Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Calculation and visualization of free energy barriers for several VOCs and TNT in HKUST-1

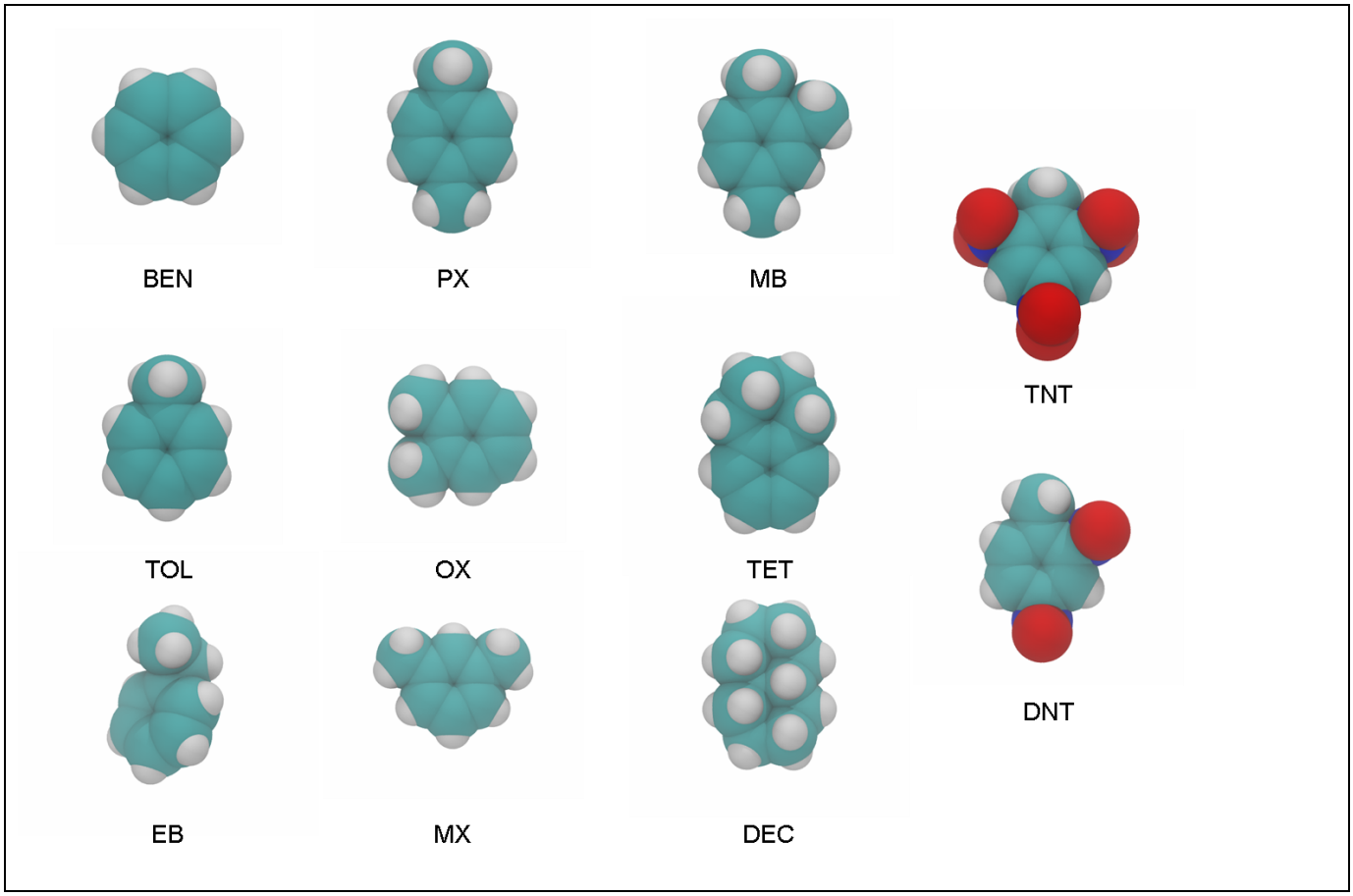
Lev Sarkisov

Institute for Materials and Processes, School of Engineering, University of Edinburgh, EH9 3JL, UK

Lev.Sarkisov@ed.ac.uk

A simple protocol based on a lattice representation of the porous space is proposed to locate and characterize the free energy bottle-necks in metal organic frameworks. As an illustration we apply this method to HKUST-1 to demonstrate that there are impassable free energy barriers for molecules of trinitrotoluene in this structure.

S1. Species considered in this work: benzene (BEN), toluene (TOL), ethylbenzene (EB) para-, ortho- and meta-xylene (PX, OX and MX, respectively), 1,2,4-trimethylbenzene (MB), tetralin (TET), decalin (DEC), trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT).

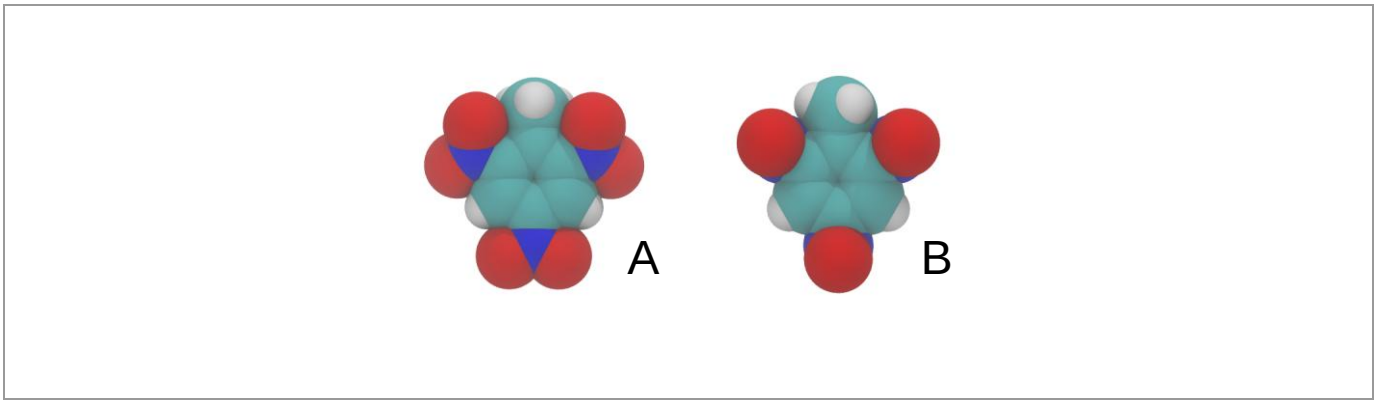


S2. Molecular forcefield details:

S2.1 UFF interaction parameters[1]:

Atom	σ (Å)	ε (K)
H	2.57	22.1
C	3.43	52.8
O	3.12	30.2
N	3.26	34.7
Cu	3.11	2.51
Zn	2.46	62.4

S2.2 Computer visualization of investigated TNT conformations:



S2.3 TNT structure **A** in the UFF representation with charges from the CHELPG method, obtained using the B3LYP/6-31G DFT method[2-5]:

Atom	x	y	z	q, CHELPG
C	1.28724	-1.1E-05	0.062265	0.207654
C	0.519507	-1.1893	0.021675	-0.07304
C	-0.87338	-1.21088	-0.01479	-0.06294
C	-1.55263	0.000005	-0.03742	0.00857
C	-0.87336	1.210887	-0.01489	-0.06286
C	0.519517	1.189257	0.021713	-0.07341
C	2.788378	0.000133	0.215958	-0.44019
N	1.160983	2.517249	0.013282	0.713758
N	1.160813	-2.51734	0.012865	0.713029
N	-3.01991	-2E-06	-0.08615	0.667433
O	0.512414	3.474389	0.519899	-0.40493
O	2.295955	2.631898	-0.52592	-0.40059
O	0.51287	-3.47416	0.520886	-0.40476
O	2.295577	-2.63215	-0.52673	-0.40039
O	-3.60329	-1.11811	-0.10581	-0.39038
O	-3.60326	1.118059	-0.10568	-0.39035
H	-1.40985	-2.14985	-0.02071	0.156755
H	-1.4098	2.149869	-0.02081	0.156708
H	3.276363	0.000897	-0.76405	0.170515
H	3.128356	-0.89073	0.742107	0.154803
H	3.127924	0.890584	0.743158	0.154616

S2.4 TNT structure **B** in the UFF representation with the geometry from B3LYP/6-31G and charges from CHELPG and Mulliken population analysis[2-5]:

Atom	x	y	z	q, CHELPG	q, Mulliken
C	1.23125	0.02783	0.00000	0.22215	0.26357
C	0.50100	-1.17092	0.00000	-0.12904	0.14407
C	-0.88798	-1.23696	0.00000	-0.08941	0.04157
C	-1.58814	-0.03355	0.00000	-0.02769	0.18202
C	-0.93977	1.19643	0.00000	-0.11852	0.04081
C	0.45344	1.19334	0.00000	-0.08265	0.13636
C	2.74006	0.03107	0.00000	-0.48240	-0.47957
N	1.13665	2.50308	0.00000	0.80791	0.04917
N	-3.06311	-0.06537	0.00000	0.80664	0.05928
N	1.25430	-2.44190	0.00000	0.82152	0.05319
O	1.40513	3.00938	-1.12099	-0.42950	-0.24956
O	1.40514	3.00937	1.12100	-0.42950	-0.24956
O	-3.63499	-0.07805	-1.12154	-0.42736	-0.25034
O	-3.63499	-0.07811	1.12154	-0.42736	-0.25034
O	1.55171	-2.93212	1.12100	-0.42555	-0.25018
O	1.55173	-2.93211	-1.12101	-0.42555	-0.25018
H	-1.40363	-2.18921	0.00000	0.16261	0.21171
H	-1.49542	2.12594	0.00000	0.16972	0.21168
H	3.12349	-0.48985	-0.88420	0.16496	0.20033
H	3.14824	1.04196	-0.00001	0.17406	0.18565
H	3.12349	-0.48984	0.88421	0.16496	0.20033

S2.5 OPLS interaction parameters[6,7]:

Atom	**σ (Å)**	**ε (K)**	**Comment**
H	2.42	15.1	Aromatic
HA	2.50	15.1	Alkane
C	3.55	35.2	Aromatic
CA	3.50	33.2	Alkane
O	2.96	85.5	Nitro
N	3.25	60.4	Nitro

CC	3.75	52.8	Carboxylic
OC	2.96	107.7	Carboxylic
Cu	3.11	2.51	from UFF
Zn	2.46	62.4	from UFF

S2.6 TNT structure **B** in the OPLS representation with the geometry and charges obtained from B3LYP/6-31G/CHELPG[2-5]:

Atom	x	y	z	Charge, q
C	1.23125	0.02783	0.00000	0.22215
C	0.50100	-1.17092	0.00000	-0.12904
C	-0.88798	-1.23696	0.00000	-0.08941
C	-1.58814	-0.03355	0.00000	-0.02769
C	-0.93977	1.19643	0.00000	-0.11852
C	0.45344	1.19334	0.00000	-0.08265
CA	2.74006	0.03107	0.00000	-0.48240
N	1.13665	2.50308	0.00000	0.80791
N	-3.06311	-0.06537	0.00000	0.80664
N	1.25430	-2.44190	0.00000	0.82152
O	1.40513	3.00938	-1.12099	-0.42950
O	1.40514	3.00937	1.12100	-0.42950
O	-3.63499	-0.07805	-1.12154	-0.42736
O	-3.63499	-0.07811	1.12154	-0.42736
O	1.55171	-2.93212	1.12100	-0.42555
O	1.55173	-2.93211	-1.12101	-0.42555
H	-1.40363	-2.18921	0.00000	0.16261
H	-1.49542	2.12594	0.00000	0.16972
HA	3.12349	-0.48985	-0.88420	0.16496
HA	3.14824	1.04196	-0.00001	0.17406
HA	3.12349	-0.48984	0.88421	0.16496

S2.7 Complete molecular structures of HKUST-1 in the UFF and OPLS representation and IRMOF-1 in the UFF representation are available upon request

S3. Variation of the Henry's constant for tetralin in HKUST-1 at 300 K as a function of the number of trial orientations R.

R	K_H [mol/kg/bar]

50	$1.530 \cdot 10^8$
100	$1.536 \cdot 10^8$
500	$1.520 \cdot 10^8$
1000	$1.510 \cdot 10^8$
1800	$1.526 \cdot 10^8$

S4. Comparison of the Henry's constants of adsorption obtained from the adsorption isotherms (generated using the GCMC simulations), the Widom insertion method and lattice method (this work).

S4.1 Details of the simulations

S4.1.1 Lattice simulations:

$$\text{Coulombic potential: } u_{Coul}(r) = \frac{q_i q_j}{4\pi\varepsilon_0}\left[\frac{\mathbf{erfc}(\alpha r)}{r} - \frac{\mathbf{erfc}(\alpha R_c)}{R_c} + \left(\frac{\mathbf{erfc}(\alpha R_C)}{R_C^2} + \frac{2\alpha}{\pi^{1/2}}\frac{\mathbf{exp}(-\alpha^2 R_C^2)}{R_C}\right)(r - R_C)\right], \quad r \le R_C \qquad (13)$$

where, ε_0 is the electric constant, r is the distance between two partial charges q_i and q_j, α is the damping parameter (here equal to 0.1), and R_C is the cutoff distance, which is taken to be 20 Å for TNT and DNT simulations and 12.8 Å for all other species.

S4.1.2 GCMC simulations: Adsorption isotherms have been generated using the MuSiC code[8]. To generate reliable estimates of the Henry's constants it is important to collect the data in the linear regime of the adsorption isotherm. This is associated with two challenges. At very low pressures, it is difficult to collect reliable statistics as the number of molecules adsorbed is very small (this necessitates consideration of a very large number of replicas of the initial unit cell). On the other hand, with increasing fugacity, as we approach capillary condensation, we reach a regime where the adsorption behavior starts to deviate from linear.

Parameters of the GCMC simulations:

Number of unit cells	Between 20x20x20 and 4x4x4 (100x100x100 in selected test cases)
Coulombic method	Ewald
Number of moves per point	40000000, with 50% allocated for equilibration
Moves	Energy biased insertions and deletions, using pre-calculated potential maps; random translations and rotations
Moves proportion	1:1:1:1

S4.1.3 The Widom insertion method:

Number of unit cells	1x1x1
Coulombic method	Ewald
Number of trail insertions	20000000

S4.2 Results: Benzene in HKUST-1

S4.2.1 Adsorption isotherms (300 K) data (yellow and purple colors will be used throughout the data to represent the reliability boundaries of linear isotherm regime):

Mulliken charges

P, kPA	mol/uc	Kh [mol/kg/bar]	Comments
1.00E-08	0.00001	-	Poor statistics
1.00E-07	0.000146	1.51E+04	
1.00E-06	0.0011	1.14E+04	
1.00E-05	0.013	1.34E+04	
1.00E-04	0.14175	-	Onset of capillary condensation
	Average	**1.33E+04**	

No charges

P, kPA	mol/uc	Kh [mol/kg/bar]
1.00E-08	0.000015	-
1.00E-07	0.00009	9.30E+03
1.00E-06	0.000975	1.01E+04
1.00E-05	0.00911	9.42E+03
1.00E-04	0.09836	-
	Average	**9.74E+03**

CHELPG charges

P, kPA	mol/uc	Kh [mol/kg/bar]
1.00E-08	0.000005	-
1.00E-07	0.00009	9.30E+03
1.00E-06	0.00103	1.06E+04
1.00E-05	0.011805	1.22E+04
1.00E-04	0.11883	-
	Average	**1.11E+04**

S4.2.2 Comparison of Kh [mol/kg/bar] between the methods (benzene):

Charges model	GCMC	Widom	Lattice
Mulliken	1.33E+04	1.34E+04	1.48E+04
No charges	9.74E+03	1.01E+04	9.64E+03
CHELPG	1.11E+04	1.16E+04	1.22E+04

S4.3 Results: TNT (conformation B) in HKUST-1:

S4.3.1 Adsorption isotherms (300 K) data:

Mulliken charges

P, kPA	mol/uc	Kh [mol/kg/bar]
1.00E-12	3.7E-06	-
1.00E-11	6.19E-05	6.40E+07
1.00E-10	0.00064	6.62E+07
1.00E-09	0.00709	7.33E+07
1.00E-08	0.0996	1.03E+08
1.00E-07	0.611	-
	Average	**7.66E+07**

No charges

P, kPA	mol/uc	Kh [mol/kg/bar]
1.00E-12	4.4E-06	-
1.00E-11	0.000025	-
1.00E-10	0.000255	2.64E+07
1.00E-09	0.00282	2.92E+07
1.00E-08	0.02919	3.02E+07
	Average	**2.86E+07**

CHELPG charges

P, kPA	mol/uc	Kh [mol/kg/bar]
1.00E-11	5.19E-05	-
1.00E-10	0.00059	6.10E+07
1.00E-09	0.00546	5.64E+07
1.00E-08	0.05665	5.86E+07
	Average	**5.87E+07**

S4.3.2 Comparison of Kh [mol/kg/bar] between the methods (TNT, conformation B):

Charges model	GCMC	Widom	Lattice
Mulliken	7.66E+07	7.89E+07	6.40E+07
No charges	2.86E+07	3.65E+07	2.69E+07
CHELPG	5.87E+07	5.36E+07	5.00E+07

Note: The lattice results systematically underestimate the Henry's adsorption constants. This is associated with the cutoff nature of the Fennel-Gezelter potential. Current results are obtained with 20 Å cutoff and longer cutoff distances are expected to further improve the agreement.

S4.4 Results: TNT (conformation B) in HKUST-1 using OPLS potentials and CHELPG charges:

Adsorption isotherm:

P, kPA	mol/uc	Kh [mol/kg/bar]
1.00E-15	1.81E-05	-
1.00E-14	0.000238	2.46E+11
1.00E-13	0.001965	2.03E+11
1.00E-12	0.02027	2.10E+11
	Average	**2.19E+11**

Comparison of Kh [mol/kg/bar] between the methods:

Charges model	**GCMC**	**Widom**	**Lattice**
CHELPG	2.19E+11	2.48E+11	1.88E+11

S4.5 Results: Benzene in IRMOF-1

S4.5.1 Adsorption isotherms data (300 K):

Mulliken charges

P, kPA	mol/uc	Kh [mol/kg/bar]
1.00E-06	0.000055	-
1.00E-05	0.00067	1.09E+03
1.00E-04	0.006975	1.13E+03
1.00E-03	0.0708	1.15E+03
	Average	**1.12E+03**

No charges

P, kPA	mol/uc	Kh [mol/kg/bar]
1.00E-07	0.000005	-
1.00E-06	0.000035	-
1.00E-05	0.000695	1.13E+03
1.00E-04	0.00671	1.09E+03
1.00E-03	0.06716	1.09E+03
	Average	**1.10E+03**

CHELPG charges

P, kPA	mol/uc	Kh [mol/kg/bar]
1.00E-07	0.000005	-

1.00E-06	0.000045	-
1.00E-05	0.000665	1.08E+03
1.00E-04	0.006745	1.10E+03
1.00E-03	6.85E-02	1.11E+03
	Average	**1.10E+03**

S4.5.2 Comparison of Kh [mol/kg/bar] between the methods (Benzene/IRMOF-1):

Charges model	GCMC	Widom	Lattice
Mulliken	1.12E+03	1.22E+03	1.11E+03
No charges	1.10E+03	1.16E+03	1.08E+03
CHELPG	1.10E+03	1.19E+03	1.09E+03

S4.6 Results: TNT (conformation B) in IRMOF-1

S4.6.1 Adsorption isotherms data (300 K):

Mulliken charges

P, kPA	mol/uc	Kh [mol/kg/bar]
1.00E-10	0.000025	-
1.00E-09	0.00017	2.76E+06
1.00E-08	0.0019531	3.17E+06
1.00E-07	0.0210937	3.43E+06
1.00E-06	4.078	-
	Average	**2.97E+06**

No charges

P, kPA	mol/uc	Kh [mol/kg/bar]
1.00E-10	0	-
1.00E-09	0.00001	1.62E+05
1.00E-08	0.0000875	1.42E+05
1.00E-07	0.0009375	1.52E+05
1.00E-06	0.2053906	-
	Average	**1.52E+05**

CHELPG charges

P, kPA	mol/uc	Kh [mol/kg/bar]
1.00E-10	0.000015	-
1.00E-09	0.00011	1.79E+06
1.00E-08	0.0017969	2.92E+06
1.00E-07	0.01125	1.83E+06
1.00E-06	0.284375	-
	Average	**2.18E+06**

S4.6.2 Comparison of Kh [mol/kg/bar] between the methods (TNT/IRMOF-1):

Charges model	GCMC	Widom	Lattice
Mulliken	2.97E+06	3.51E+06	2.68E+06
No charges	1.52E+05	1.55E+05	1.36E+05
CHELPG	2.18E+06	3.35E+06	2.13E+06

(1) Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. *Journal of the American Chemical Society* **1992**, *114*, 10024.
(2) Becke, A. D. *Journal of Chemical Physics* **1993**, *98*, 5648.
(3) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *Journal of Physical Chemistry* **1994**, *98*, 11623.
(4) Breneman, C. M.; Wiberg, K. B. *Journal of Computational Chemistry* **1990**, *11*, 361.
(5) Gaussian09.
(6) Jorgensen, W. L.; Maxwell, D. S.; TiradoRives, J. *Journal of the American Chemical Society* **1996**, *118*, 11225.
(7) Price, M. L. P.; Ostrovsky, D.; Jorgensen, W. L. *Journal of Computational Chemistry* **2001**, *22*, 1340.
(8) Gupta, A.; Chempath, S.; Sanborn, M. J.; Clark, L. A.; Snurr, R. Q. *Molecular Simulation* **2003**, *29*, 29.