
Article:
Greer, AJ, Taylor, SFR, Daly, H et al. (5 more authors) (2021) Combined Experimental and Theoretical Study of the Competitive Absorption of CO2 and NO2 by a Superbase Ionic Liquid. ACS Sustainable Chemistry and Engineering, 9 (22). pp. 7578-7586. ISSN 2168-0485

https://doi.org/10.1021/acssuschemeng.1c01451

Supporting Information

Combined Experimental and Theoretical Study of the Competitive Absorption of CO_2 and NO_2 by a Superbase Ionic Liquid

Adam J. Greer[†,‡,], S. F. Rebecca Taylor[‡], Helen Daly[‡], Matthew G. Quesne[#,⊣], Nora H. de Leeuw[#,⁘], C. Richard A. Catlow[#,⊣], Johan Jacquemin[§,ν,]*, Christopher Hardacre[‡,]**

[†] School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast, BT9 5AG, Northern Ireland

[‡] Department of Chemical Engineering and Analytical Science, The University of Manchester, The Mill, Sackville Street, Manchester, M13 9PL, United Kingdom

[#] School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, United Kingdom

[⊣] UK Catalysis Hub, Research Complex at Harwell, STFC Rutherford Appleton Laboratory, Didcot, Oxfordshire, OX11 0FA, United Kingdom

[⁘] School of Chemistry, University of Leeds, Leeds, LS2 9JT, United Kingdom

[§] Université de Tours, Laboratoire PCM2E, Parc de Grandmont, 37200, Tours, France

[v] Materials Science and Nano-Engineering, Mohammed VI Polytechnic University, Lot 660-Hay Moulay Rachid, Ben Guerir 43150, Morocco

AUTHOR INFORMATION

Co-Corresponding Authors:

* Christopher Hardacre, Tel: +44 (0) 161 3062672, E-mail: c.hardacre@manchester.ac.uk

* Johan Jacquemin, Tel: +33 (0) 2 47 36 73 29, Fax: +33 (0) 2 47 36 70 73, E-mail: jj@univ-tours.fr

* Adam Greer, Tel: +44 (0) 161 3062227, E-mail: adam.greer@manchester.ac.uk

SI Table of Contents (22 pages, 9 Figures, 5 Tables)

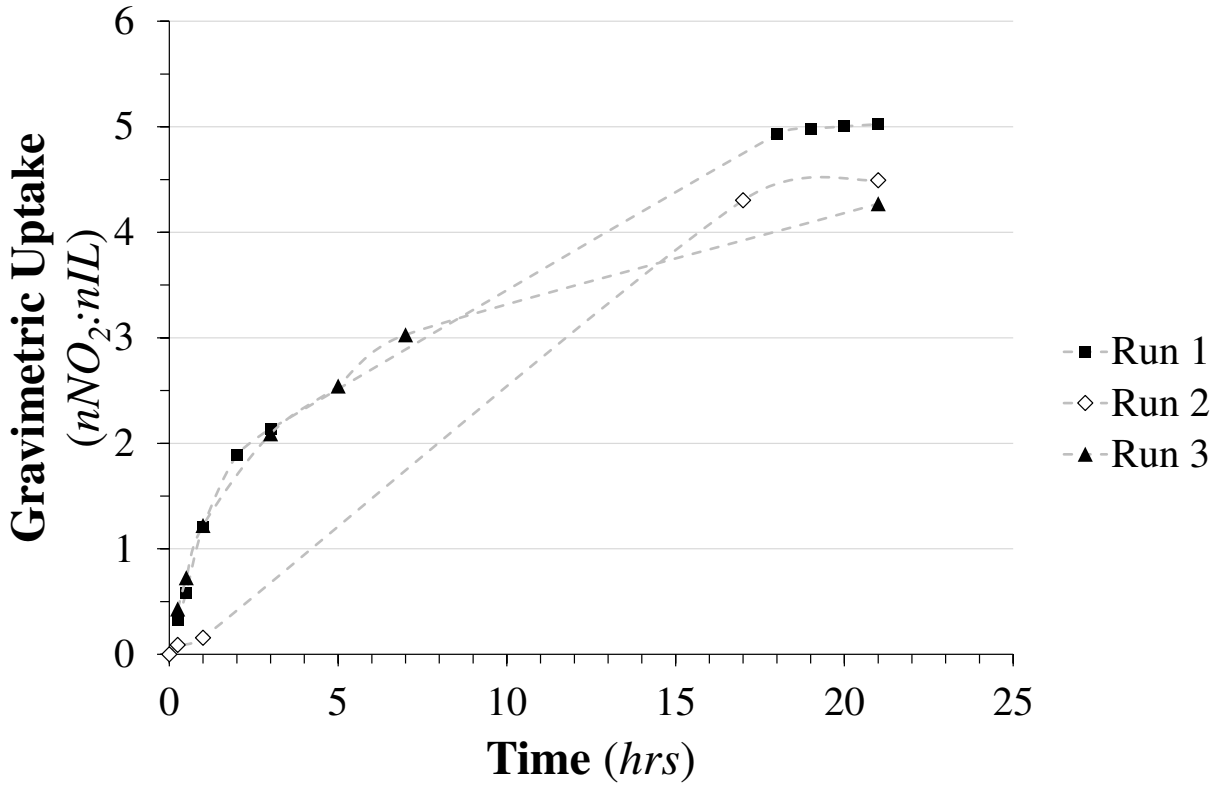

Figure S1. Gravimetric uptake of 1% NO_2 in argon by $[P_{66614}][Benzim]$ over a period of 21 hours.

Table S1. Experimental data from the gas absorption rig displaying the CO_2 uptake (nCO_2/nIL) versus calculated amount of exposure to NO_2 (nNO_2/nIL), by $[P_{66614}][Benzim]$, after 10 cycles of a 2 hour absorption under a feed of 14% CO_2 and 0.2% NO_2 in argon at 22 °C and atmospheric pressure, and a 2 hour desorption at 90 °C. Weight percent (wt.%) values are displayed in brackets.

		nCO_2/nIL / nNO_2/nIL (*wt.%)*									
IL		1	2	3	4	5	6	7	8	9	10
$[P_{66614}][Benzim]$	CO_2 Uptake	0.79 (5.79)	0.78 (5.72)	0.66 (4.84)	0.69 (5.06)	0.52 (3.81)	0.49 (3.59)	0.45 (3.30)	0.40 (2.93)	0.31 (2.27)	0.31 (2.27)
	NO_2 Exposure	0.13 (1.00)	0.25 (1.92)	0.38 (2.91)	0.50 (3.83)	0.63 (4.83)	0.75 (5.75)	0.88 (6.74)	1.00 (7.66)	1.13 (8.66)	1.25 (9.58)

u(T) = 0.5 °C; u(nGas:nIL) = 0.04; u(p) = 4 kPa; water content <0.1 wt.%

[P_{66614}][Benzim]: ^{1}H NMR (500 MHz, DMSO–d_6): δ (ppm) = 0.32-0.40 (s, 12H, CH_3(P)), 0.58-0.77 (m, 48H, CH_2(P)), 0.95 (s, 8H, CH_2(P)), 6.34 (s, 2H, C4 and C5), 6.91 (s, 2H, C3 and C6), 7.36 (s, 1H, C1); ^{13}C NMR (126 MHz, DMSO–d_6): δ (ppm) = 12.96, 16.81, 18.41, 20.19, 21.39, 21.77, 24.96, 26.47, 28.48, 28.81, 30.02, 31.02, 54.77, 114.91, 117.26, 143.02, 147.58.

[P_{66614}][Benzim] (*NO_2 only*)**:** ^{1}H NMR (500 MHz, DMSO–d_6): δ (ppm) = 0.20-0.29 (s, 12H, CH_3(P)), 0.57-0.84 (m, 48H, CH_2(P)), 1.61 (s, 8H, CH_2(P)), 6.57 (s, 2H, C4 and C5), 6.71, 7.10 (s, 2H, C3 and C6), 7.31, 7.65 (s, 1H, C1), 8.23, 8.74, 10.43, 13.19; ^{13}C NMR (126 MHz, DMSO–d_6): δ (ppm) = 12.82, 17.01, 20.25, 21.27, 21.70, 27.81, 28.71, 29.88, 30.95, 114.56, 120.6, 137.62, 140.64, 143.20, 143.71.

[P_{66614}][Benzim] (*CO_2/NO_2 co-feed*)**:** ^{1}H NMR (500 MHz, DMSO–d_6): δ (ppm) = 0.22-0.33 (s, 12H, CH_3(P)), 0.58-0.70 (m, 48H, CH_2(P)), 1.49 (s, 8H, CH_2(P)), 6.81 (s, 2H, C4 and C5), 7.07 (s, 2H, C3 and C6), 7.57 (s, 1H, C1), 7.96, 8.45, 10.61, 15.13; ^{13}C NMR (126 MHz, DMSO–d_6): δ (ppm) = 12.89, 16.96, 20.27, 21.32, 21.74, 28.45, 28.74. 29.33, 29.94, 30.99, 114.70, 119.47, 131.71, 139.51, 142.86.

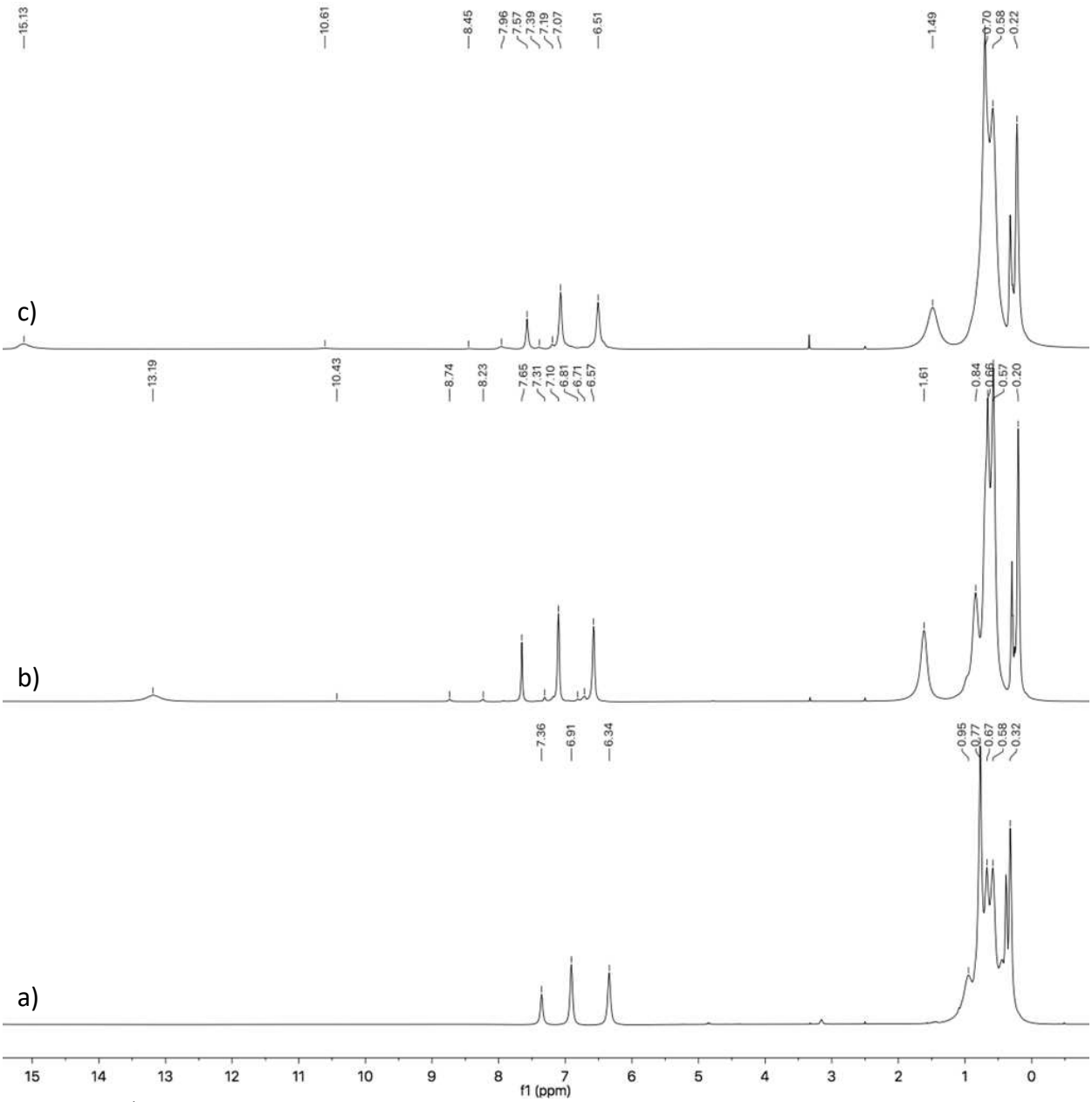

Figure S2. ^{1}H NMR of [P_{66614}][Benzim] under (a) blank IL, (b) 1% NO_2 after 6 hrs, (c) 14% CO_2 + 0.2% NO_2 in Ar after 10 absorption/desorption cycles.

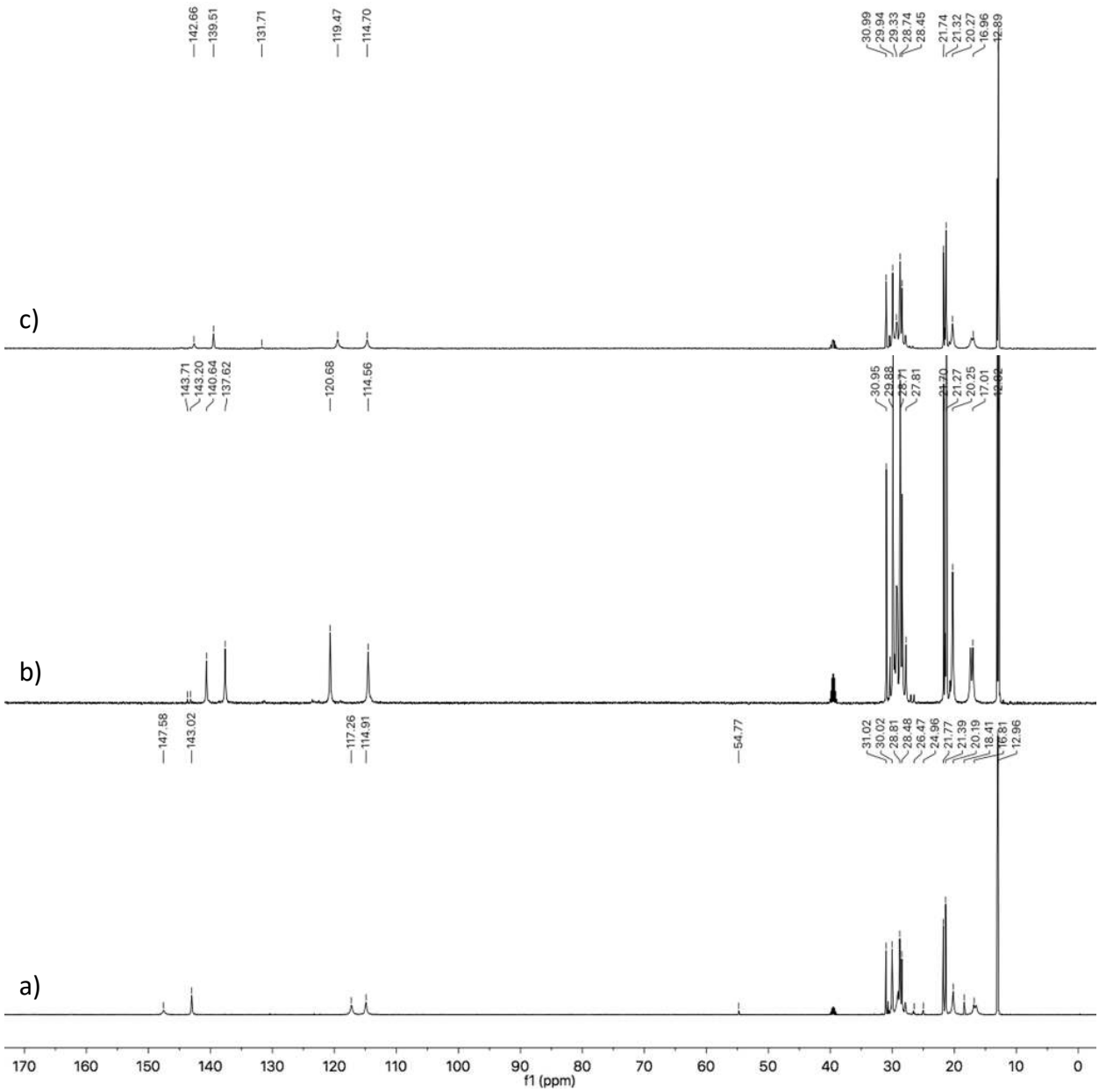

Figure S3. ^{13}C NMR of $[P_{66614}][Benzim]$ under (a) blank IL, (b) 1 % NO_2 after 6 hrs, (c) 14% CO_2 + 0.2% NO_2 in Ar after 10 absorption/desorption cycles.

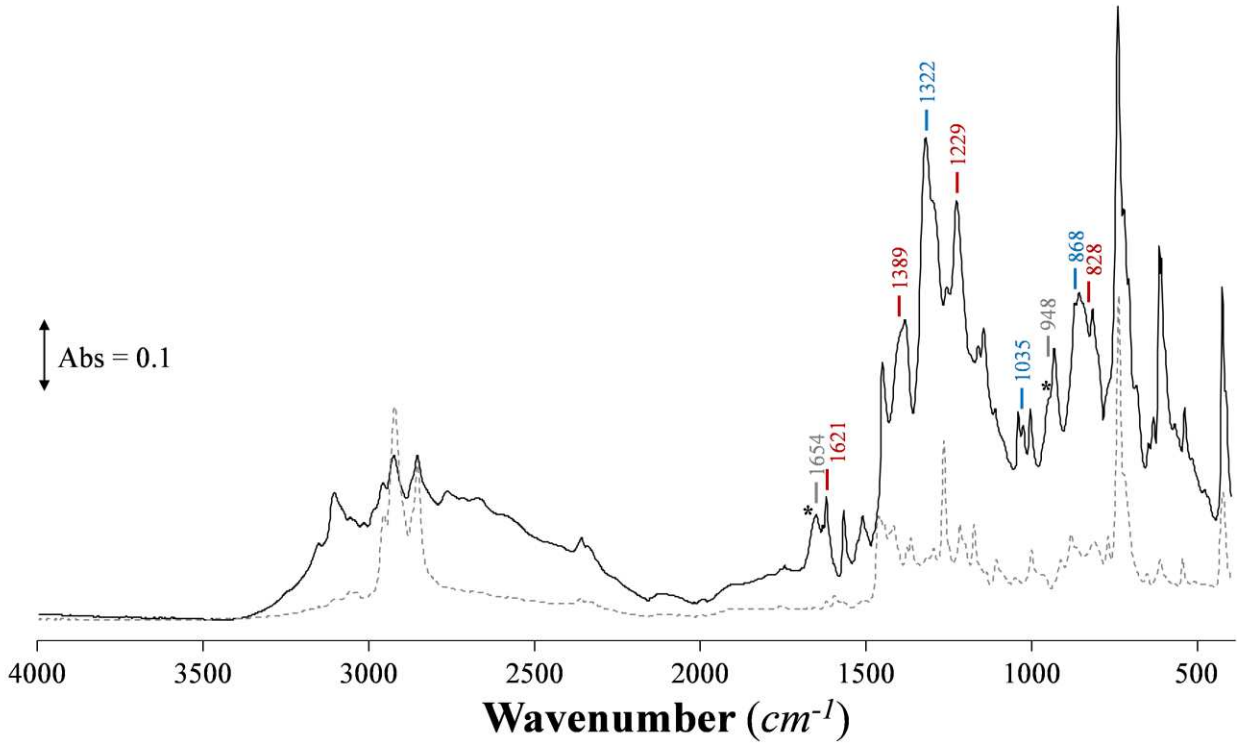

Figure S4. ATR-IR spectra of $[P_{66614}][Benzim]$ after exposure to 1% NO_2 in Ar for 24 hours. Carried out at 22 °C with a flow rate of 40 $cm^3 \cdot min^{-1}$. --- $[P_{66614}][Benzim]$ before exposure to the feed. *Small peaks at 1654 and 948 cm^{-1} indicate HNO_3 production. *In-silico* modelling found that nitric acid would be expected to protonate the $[Benzim]^-$ anion, leading to further changes in aromaticity of the ring structure.

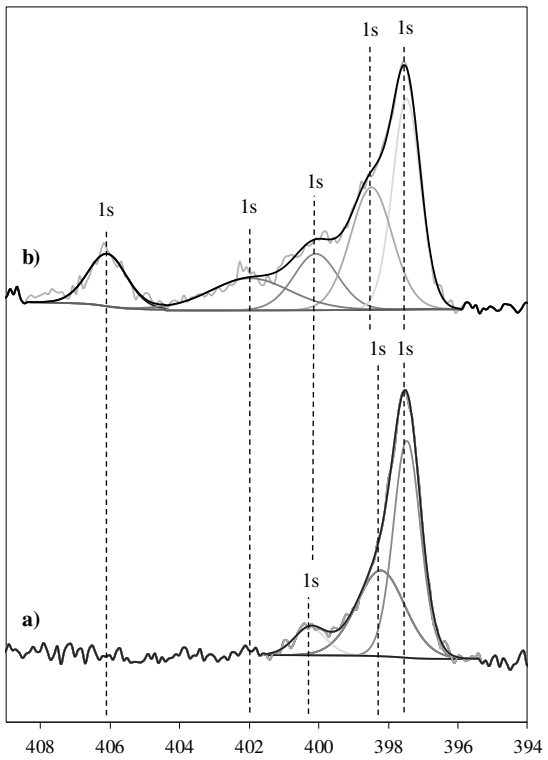

Figure S5. XPS spectra of the nitrogen 1s region of $[P_{66614}][Benzim]$ (a), and after 10 cycles of 14% CO_2 and 0.2% NO_2 in argon, with desorption occurring at 90 °C under argon (b). Peaks for the benzimidazolide anion were assigned previously.[1] The spectra were analyzed using CasaXPS and corrected for charging using the C 1s feature at 284.8 eV.

Table S2. Gas phase absorption energies for various absorbates to a model of $[P_{3333}][Benzim]$ IL. All energies were obtained at B3LYP/6-311+G* level of theory and are given in $kJ \cdot mol^{-1}$. Enthalpies (**E**) and free energies (**G**) are both given, with the subscript, ZPE, representing the zero-point corrected values. (Physisorption is indicated by …).

	E	**E_{ZPE}**	**ΔG**	**Reference**
$[Benzim\text{-}CO_2]^-$	-63.81	-52.12	-9.60	
$[Benzim]^-$…NO	-32.44	-29.61	+5.47	[1]
$[BenzimNONO]^-$	-105.95	-91.09	-33.15	[1]
$[Benzim]^-$…N_2O_4	-128.08	-107.82	-7.39	
$[Benzim]^-$…$(N_2O_4)_2$	-249.57	-210.53	-28.78	
$[Benzim\text{-}CO_2]^-$…(N_2O_4)	-175.05	-147.32	-5.87	

Table S3. Solvent phase absorption energies for various absorbates to a model of $[P_{3333}][Benzim]$ IL. All energies were obtained at B3LYP/6-311+G* level of theory and are given in $kJ \cdot mol^{-1}$. Enthalpies (**E**), free energies (**G**) and zero-point energies (ZPE) are provided. (Physisorption is indicated by …).

	E	**E_{ZPE}**	**ΔG**	**Reference**
$[Benzim\text{-}CO_2]^-$	-61.53	-52.58	-7.56	
$[Benzim]^-$…NO	-21.92	-19.09	+15.99	[1]
$[BenzimNONO]^-$	-87.26	-72.40	-14.46	[1]
$[Benzim]^-$…N_2O_4	-105.95	-85.69	+14.74	
$[Benzim]^-$…$(N_2O_4)_2$	-213.56	-174.52	+22.31	
$[Benzim\text{-}CO_2]^-$…N_2O_4	-158.89	-131.15	+10.30	

Table S4. Grouped Mulliken spin population for absorbates to a model of $[P_{3333}][Benzim]$ IL. Total spin populations are grouped into contributions for the cation ($[P_{3333}]$), anion ([Benzim]), and various absorbates. (Physisorption is indicated by …).

	$[P_{3333}]$	**[Benzim]**	**Absorbate**
$[Benzim\text{-}CO_2]^-$	0.00	0.00	0.00
$[Benzim]^-$…NO	0.01	-0.02	1.00
$[BenzimNONO]^-$	0.00	0.00	0.00
$[Benzim]^-$…N_2O_4	0.00	0.00	0.00

Table S5. Grouped Mulliken charges for absorbates to a model of $[P_{3333}][Benzim]$ IL. Total Mulliken charges are grouped into contributions for the cation ($[P_{3333}]$), anion ([Benzim]), and various absorbates. (Physisorption is indicated by …).

	$[P_{3333}]$	**[Benzim]**	**Absorbate**
$[Benzim\text{-}CO_2]^-$	1.03	-0.09	-0.94
$[Benzim]^-$…NO	1.02	-0.95	-0.07
$[BenzimNONO]^-$	0.88	-0.12	-0.76
$[Benzim]^-$…N_2O_4	0.96	-1.05	0.09

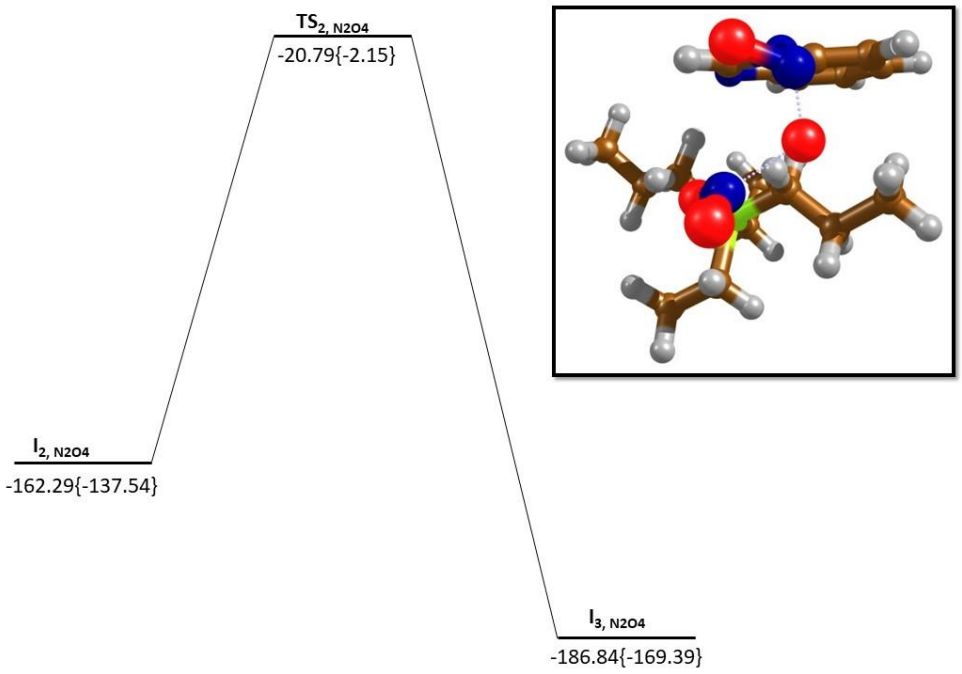

Figure S6. Calculated reaction landscapes showing intermediates (I) and transition states (TS) for oxygen transfer from the NO_2^+ bound to $[P_{3333}][Benzim]$ to free $[NO_2]^-$. Values are given in $kJ \cdot mol^{-1}$ with zero-point corrected gas phase and {solvent} corrected energies calculated at B3LYP/6-311+G* level of theory.

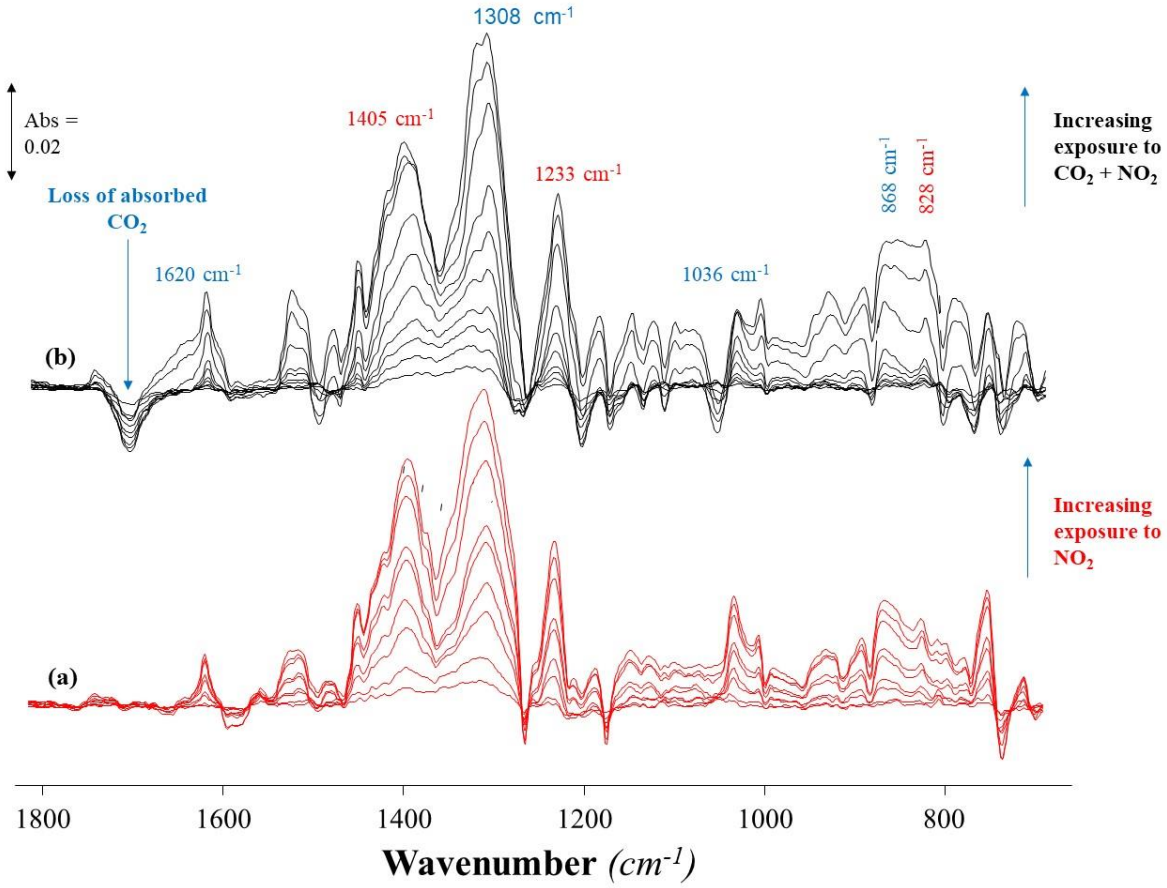

Figure S7. ATR-IR subtracted spectra of $[P_{66614}][Benzim]$ showing increasing exposure to a feed of (a) 0.2% NO_2 in Ar, and (b) 0.2% NO_2 + 14% CO_2 in Ar. Carried out at 22 °C with a flow rate of 15 $cm^3 \cdot min^{-1}$.

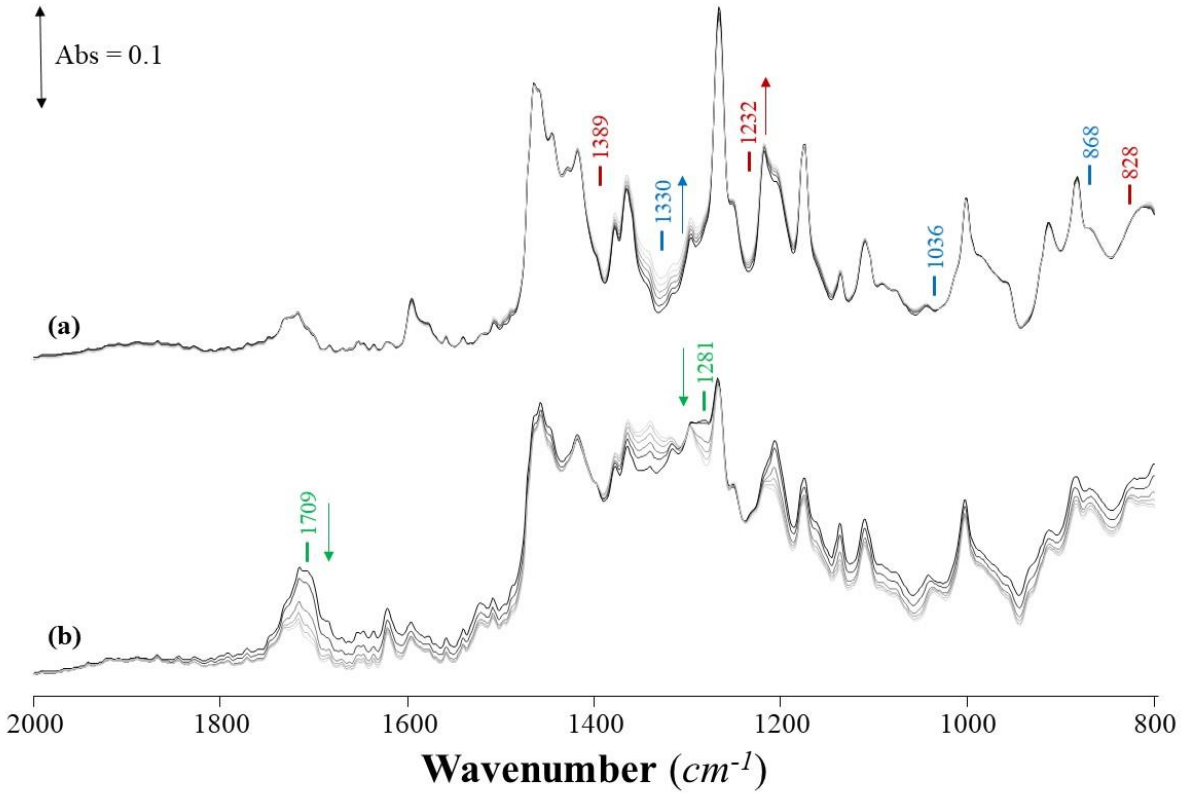

Figure S8. ATR-IR subtracted spectra of [P_{66614}][Benzim] showing desorption under Ar for 30 mins after exposure to (a) 0.2% NO_2 in Ar and (b) 14% CO_2 + 0.2% NO_2, for 15 mins. Carried out at 90 °C with a flow rate of 40 $cm^3 \cdot min^{-1}$. – CO_2 – [Benzim-NO_2] – [P_{66614}][NO_2].

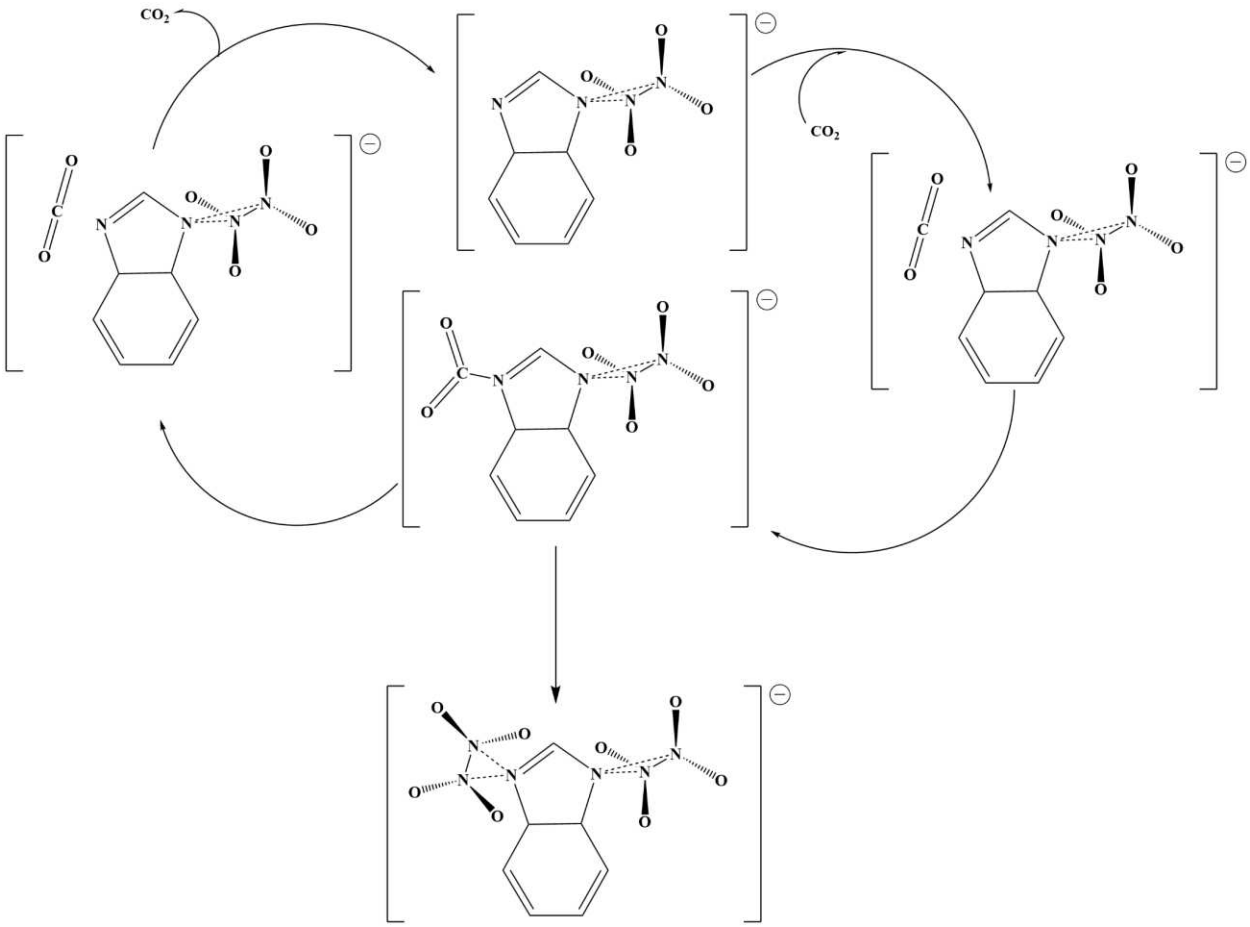

Figure S9. Proposed mechanism showing the effect of N_2O_4 absorption on the CO_2 recyclability of $[P_{66614}][Benzim]$.

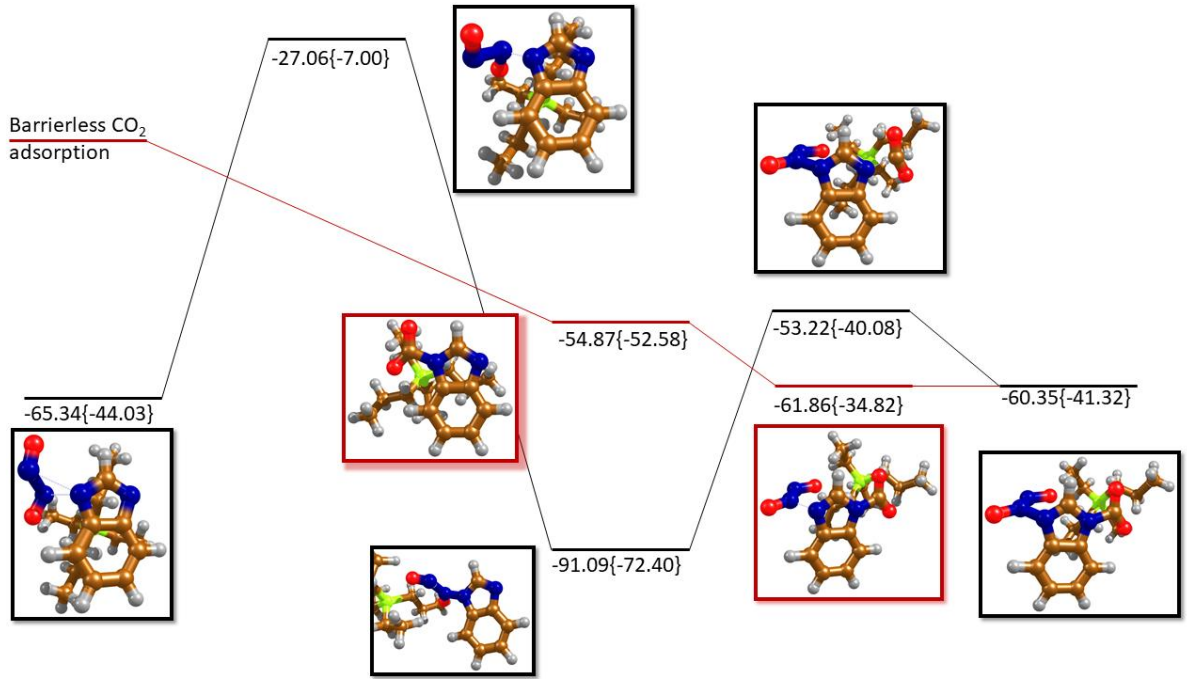

Figure S10. Potential energy landscapes of the co-adsorption of CO_2/NONO by a truncated $[P_{3333}]$[Benzim] model.

Cartesian Co-Ordinates

B3LYP

[P_{3333}][Benzim]

	X	Y	Z
15	-0.159066000	-1.768462000	2.245933000
6	3.062669000	0.878148000	2.406248000
1	2.797105000	1.409396000	3.324542000
1	3.853997000	0.166734000	2.653049000
6	1.849672000	0.157019000	1.815332000
1	1.077464000	0.890061000	1.553893000
1	2.143506000	-0.329848000	0.879925000
1	3.468760000	1.608449000	1.702035000
6	1.318475000	-0.892512000	2.798873000
1	2.064281000	-1.678371000	2.991620000
1	1.086875000	-0.453858000	3.772901000
6	-0.670449000	-3.097737000	3.372388000
1	-1.431479000	-3.660870000	2.816849000
1	0.187316000	-3.763589000	3.499386000
6	-1.215943000	-2.670745000	4.741810000
1	-1.996646000	-1.911723000	4.626253000
1	-0.411980000	-2.231777000	5.336077000
6	-1.799447000	-3.879336000	5.473830000
1	-1.059437000	-4.676050000	5.552240000
1	-2.676912000	-4.272654000	4.949205000
1	-2.104170000	-3.604988000	6.485762000
6	0.161066000	-2.512784000	0.609598000
1	-0.793788000	-2.902259000	0.241681000
1	0.441704000	-1.693203000	-0.058074000
6	1.235937000	-3.605186000	0.630511000
1	0.904471000	-4.478997000	1.191480000
1	2.161283000	-3.261015000	1.094096000
1	1.455354000	-3.923250000	-0.390747000
6	-1.536979000	-0.580825000	2.007105000
1	-1.413981000	-0.151996000	1.008165000
1	-2.460185000	-1.167733000	1.980506000
6	-1.624578000	0.535140000	3.054727000
1	-0.734798000	1.166039000	3.043617000
1	-1.741867000	0.145125000	4.065353000
1	-2.484643000	1.173260000	2.842091000
1	2.645698000	-5.288430000	2.888311000
6	2.438536000	-4.692583000	3.771281000
7	1.789382000	-5.213824000	4.826241000
6	1.759866000	-4.161293000	5.715402000
6	2.404129000	-3.033732000	5.112135000
6	2.493907000	-1.814626000	5.801073000
6	1.928339000	-1.728964000	7.069311000
1	3.015791000	-0.964909000	5.369026000
1	1.994715000	-0.798170000	7.625205000
6	1.296605000	-2.842447000	7.664507000
1	0.883075000	-2.744079000	8.663786000
6	1.216956000	-4.062711000	7.003922000
1	0.745778000	-4.922442000	7.470705000
7	2.827291000	-3.397267000	3.849788000

[P_{3333}][Benzim]CO_2

	X	Y	Z
15	-0.152713000	-1.683088000	2.150301000
6	3.028318000	0.982835000	2.540408000
1	2.791023000	1.418240000	3.515663000
1	3.816663000	0.240983000	2.683528000
6	1.796110000	0.333379000	1.908844000
1	1.022838000	1.089185000	1.727758000
1	2.072826000	-0.074262000	0.932197000
1	3.420570000	1.780391000	1.904805000
6	1.275948000	-0.798309000	2.804396000
1	2.067710000	-1.548883000	2.932305000
1	1.010912000	-0.438756000	3.802617000
6	-0.562386000	-3.135354000	3.168699000
1	-1.260724000	-3.729917000	2.567924000
1	0.350906000	-3.726932000	3.268748000
6	-1.163572000	-2.836103000	4.550604000
1	-1.981408000	-2.114887000	4.458203000

1	-0.402621000	-2.384253000	5.191035000
6	-1.702996000	-4.109224000	5.203835000
1	-0.926038000	-4.867291000	5.308212000
1	-2.522550000	-4.534227000	4.615160000
1	-2.087682000	-3.889753000	6.202254000
6	0.165337000	-2.243482000	0.444375000
1	-0.775456000	-2.674686000	0.084386000
1	0.338760000	-1.340529000	-0.148893000
6	1.328101000	-3.230819000	0.303581000
1	1.151280000	-4.161237000	0.842987000
1	2.267768000	-2.824409000	0.677183000
1	1.460843000	-3.484876000	-0.749779000
6	-1.604484000	-0.563595000	2.057772000
1	-1.551546000	-0.066422000	1.084968000
1	-2.495464000	-1.198312000	2.030552000
6	-1.701936000	0.478133000	3.178132000
1	-0.857984000	1.168990000	3.156314000
1	-1.733885000	0.022758000	4.167970000
1	-2.613069000	1.066883000	3.054346000
1	2.198103000	-6.343858000	3.830025000
6	2.103086000	-5.519162000	4.519424000
7	1.460689000	-5.541157000	5.663967000
6	1.615708000	-4.258773000	6.178604000
6	2.381215000	-3.465892000	5.285438000
6	2.694189000	-2.135958000	5.573293000
6	2.183896000	-1.603751000	6.753533000
1	3.321208000	-1.560179000	4.907982000
1	2.413317000	-0.574666000	7.011924000
6	1.399881000	-2.374232000	7.633864000
1	1.028652000	-1.921925000	8.547783000
6	1.117604000	-3.707563000	7.362455000
1	0.531074000	-4.315181000	8.042866000
7	2.675634000	-4.305747000	4.216404000
6	3.313867000	-3.978261000	2.886591000
8	3.428130000	-4.946651000	2.143030000
8	3.560803000	-2.765237000	2.749161000

$[P_{3333}][Benzim]2CO_2$

	X	Y	Z
15	-1.056374000	-2.127459000	1.787895000
6	2.934618000	-1.213949000	0.936764000
1	3.308887000	-1.132976000	1.959846000
1	3.266810000	-2.176333000	0.541419000
6	1.410258000	-1.092003000	0.891118000
1	1.108849000	-0.102605000	1.249664000
1	1.066984000	-1.164755000	-0.146139000
1	3.404604000	-0.427024000	0.342328000
6	0.752112000	-2.189370000	1.738132000
1	1.013435000	-3.173462000	1.347847000
1	1.098077000	-2.161209000	2.775146000
6	-1.745952000	-3.501064000	2.752017000
1	-2.818567000	-3.523132000	2.525530000
1	-1.311417000	-4.412231000	2.325593000
6	-1.507087000	-3.447788000	4.269286000
1	-2.064239000	-2.612916000	4.706098000
1	-0.452306000	-3.268788000	4.489648000
6	-1.951322000	-4.755691000	4.925948000
1	-1.409554000	-5.608720000	4.509539000
1	-3.019467000	-4.939818000	4.774720000
1	-1.764419000	-4.728616000	6.001666000
6	-1.704491000	-2.257019000	0.087080000
1	-2.796261000	-2.253695000	0.165901000
1	-1.426087000	-1.339050000	-0.438562000
6	-1.205540000	-3.499483000	-0.664052000
1	-1.416877000	-4.427355000	-0.132160000
1	-0.128296000	-3.465054000	-0.833763000
1	-1.688273000	-3.551761000	-1.641537000
6	-1.579806000	-0.518860000	2.487230000
1	-1.540367000	0.214533000	1.676612000
1	-2.634464000	-0.625043000	2.759771000
6	-0.743499000	-0.045528000	3.684561000
1	0.288910000	0.159422000	3.400249000
1	-0.716145000	-0.775947000	4.491314000

1	-1.166849000	0.879532000	4.080708000
6	4.093247000	-5.442074000	0.233436000
6	3.388199000	-5.136348000	1.398229000
6	3.956873000	-4.343295000	2.418721000
6	5.251835000	-3.835081000	2.312076000
6	5.949954000	-4.144314000	1.152164000
6	5.381268000	-4.931204000	0.132342000
7	2.088840000	-5.448789000	1.815024000
6	1.903200000	-4.863827000	3.002683000
7	2.977623000	-4.190346000	3.404622000
1	3.638907000	-6.043324000	-0.540909000
1	5.668879000	-3.227693000	3.102807000
1	6.960557000	-3.770287000	1.028722000
1	5.965400000	-5.146496000	-0.755889000
1	0.974857000	-4.894836000	3.542094000
8	-0.172801000	-5.922579000	1.568153000
6	0.885761000	-6.004686000	0.943726000
8	1.238347000	-6.342919000	-0.168367000
8	1.738634000	-2.867551000	4.887917000
6	2.906938000	-3.041286000	4.556714000
8	4.000229000	-2.579766000	4.790683000

$[P_{3333}][Benzim]N_2O_4$

	X	Y	Z
15	-0.106862000	-1.827890000	2.279366000
6	2.988138000	0.969451000	2.267279000
1	2.669085000	1.576875000	3.119143000
1	3.802306000	0.324909000	2.606359000
6	1.828973000	0.135658000	1.719116000
1	1.028415000	0.798804000	1.370782000
1	2.171637000	-0.422907000	0.842374000
1	3.383209000	1.644790000	1.504442000
6	1.322362000	-0.845166000	2.783302000
1	2.105326000	-1.568105000	3.058971000
1	1.045784000	-0.331301000	3.708247000
6	-0.554685000	-3.105392000	3.489733000
1	-1.269020000	-3.753177000	2.968351000
1	0.337451000	-3.708399000	3.671547000
6	-1.146619000	-2.597462000	4.812547000
1	-1.904738000	-1.830950000	4.623376000
1	-0.357390000	-2.137626000	5.410673000
6	-1.792632000	-3.741509000	5.592639000
1	-1.081209000	-4.546378000	5.769430000
1	-2.649261000	-4.156012000	5.051250000
1	-2.142727000	-3.390709000	6.565876000
6	0.227605000	-2.648734000	0.683428000
1	-0.709866000	-3.124799000	0.377559000
1	0.425065000	-1.854012000	-0.042002000
6	1.372959000	-3.664319000	0.723092000
1	1.145743000	-4.502849000	1.380284000
1	2.302162000	-3.212709000	1.072280000
1	1.541581000	-4.060995000	-0.280236000
6	-1.547358000	-0.728524000	1.980487000
1	-1.480199000	-0.397000000	0.940382000
1	-2.440725000	-1.356964000	2.046465000
6	-1.657639000	0.482246000	2.914611000
1	-0.807606000	1.156355000	2.801040000
1	-1.714412000	0.193092000	3.963912000
1	-2.560610000	1.048645000	2.677619000
1	3.191563000	-4.905312000	2.824741000
6	2.857251000	-4.422920000	3.735735000
7	2.200177000	-5.114319000	4.686246000
6	1.974986000	-4.169771000	5.667342000
6	2.518276000	-2.925102000	5.218504000
6	2.408201000	-1.774538000	6.011036000
6	1.759274000	-1.880527000	7.237708000
1	2.842374000	-0.831910000	5.689208000
1	1.671993000	-1.006324000	7.875994000
6	1.235239000	-3.112004000	7.683507000
1	0.750567000	-3.159887000	8.653802000
6	1.341470000	-4.264376000	6.912486000
1	0.949090000	-5.213177000	7.264310000
7	3.077247000	-3.114550000	3.968186000
7	0.246925000	-6.815974000	3.927357000
8	-0.365227000	-6.912187000	4.942481000
8	-0.020697000	-6.334116000	2.864836000

7	1.815519000	-7.629326000	3.965191000
8	2.397664000	-7.541485000	2.933087000
8	2.001920000	-8.205401000	4.982294000

$[P_{3333}][Benzim]\ N_2O_4\_TS1$

	X	Y	Z
15	-0.530483000	-1.952574000	2.328559000
6	3.104773000	0.056402000	2.739303000
1	2.856690000	0.600709000	3.654867000
1	3.786461000	-0.751966000	3.008086000
6	1.842331000	-0.484475000	2.066928000
1	1.195322000	0.352150000	1.779432000
1	2.113014000	-0.995897000	1.137961000
1	3.627779000	0.744924000	2.070857000
6	1.086202000	-1.462982000	2.980068000
1	1.655581000	-2.380876000	3.122779000
1	0.935714000	-1.046942000	3.979900000
6	-1.349251000	-3.167867000	3.397771000
1	-2.177089000	-3.580964000	2.809829000
1	-0.630206000	-3.981696000	3.539231000
6	-1.851126000	-2.645034000	4.749938000
1	-2.600709000	-1.861269000	4.601956000
1	-1.020548000	-2.202180000	5.304760000
6	-2.461217000	-3.779497000	5.573336000
1	-1.740172000	-4.583581000	5.730033000
1	-3.332988000	-4.210413000	5.072319000
1	-2.784341000	-3.418091000	6.552416000
6	-0.318374000	-2.686695000	0.671948000
1	-1.318413000	-2.972045000	0.329033000
1	0.021272000	-1.883707000	0.011214000
6	0.642966000	-3.880087000	0.637154000
1	0.331766000	-4.688140000	1.297739000
1	1.654284000	-3.594047000	0.929739000
1	0.695558000	-4.275431000	-0.378711000
6	-1.580762000	-0.463476000	2.123989000
1	-1.308805000	-0.012755000	1.165799000
1	-2.610553000	-0.817988000	2.017189000
6	-1.467754000	0.570762000	3.250813000
1	-0.461314000	0.986246000	3.315345000
1	-1.718452000	0.151107000	4.224591000
1	-2.153375000	1.398519000	3.059442000
1	4.258989000	-4.488200000	2.668184000
6	3.778893000	-4.028445000	3.518768000
7	2.666408000	-4.580967000	4.075660000
6	2.287207000	-3.783108000	5.134006000
6	3.249389000	-2.736411000	5.148895000
6	3.137936000	-1.704642000	6.087263000
6	2.076384000	-1.746283000	6.983480000
1	3.869781000	-0.904369000	6.110588000
1	1.974385000	-0.963614000	7.728283000
6	1.144761000	-2.804823000	6.967996000
1	0.349846000	-2.820376000	7.706813000
6	1.235930000	-3.843665000	6.049098000
1	0.550325000	-4.679378000	6.048019000
7	4.169324000	-2.920237000	4.123787000
7	1.805750000	-5.833303000	3.373304000
8	0.590896000	-5.605683000	3.496496000
8	2.385159000	-6.194911000	2.359620000
7	2.245122000	-7.090685000	4.770248000
8	3.247120000	-7.734874000	4.592888000
8	1.470662000	-7.132442000	5.698765000

$[P_{3333}][Benzim]\ NO_2\_NO_2$

	X	Y	Z
15	-1.625095000	1.550530000	-0.482485000
6	2.186728000	3.166029000	0.097015000
1	2.226542000	3.215945000	1.189131000
1	2.759327000	2.292936000	-0.222530000
6	0.746857000	3.069382000	-0.406900000
1	0.193935000	3.974866000	-0.130205000
1	0.758335000	3.012277000	-1.497545000
1	2.680398000	4.056583000	-0.299867000
6	0.054732000	1.824427000	0.155279000
1	0.615332000	0.930043000	-0.104050000
1	-0.012521000	1.859511000	1.245861000
6	-2.290014000	0.036675000	0.281230000
1	-1.730364000	-0.791261000	-0.149858000
1	-1.979055000	0.097848000	1.328592000

6	-3.802233000	-0.193379000	0.194319000
1	-4.098816000	-0.342877000	-0.845782000
1	-4.353263000	0.682778000	0.552445000
6	-4.202914000	-1.417772000	1.020224000
1	-3.969319000	-1.273563000	2.079182000
1	-3.663908000	-2.308280000	0.689608000
1	-5.274661000	-1.615043000	0.937026000
6	-1.664644000	1.653901000	-2.306419000
1	-1.878488000	2.700895000	-2.546895000
1	-0.643921000	1.421390000	-2.618986000
6	-2.652195000	0.713170000	-2.996820000
1	-3.691922000	0.913105000	-2.726067000
1	-2.409803000	-0.323720000	-2.764276000
1	-2.564894000	0.837649000	-4.078322000
6	-2.659444000	2.945684000	0.113813000
1	-2.245342000	3.855736000	-0.328972000
1	-3.653922000	2.819876000	-0.324228000
6	-2.742385000	3.075035000	1.636276000
1	-1.758973000	3.241379000	2.080389000
1	-3.171208000	2.183802000	2.098891000
1	-3.373619000	3.922872000	1.910758000
8	2.371969000	-3.605700000	-1.464368000
7	2.643044000	-2.698743000	-0.707905000
8	3.665007000	-2.049007000	-0.647826000
7	1.666661000	-2.399510000	0.263786000
6	1.716881000	-1.405056000	1.245270000
6	0.470231000	-1.533105000	1.897712000
7	-0.302820000	-2.536609000	1.304415000
6	0.415111000	-3.007414000	0.333960000
1	0.141563000	-3.775611000	-0.369571000
6	2.662279000	-0.457156000	1.619147000
1	3.603324000	-0.362328000	1.098556000
6	2.325784000	0.368086000	2.690865000
1	3.035101000	1.122318000	3.012592000
6	1.099654000	0.245907000	3.361605000
1	0.885996000	0.900175000	4.200200000
6	0.158943000	-0.704362000	2.973319000
1	-0.787116000	-0.815790000	3.491439000
8	1.309304000	0.493381000	-2.447242000
7	1.049619000	-0.651798000	-2.031794000
8	-0.117755000	-0.810243000	-1.552445000

$[P_{3333}][Benzim]$ NO_2_NO_2_TS2

	X	Y	Z
15	0.171746000	-2.151489000	1.680919000
6	4.206777000	-1.092394000	1.982038000
1	4.296457000	-1.102208000	3.069391000
1	4.659921000	-2.014240000	1.612051000
6	2.742752000	-0.997675000	1.550941000
1	2.312585000	-0.059210000	1.920891000
1	2.686483000	-0.956010000	0.457951000
1	4.779772000	-0.246582000	1.592946000
6	1.939839000	-2.195032000	2.074460000
1	2.335723000	-3.137835000	1.693386000
1	2.016943000	-2.277633000	3.160864000
6	-0.585073000	-3.761957000	2.023490000
1	-0.308554000	-4.412777000	1.187199000
1	-0.047731000	-4.161082000	2.900866000
6	-2.099166000	-3.782670000	2.271664000
1	-2.655632000	-3.378377000	1.420857000
1	-2.339963000	-3.147057000	3.128843000
6	-2.563711000	-5.211238000	2.562183000
1	-2.024385000	-5.627527000	3.415972000
1	-2.383334000	-5.866424000	1.705008000
1	-3.633321000	-5.239412000	2.784520000
6	-0.021911000	-1.693447000	-0.079506000
1	0.387673000	-0.685760000	-0.189931000
1	0.637988000	-2.362574000	-0.638026000
6	-1.449175000	-1.765471000	-0.627910000
1	-2.142140000	-1.136836000	-0.064512000
1	-1.832615000	-2.786509000	-0.618966000
1	-1.463497000	-1.419923000	-1.663519000
6	-0.633108000	-0.859724000	2.688192000
1	-0.218078000	0.101093000	2.370246000
1	-1.692189000	-0.848936000	2.417814000
6	-0.448483000	-1.066593000	4.195878000
1	0.598641000	-1.007942000	4.492909000

1	-0.818041000	-2.039553000	4.522329000
1	-0.997259000	-0.297579000	4.743205000
8	4.166867000	-6.573498000	0.737275000
7	4.685288000	-5.545779000	1.012910000
8	4.362188000	-4.471878000	0.319269000
7	3.458443000	-5.061851000	3.234349000
6	3.518185000	-4.135024000	4.250829000
6	2.213803000	-4.029317000	4.834633000
7	1.365119000	-4.890242000	4.170167000
6	2.176723000	-5.461834000	3.253869000
1	1.807844000	-6.206730000	2.555249000
6	4.575906000	-3.347135000	4.720769000
1	5.567091000	-3.436494000	4.286889000
6	4.319445000	-2.447690000	5.749721000
1	5.123979000	-1.827086000	6.132683000
6	3.033177000	-2.334687000	6.320211000
1	2.875392000	-1.633845000	7.134742000
6	1.975797000	-3.123863000	5.878288000
1	0.994720000	-3.054836000	6.339867000
8	3.468375000	-5.052522000	-1.888921000
7	3.084022000	-4.745490000	-0.814327000
8	2.004219000	-4.506267000	-0.370588000

$[P_{3333}][Benzim]$ NO_3_NO

	X	Y	Z
15	0.188319000	-1.995959000	1.423538000
6	3.991097000	-0.708553000	2.584643000
1	3.793553000	-0.502089000	3.640615000
1	4.524187000	-1.657117000	2.513834000
6	2.696967000	-0.777393000	1.775564000
1	2.192911000	0.197207000	1.790675000
1	2.944871000	-0.993784000	0.733993000
1	4.644378000	0.079086000	2.201057000
6	1.766384000	-1.873669000	2.314075000
1	2.243921000	-2.850720000	2.246557000
1	1.527542000	-1.712361000	3.368787000
6	-0.700801000	-3.511240000	1.901589000
1	-1.420892000	-3.723076000	1.105983000
1	0.046235000	-4.306319000	1.871888000
6	-1.411670000	-3.456077000	3.259149000
1	-2.171494000	-2.667424000	3.254965000
1	-0.692694000	-3.197485000	4.040478000
6	-2.063901000	-4.797787000	3.593535000
1	-1.310418000	-5.585148000	3.644183000
1	-2.804343000	-5.074971000	2.836720000
1	-2.578130000	-4.751189000	4.557352000
6	0.411541000	-1.927982000	-0.381983000
1	0.951649000	-0.999311000	-0.586746000
1	1.077379000	-2.744502000	-0.668422000
6	-0.901554000	-1.972231000	-1.168867000
1	-1.580457000	-1.154942000	-0.911138000
1	-1.431139000	-2.915774000	-1.024939000
1	-0.680476000	-1.890335000	-2.234541000
6	-0.827598000	-0.520320000	1.844756000
1	-0.537414000	0.262567000	1.138110000
1	-1.866393000	-0.770076000	1.612537000
6	-0.698743000	-0.005655000	3.281791000
1	0.316628000	0.331000000	3.497897000
1	-0.964126000	-0.764169000	4.018429000
1	-1.365366000	0.846688000	3.429719000
8	4.294910000	-7.165453000	1.363373000
7	4.483780000	-6.309719000	2.181004000
8	2.017630000	-4.483531000	0.633690000
7	3.347604000	-5.972364000	2.904494000
6	3.320991000	-4.968291000	3.871090000
6	1.991112000	-4.963985000	4.334443000
7	1.232419000	-5.917426000	3.636980000
6	2.050664000	-6.473948000	2.796167000
1	1.812362000	-7.237356000	2.074165000
6	4.286649000	-4.092865000	4.344872000
1	5.292884000	-4.093748000	3.947057000
6	3.883182000	-3.202910000	5.338036000
1	4.601998000	-2.495434000	5.736186000
6	2.569247000	-3.200235000	5.833957000
1	2.302501000	-2.502392000	6.620655000
6	1.607749000	-4.079758000	5.340951000
1	0.596918000	-4.092592000	5.731922000

8	4.055087000	-3.787788000	0.965949000	8	3.092315000	-3.458196000	-0.959956000
7	3.075162000	-3.916292000	0.199864000				

References

1. Greer, A. J., Taylor, S. F. R., Daly, H., Quesne, M., Catlow, C. R. A., Jacquemin, J. & Hardacre, C. Investigating the Effect of NO on the Capture of CO_2 Using Superbase Ionic Liquids for Flue Gas Applications. *ACS Sustain. Chem. Eng.* **2019**, *7*, 3567–3574, DOI 10.1021/acssuschemeng.8b05870.