7.3
CH_3NO_2	1.6	0.8	2.4
HCN	1.7	0.0	1.7
$HCONH_2$	1.1	0.4	1.5
Methanesulfonamide	3.7	6.0	9.7
NH_2CN	3.9	0.9	4.8
Dinitromethane	5.3	11.1	16.4
Malononitrile	5.9	1.0	6.9

Table S2. CE-B3LYP model interaction energies (kJ mol^{-1}) between 18-crown-6 and neutral guest molecules. Individual components have been scaled as described in the original publication.[1]

Guest	Electrostatic	Polarisation	Dispersion	Repulsion	Total
CO	-17.2	-1.3	-22.7	23.9	-17.3
CF_4	-11.3	-2.7	-32.6	12.4	-34.2
Methylcyclopentane	-12.2	-6.6	-45.8	24.7	-39.9
SiH_4	-26.4	-6.8	-34.9	32.5	-35.5
C_3H_8	-8.0	-5.2	-33.6	17.1	-29.7
Methylcyclobutane	-9.6	-5.9	-41.1	20.6	-35.9
C_2H_6	-4.1	-4.5	-27.4	12.1	-23.9
CH_4	-7.4	-3.8	-17.8	10.7	-18.4
PH_3	-20.0	-5.0	-25.3	21.2	-29.1
C_2H_4	-8.7	-4.3	-24.7	11.8	-25.9
CH_3COCH_3	-31.9	-8.1	-37.0	27.4	-49.6
CH_3OCH_3	-22.3	-6.4	-32.2	22.1	-38.9
Methylcyclohexane	-12.2	-6.7	-45.7	25.3	-39.2
NH_3	-43.7	-6.1	-22.8	24.5	-48.1
CH_3CHO	-37.7	-7.9	-32.5	29.3	-48.8
NH_2CH_3	-37.8	-7.2	-27.2	24.8	-47.4
H_2S	-40.0	-6.0	-20.7	27.0	-39.7
$NH_2CH_2CH_3$	-38.6	-7.6	-31.8	27.5	-50.4
CO_2	-39.9	-2.9	-33.4	25.2	-51.0
CH_3COOH	-77.5	-16.3	-36.0	46.9	-82.9
Toluene	-20.5	-6.9	-43.2	27.5	-43.1
C_2H_2	-12.5	-3.4	-17.0	6.2	-26.7
CCl_4	-12.0	-3.6	-30.2	19.2	-26.6
CH_3Cl	-37.6	-6.8	-29.8	24.8	-49.5
CS_2	-16.7	-4.2	-26.9	25.9	-21.9

HCHO	-33.8	-5.6	-26.4	19.0	-46.8
CH_3CH_2OH	-45.7	-9.6	-34.3	31.7	-57.9
CH_3OH	-48.5	-8.8	-24.7	30.3	-51.7
HCl	-28.1	-4.2	-17.1	10.0	-39.4
$CHCl_3$	-36.7	-4.6	-31.3	25.9	-46.7
CH_2F_2	-37.4	-6.0	-30.8	19.3	-54.9
H_2O	-52.3	-7.0	-17.1	21.3	-55.1
Benzene	-16.2	-6.1	-36.1	19.5	-38.8
HF	-76.9	-14.8	-11.3	49.8	-53.2
CH_3CN	-48.6	-9.1	-35.5	29.9	-63.3
CH_2Cl_2	-47.1	-8.4	-35.9	30.1	-61.3
Aniline	-54.0	-9.8	-42.9	35.7	-71.0
Dimethylsulfone	-69.6	-13.0	-41.7	47.1	-77.3
HCOOH	-83.3	-15.3	-32.6	40.4	-90.8
Phenol	-50.6	-10.1	-41.5	29.1	-73.1
Benzoic acid	-69.2	-13.4	-45.2	51.8	-75.9
CH_3NO_2	-60.1	-9.8	-37.0	32.8	-74.1
HCN	-37.8	-5.4	-20.3	9.8	-53.8
$HCONH_2$	-74.4	-13.1	-34.2	39.4	-82.3
Methylsulfonamide	-79.1	-14.4	-43.4	41.9	-95.1
NH_2CN	-98.0	-16.8	-36.8	53.5	-98.1
Dinitromethane	-94.2	-15.8	-49.7	46.3	-113.4
Malononitrile	-84.3	-16.3	-47.7	45.9	-102.4

[1] M. J. Turner, S. Grabowsky, D. Jayatilaka, M. A. Spackman, *J. Phys. Chem. Lett.* **2014**, *5*, 4249-4255.