

Supporting Information for

A survey of carbon dioxide capture in phosphonium-

based ionic liquids and end-capped polyethylene glycol

using DETA (DETA = diethylenetriamine) as a model

absorbent

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Table of Contents

S1 – General Experimental.....	S4
S1.1 – Materials and General Procedures.....	S4
S1.2 – Instrumentation.....	S8
S1.3 – Preparation of Solvents.....	S8
S1.3.1 - Purification of Phosphonium Ionic Liquids.....	S8
S1.3.2 - Synthesis of 1-butyl-3-methylimidazolium bistriflamide...	S10
S1.3.3 - Drying of Polymeric Solvents.....	S11
S2 – Thermogravimetric Analysis Experiments.....	S11
S2.1 - Onset of Decomposition Determination.....	S12
S2.2 - TGA Decomposition Curves.....	S13
S2.3 - Useful Working Temperature Range Determination.....	S19
S2.4 - Isothermal TGA Plots.....	S21
S3 – Long-Term Thermal Stability Testing.....	S27
S3.1 - Observation of Colour Changes.....	S27
S3.2 - Determining Cause for Colour Change.....	S28
S3.3 - Colour Change Photographs.....	S29
S3.4 - Infrared Spectra.....	S40
S3.5 - ^1H NMR Spectra.....	S51
S3.6 - ^{31}P NMR Spectra.....	S54
S3.7 - Infrared Spectra and ^1H NMR Spectra of Pure & Distilled Polyethylene Glycol Dimethyl Ether ($M_N = \sim 250$).....	S56
S4 – Heat Capacity Measurements.....	S57
S4.1 - Sample Preparation.....	S57
S4.2 - Experimentation.....	S57
S4.3 - Heat Capacity Data.....	S59
S5 – Vapour Pressure Measurements.....	S64
S5.1 – Experimental.....	S64
S5.2 – Vapour Pressure Data.....	S65
S6 – Carbon Dioxide Capture.....	S66

S6.1 - CO ₂ Capture Experimental Procedure.....	S66
S6.2 - CO ₂ Capture Results.....	S67
S6.3 - DETA-CO ₂ Adduct Formation and Data.....	S69
S7 – Theoretical Calculations.....	S72
S7.1 – Experimental.....	S72
S7.2 – Summary.....	S72
References.....	S82

NOTE: For size reasons, the Supporting Information has been divided into 3 files. Each file contains the Table of Contents and References. Page numbering is consistent between files.

PART 1	Pages S1 – S26
PART 2	Pages S27 – S56
PART 3	Pages S57 – S83

S5 – Heat Capacity Measurements

S5.1 – Sample preparation

The samples as submitted were moisture sensitive liquids. As a result, they had to be hermetically sealed in an aluminum pan before mounting on the calorimetry puck for heat capacity measurements. Hermetic aluminum pans from Perkin Elmer were used as they isolate the sample from the atmosphere and the subsequent vacuum in the cryostat and they have the added benefit of being inexpensive.

The samples were stable enough to be exposed to the atmosphere for a few minutes. This gave enough time to transfer them from the vial to the sample pan and hermetically seal the lid using the crimp. It is well known that large sample sizes often have longer relaxation times and this can lead to lower heat capacity measurements.⁴ For these samples, it was found that using a mass of between 5 and 8 mg gave reproducible data with a good S/N ratio.

S5.2 – Experimentation

A commercial relaxation calorimeter from Quantum Design (Physical Property Measurement System) was used to measure the heat capacities of various ionic liquids over the specified temperature range, 298.15 to 373.15 kelvin. The two-tau method of heat capacity data analysis, which allows

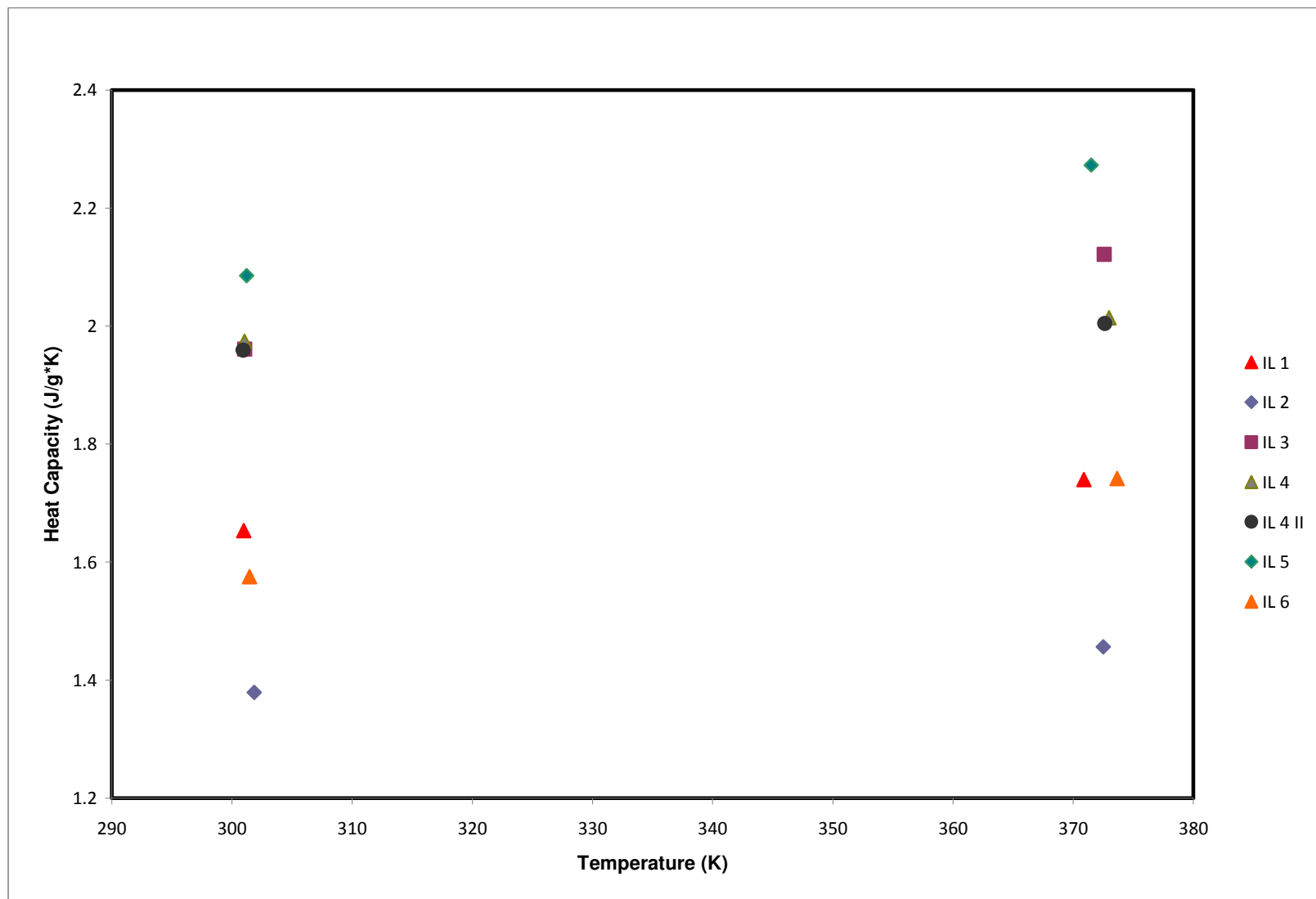
separately for relaxation of the temperature within the sample and within the addenda, was used.⁵ Due to the air sensitivity and liquid nature of the samples, the method used for data collection involved 4 separate runs, as described by Marriott *et al.*⁶ for volatile samples where the sample has been hermetically sealed in an aluminum pan.

First, the background data (addenda) was collected. A very thin layer of Apiezon® H grease (ca. 1.5 mg) was spread over the platform (to provide a good thermal contact between the pan and platform in the following run) and data was collected. Then a second run, with the unsealed volatile pan added (and with a very thin layer of grease between the lid and pan lip for thermal contact), was collected; this gives the specific heat of the sample pan and grease. The third run was another addenda run (same as the first) and finally the fourth run added the sample pan (from run 2) with the sample sealed in it. With the data from runs 2 and 4, the specific heat of the pan and grease can be subtracted from the specific heat of the pan, grease and sample (i.e. 4-2) giving the specific heat of the sample. Figure S74 shows the temperature dependence of the measured ionic liquids and Table S2 summarizes the results. IL103 II is a complete repeat of the procedure used to show the reproducibility of the method, which was ~0.5%, well within the manufacturer's specifications of 2%. All samples were repeated with <0.6% variability; for clarity only the results for IL103 are shown.

Table S2: Specific heats of the ionic liquids measured.

Sample	Molecular Weight (g/mol)	Average Temperature K	Average Specific Heat Capacity (J/g*K)	Density (g/ml) ^a	Average Volumetric Heat Capacity (J/ml*K)	Average Molar Heat Capacity (J/mol*K)
IL 1 1-butyl-3-methylimidazolium chloride	174.67	300.94	1.657	1.08	1.79	289.43
		370.86	1.756			306.67
IL 2 1-butyl-3-methylimidazolium bistriflamide	419.36	301.81	1.377	1.43	1.97	577.39
		372.07	1.452			608.78
IL 3 tetradecyl(trihexyl)phosphonium chloride	519.31	301.08	1.962	0.882	1.461	1019.09
		372.09	2.107	0.845	1.483	1094.19
IL 4 tetradecyl(trihexyl)phosphonium decanoate	655.11	301.00	1.967	0.885	1.741	1288.46
		372.81	2.009	0.840	1.687	1316.80
IL 5 tetradecyl(trihexyl)phosphonium dicyanamide	549.90	301.34	2.079	0.919	1.911	1143.46
		371.59	2.280	0.882	2.011	1253.97
IL 6 tetradecyl(trihexyl)phosphonium bistriflamide	764.00	301.61	1.582	1.049	1.659	1208.66
		373.04	1.748	1.006	1.758	1335.69

a Values in the table were taken from references 7 (IL 1 and 2), 8 (IL 3, 5 and 6) and 9 (IL 4). Single density measurements at 298.1 K were all that were available for IL1 and IL2. These literature values were assumed to be close to the density of the experimental ILs at the lower temperatures (~300 K) measured. For the phosphonium ILs literature values allowed a linear regression of the data to be applied giving the following equations for density. IL3 $\rho = 1.040 - 5.267 \times 10^{-4} \times T$ (K); IL4 $\rho = 0.903 - 6.34 \times 10^{-4} \times T$ (°C); IL5 $\rho = 1.077 - 5.248 \times 10^{-4} \times T$ (K); IL6 $\rho = 1.230 - 6.002 \times 10^{-4} \times T$ (K). These equations were used to calculate the density of the ILs at the experimental temperatures.



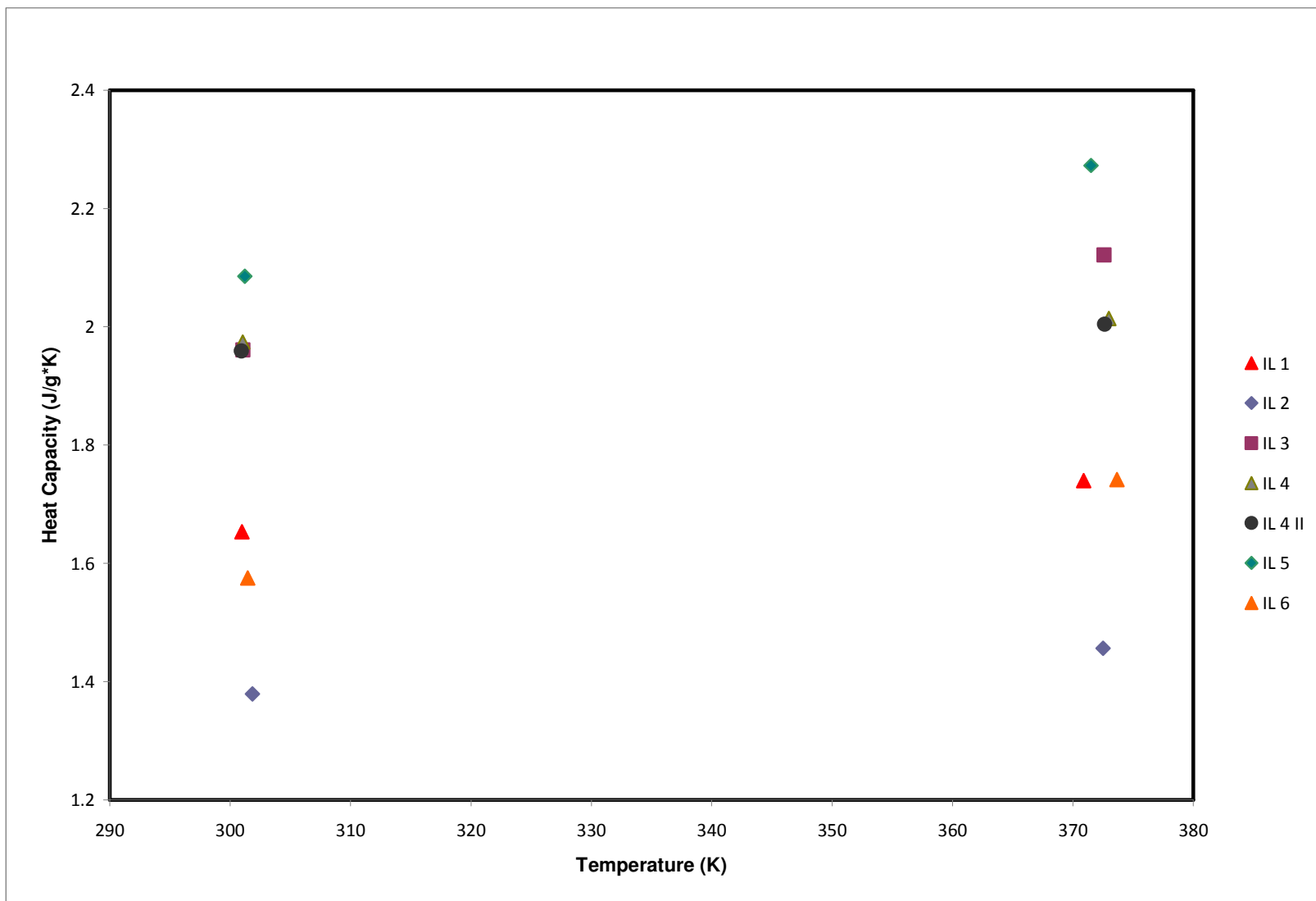


Figure S70: Temperature dependence of the specific heat of ionic liquids (data and labels as in Table S2).

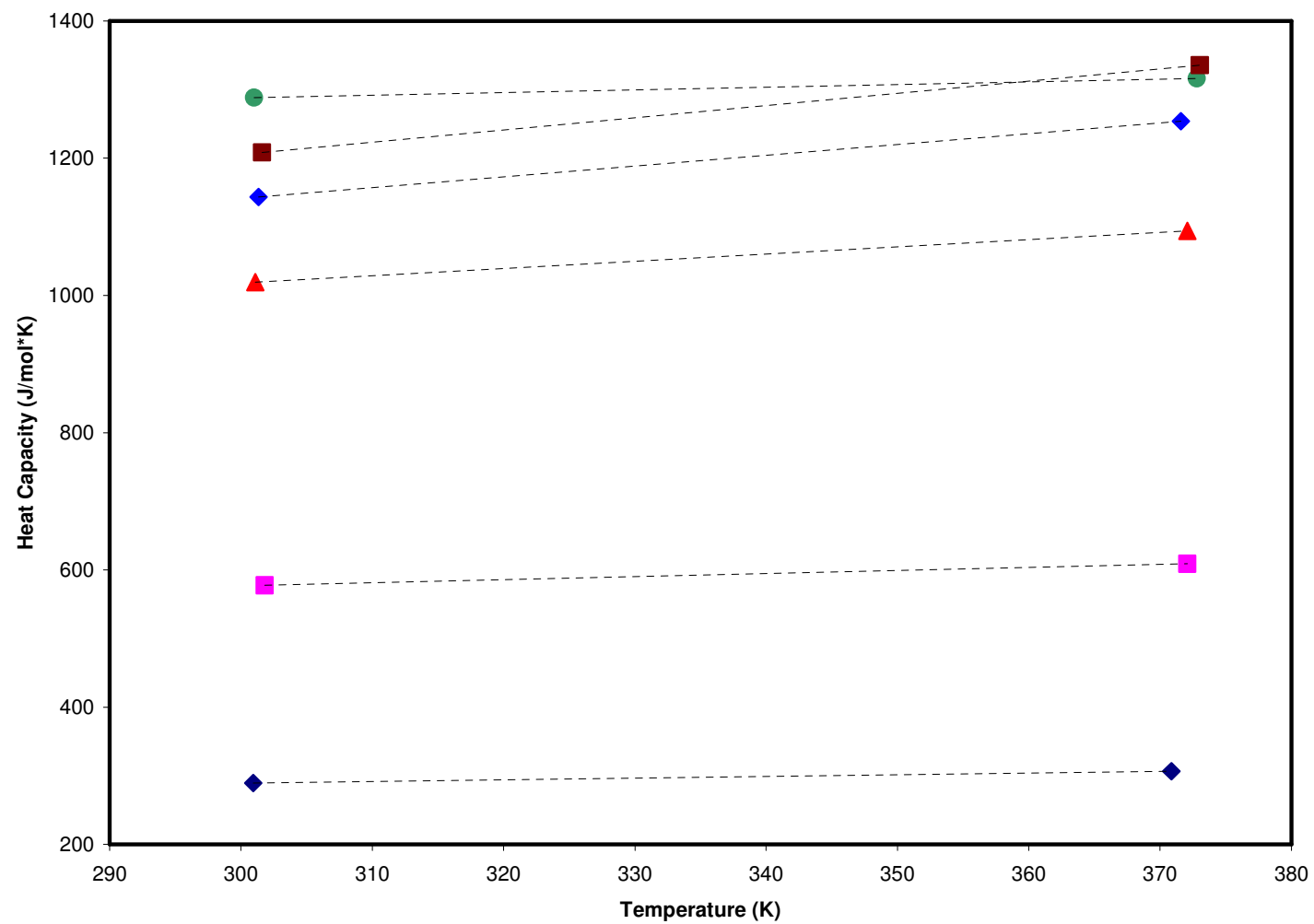


Figure S71: Temperature dependence of the molar heat capacity of ionic liquids (data and labels as in Table S2).

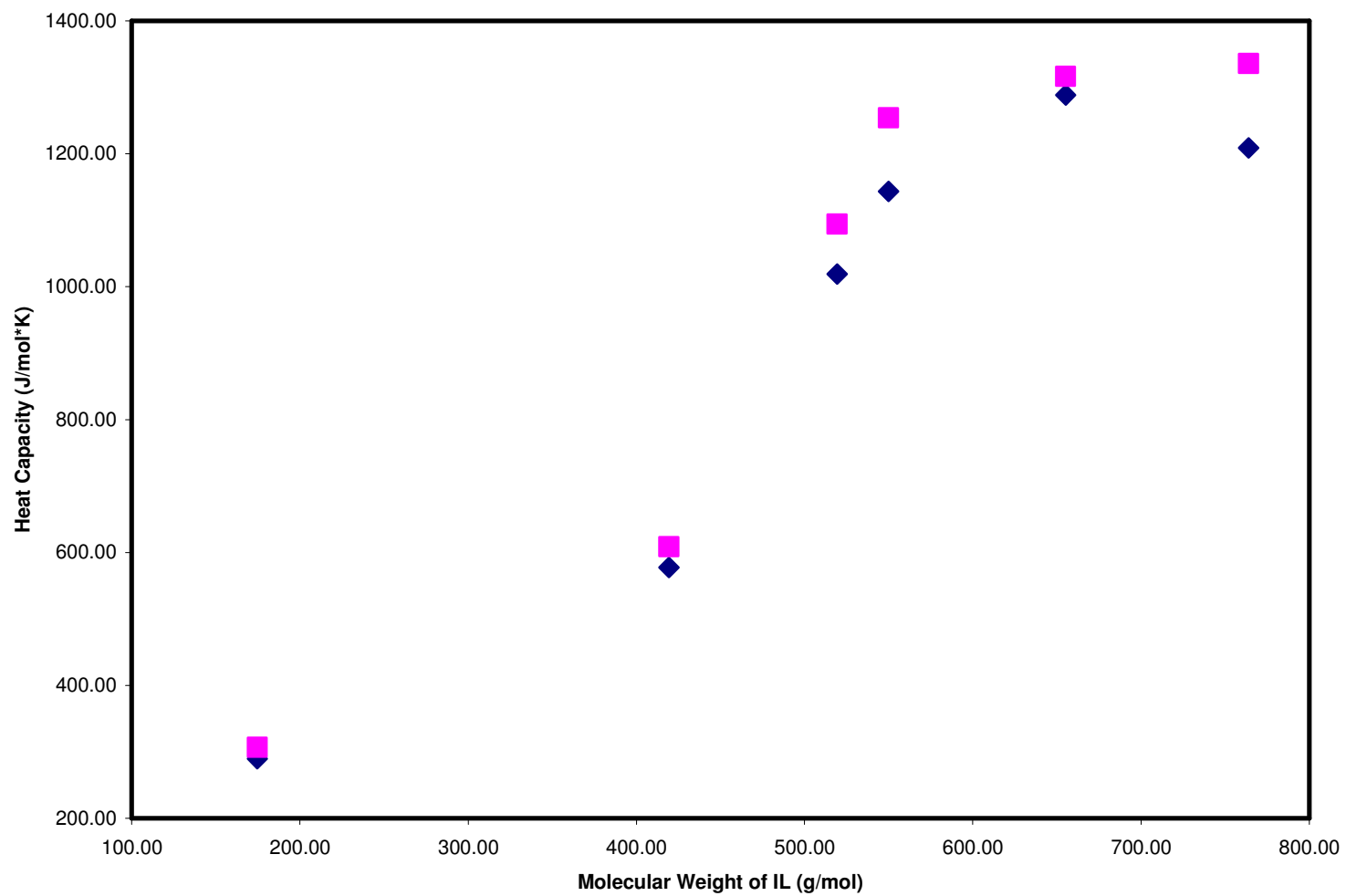


Figure S72: Dependence of the molar heat capacity of ionic liquids on their molecular weights (see Table S2 for data).

S5 – Vapour Pressure Measurements

S5.1 – Experimental

Trihexyl(tetradecyl)phosphonium chloride (IL 101) was purified by addition of sodium bicarbonate, the resulting solution was extracted four times with deionized water and once with hexanes. The hexanes were removed on a rotary evaporator and the ionic liquid was dried under suction with liquid nitrogen. The ionic liquid was then sparged with argon for 17 hours. Diethylenetriamine (DETA) was also dried under suction with liquid nitrogen and sparged with argon before addition to IL 101.

The solution to be measured was added to a three-necked round bottom flask connected to a vacuum line, a Vernier temperature probe and a Vernier pressure sensor. With light stirring the flask was evacuated and brought to equilibrium before increasing the temperature of the flask. Using LoggerPro 3.6.0 the pressure was measured as a function of temperature with one reading taken per second, the solutions were stirred continuously throughout data collection. The final results were averaged to construct Figure S71.

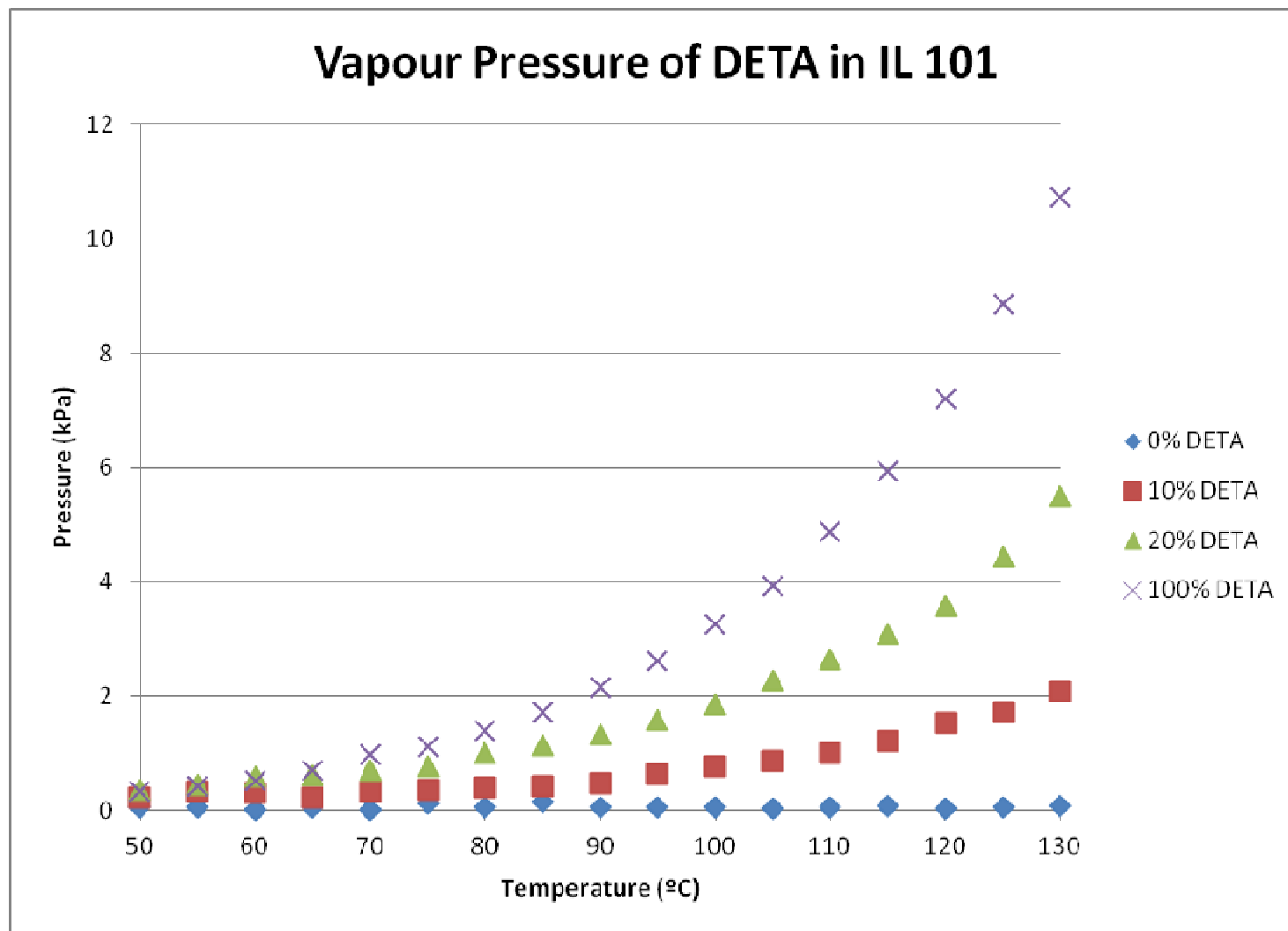


Figure S73: Vapour pressure of varying concentrations of diethylenetriamine (DETA) by volume in trihexyl(tetradecyl)phosphonium chloride (IL 101) between 50-130°C.

S6 – Carbon Dioxide Capture

S6.1 – CO₂ Capture Experimental Procedure

5, 10, and 20% fractions of diethylenetriamine (DETA) were added to 5 mL of solvent [tetradecyl(trihexyl)phosphonium chloride *OR* polyethylene glycol dimethyl ether ($M_N = \sim 250$)]. The solution was then exposed to an atmosphere of CO₂ while swirling for 3 minutes. A gooey white precipitate was found to form in the solutions upon exposure to CO₂. Overall, precipitate formation was observed to be more prevalent in the polymeric solvent solutions. After exposure to CO₂ the atmosphere in the flask was allowed to equilibrate with the atmosphere in the laboratory with the help of a Hagen Elite 802 Air Pump.

In addition, a solution containing 10% DETA, 10% H₂O, and 5 mL of solvent [tetradecyl(trihexyl)phosphonium chloride *OR* polyethylene glycol dimethyl ether ($M_N = \sim 250$)] was also tested using the above method.

Large scale reactions were also performed for 5, 10, and 20% DETA plus the 10% DETA/10% water mixture using 20 mL of solvent and the above described process.

S6.2 – CO₂ Capture Results

Table S3: CO₂ capture results.

SAMPLE	Solvent: IL101 or PEG		DETA		H ₂ O		AMOUNT CO ₂ BOUND*		MOLE RATIO CO ₂ : DETA
	g	mmol	g	mmol	g	mmol	g	mmol	
5% DETA									
IL 101 + DETA	4.45	8.57	0.26	2.52	-----	-----	0.07	1.59	0.63 : 1
IL 101 + DETA	4.63	8.92	0.25	2.42	-----	-----	0.06	1.36	0.56 : 1
IL 101 + DETA	4.55	8.76	0.25	2.42	-----	-----	0.08	1.82	0.75 : 1
PEG + DETA	5.35	-----	0.26	2.52	-----	-----	0.18	4.09	1.62 : 1
PEG + DETA	5.32	-----	0.25	2.42	-----	-----	0.15	3.41	1.41 : 1
PEG + DETA	5.50	-----	0.24	2.33	-----	-----	0.16	3.64	1.56 : 1
10% DETA									
IL 101 + DETA	4.68	9.01	0.47	4.56	-----	-----	0.08	1.82	0.40 : 1
IL 101 + DETA	4.65	8.95	0.47	4.56	-----	-----	0.07	1.59	0.35 : 1
IL 101 + DETA	4.53	8.72	0.47	4.56	-----	-----	0.07	1.59	0.35 : 1
PEG + DETA	5.38	-----	0.49	4.75	-----	-----	0.25	5.68	1.20 : 1
PEG + DETA	5.32	-----	0.50	4.85	-----	-----	0.24	5.45	1.12 : 1
PEG + DETA	5.29	-----	0.50	4.85	-----	-----	0.25	5.68	1.17 : 1
20% DETA									
IL 101 + DETA	3.90	7.51	0.96	9.31	-----	-----	0.08	1.82	0.20 : 1
IL 101 + DETA	4.11	7.91	0.96	9.31	-----	-----	0.09	2.05	0.22 : 1
IL 101 + DETA	4.56	8.78	0.95	9.21	-----	-----	0.07	1.59	0.17 : 1
PEG + DETA	5.33	-----	0.95	9.21	-----	-----	0.14	3.18	0.35 : 1
PEG + DETA	5.30	-----	0.94	9.11	-----	-----	0.20	4.54	0.50 : 1
PEG + DETA	5.26	-----	1.03	9.98	-----	-----	0.16	3.64	0.36 : 1
10% DETA + 10% Water									
IL 101 + DETA + H ₂ O	4.59	8.84	0.48	4.65	0.48	26.64	0.03	0.68	0.15 : 1
IL 101 + DETA + H ₂ O	4.62	8.90	0.45	4.36	0.49	27.20	0.03	0.68	0.16 : 1
IL 101 + DETA + H ₂ O	4.58	8.82	0.45	4.36	0.51	28.31	0.02	0.45	0.10 : 1
PEG + DETA + H ₂ O	5.30	-----	0.50	4.85	0.46	25.53	0.16	3.64	0.75 : 1
PEG + DETA + H ₂ O	5.25	-----	0.50	4.85	0.47	26.09	0.15	3.41	0.70 : 1
PEG + DETA + H ₂ O	5.36	-----	0.49	4.75	0.48	26.64	0.16	3.64	0.77 : 1

* Exposure to CO₂ lasted for 3 minutes at ambient temperature and pressure.

Table S4: CO₂ capture results for large scale reactions.

SAMPLE	Solvent: IL101 or PEG		DETA		H ₂ O		AMOUNT CO ₂ BOUND*		MOLE RATIO CO ₂ : DETA
	g	mmol	g	mmol	g	mmol	g	mmol	
5% DETA									
IL 101 + DETA	18.28	35.20	1.17	11.34	-----	-----	0.28	6.36	0.56 : 1
PEG + DETA	21.03	-----	1.14	11.05	-----	-----	0.54	12.27	1.11 : 1
10% DETA									
IL 101 + DETA	18.25	35.14	2.05	19.87	-----	-----	0.37	8.41	0.42 : 1
PEG + DETA	20.50	-----	2.02	19.58	-----	-----	0.85	19.31	0.99 : 1
20% DETA									
IL 101 + DETA	18.27	35.18	3.94	38.19	-----	-----	0.35	7.95	0.21 : 1
PEG + DETA	20.60	-----	3.87	37.51	-----	-----	0.59	13.41	0.36 : 1
10% DETA + 10% Water									
IL 101 + DETA + H ₂ O	18.32	35.28	2.04	19.77	2.17	120.46	0.27	6.14	0.31 : 1
PEG + DETA + H ₂ O	20.40	-----	2.03	19.68	2.16	119.90	0.72	16.36	0.83 : 1

* Exposure to CO₂ lasted for 3 minutes at ambient temperature and pressure.

S6.3 – DETA-CO₂ Adduct Formation and Data

A mixture of 10% DETA in tetradecyl(trihexyl)phosphonium chloride was prepared and exposed to pure CO₂ for one minute, forming a gooey white precipitate. The flask was then heated in the microwave, capped and left sealed for over a week. The DETA/ionic liquid mixture was found to precipitate white, plate-like crystals upon being left sealed under an atmosphere of CO₂. The DETA-CO₂ adduct once isolated was found to be extremely hygroscopic and temperature sensitive. Thermogravimetric studies (**Figure S70**) indicated that the adduct has an onset of decomposition temperature of 82°C (corresponding to 5% mass loss at a heating rate of 5°C/min in a nitrogen atmosphere). Furthermore, mass spectrometry demonstrated that the adduct releases CO₂ between the temperatures of 75 and 145°C (**Figure S71**). The crystal structure of the adduct was obtained and is shown in **Figure S72**. Mp: 132-136°C. Analysis: found for C₅H₁₃N₃O₂: C 39.88, H 9.75, N 27.96; calc.: C 40.80, H 8.90, N 28.55. IR: 3361 (m, N–H stretch), 3248 (m, N–H stretch), 1649 (m, C=O stretch), 1572 (m, N–H bend).

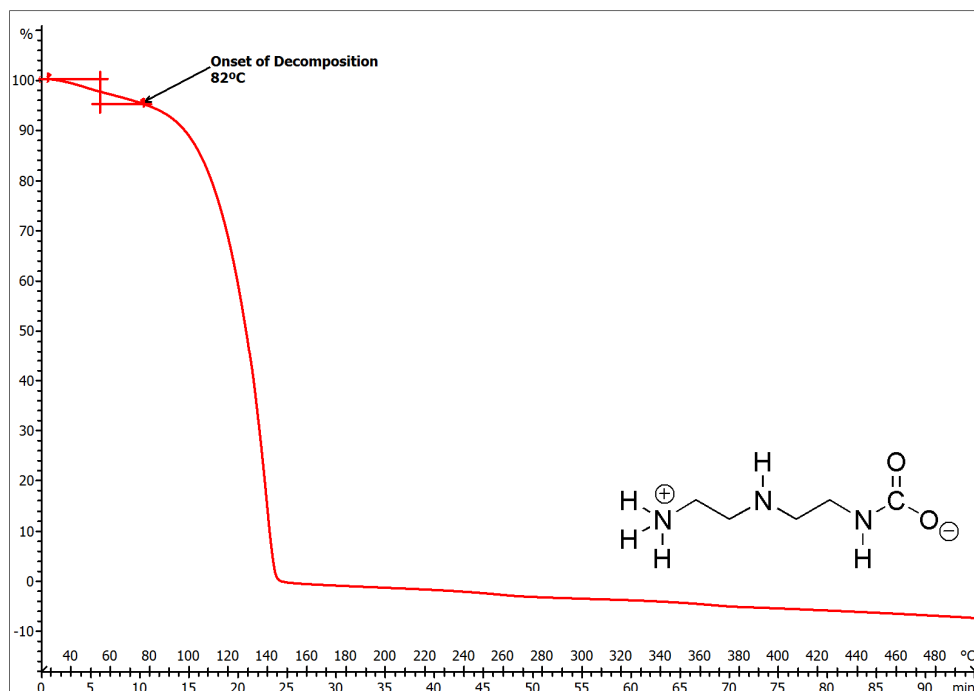


Figure S74: Decomposition curve of the DETA-CO₂ adduct in a nitrogen atmosphere when heated at 5°C/min.

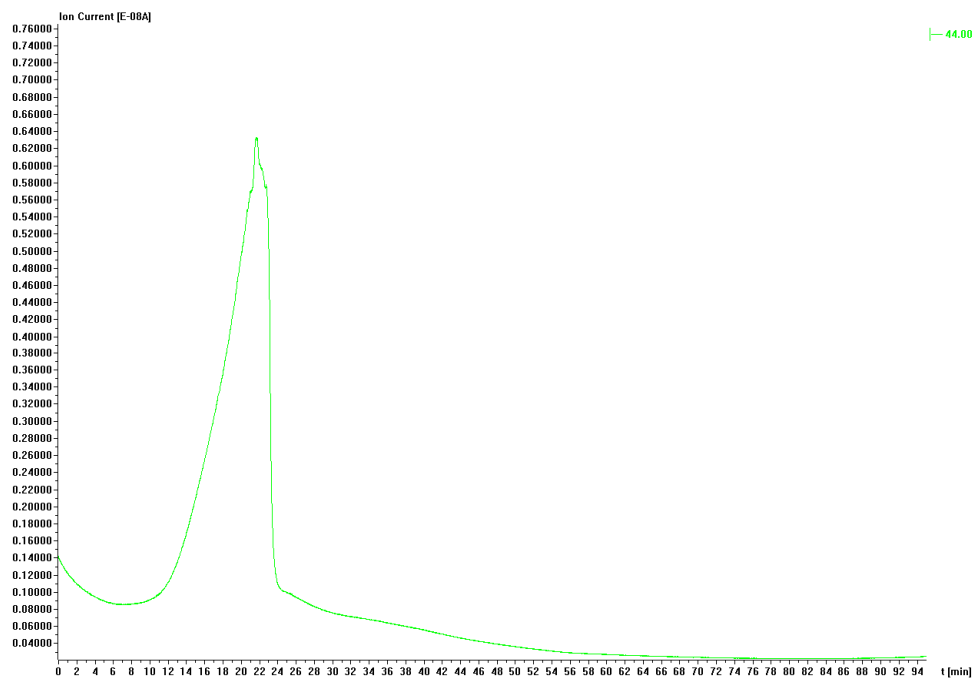


Figure S75: TGA- mass spectrometry scan of DETA-CO₂ adduct showing release of carbon dioxide during TGA decomposition scan.

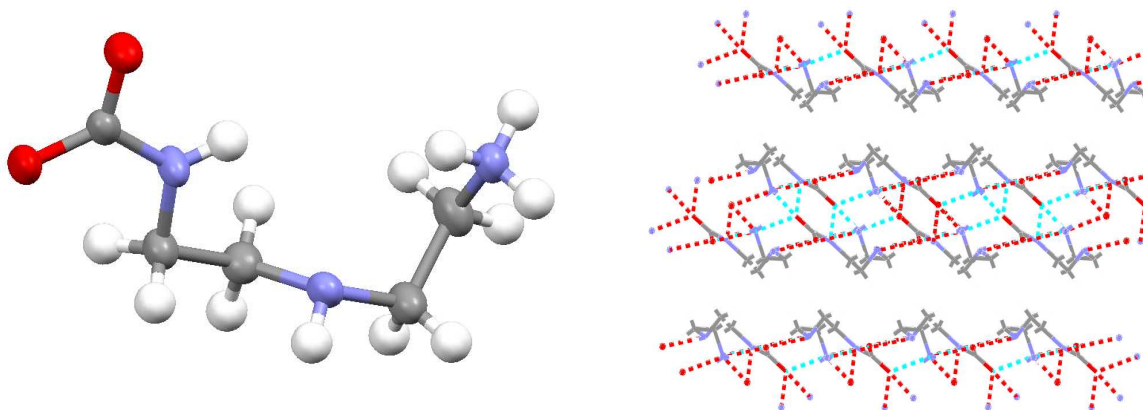


Figure S76: Molecular structure (left) and packing diagram (right) of the DETA-CO₂ adduct.

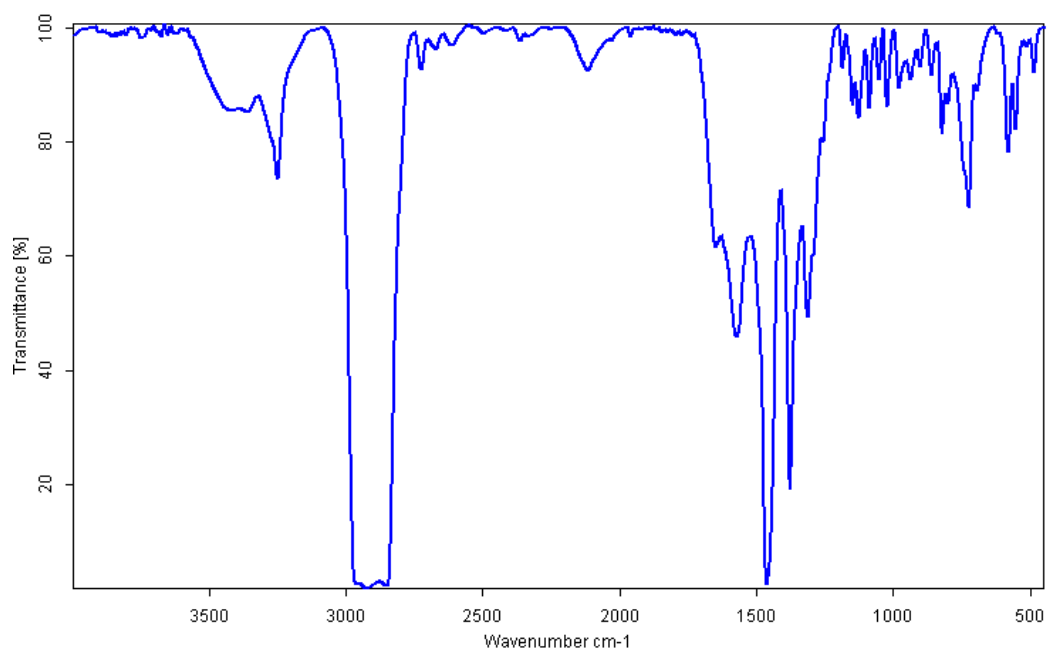


Figure S77: Infrared spectrum of the DETA-CO₂ adduct.

S7 – Theoretical Calculations

S7.1 – Experimental

Calculations were performed using Gaussian 03,¹⁰ using a stepping stone approach in which the geometries at the levels HF/STO-3G, HF/3-21G, HF/6-31G*, HF/6-31+G*, MP2/6-31G* and MP2/6-31+G* were sequentially optimized using default specifications. After each level, a frequency calculation was performed to verify the nature of the stationary point. Z-matrix coordinates constrained to the appropriate symmetry were used for efficiency, as any problems would manifest themselves by an imaginary mode orthogonal to the spanned Z-matrix space. The Hessian was also evaluated at the starting STO-3G geometry to aid convergence.

S7.2 – Summary

Some calculations were carried out on simple model systems to get accurate HF/STO-3G geometries to start more complex calculations with. We found: **NH₃**, $r(\text{N-H}) = 1.032 \text{ \AA}$; **CO₂**, $r(\text{C=O}) = 1.188 \text{ \AA}$; **NH₂CH₃**, $r(\text{N-C}) = 1.486 \text{ \AA}$, $r(\text{N-H}) = 1.033 \text{ \AA}$, $r(\text{C-H}) = 1.09 \text{ \AA}$; **NH(CH₃)₂**, $r(\text{N-C}) = 1.484 \text{ \AA}$, $r(\text{N-H}) = 1.034 \text{ \AA}$; **HCO₂H**, $r(\text{C=O})=1.214 \text{ \AA}$, $r(\text{C-O})=1.386 \text{ \AA}$, $r(\text{O-H})=0.990 \text{ \AA}$; **NH₄⁺**, $r(\text{N-H}) = 1.043 \text{ \AA}$; **NH₃CH₃⁺**, $r(\text{N-C}) = 1.528 \text{ \AA}$, $r(\text{N-H}) = 1.048 \text{ \AA}$; **NH₂(CH₃)₂⁺**, $r(\text{N-C}) = 1.525 \text{ \AA}$, $r(\text{N-H}) = 1.042 \text{ \AA}$; **HCO₂⁻**, $r(\text{C-O})=1.266 \text{ \AA}$;

NH₂CO₂⁻, $r(\text{N-H}) = 1.037 \text{ \AA}$; $r(\text{N-C}) = 1.561 \text{ \AA}$, $r(\text{C-O})=1.258 \text{ \AA}$. The amine hydrogens of the carbamate ion lay out of the NCO₂ plane.

A more complicated model system we examined was diethylamine. We examined three different C_s structures and five different C_1 structures. Of the C_s structures, only one was a local minimum (#1), and two of the C_1 structures are derived from the unstable C_s structures. Of the six stable structures, the energy ranking was as follows: $C_s \text{ \#1} < C_1 \text{ \#5} < C_1 \text{ \#4} < C_1 \text{ \#6} < C_1 \text{ \#3} < C_1 \text{ \#2}$. The three lowest energy forms feature at least one trans C-C-N-C arrangement. To simplify the following conformational possibilities, we assume that the CCNCC fragment is arranged in an all-trans fashion.

Table S5: Energy (kJ/mol) of diethylamine relative to most stable conformer (C_s #1).

	HF/6-31G*	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
$C_s \text{ \#2}$	18.41	19.38	16.21	18.39
$C_s \text{ \#3}$	16.86	16.43	14.20	13.86
$C_1 \text{ \#2}$	17.74	18.48	15.18	16.70
$C_1 \text{ \#3}$	15.41	15.04	12.54	11.85
$C_1 \text{ \#4}$	6.07	6.51	4.55	5.52
$C_1 \text{ \#5}$	5.17	4.91	3.77	3.35
$C_1 \text{ \#6}$	11.71	11.97	8.49	8.63

The next system we investigated was the reactant itself, diethylenetriamine. We looked at nine different minimum-energy C_s systems. The energy ranking was $6 < 5,7,9 < 4 < 1,2,3 < 8$.

Table S6: Energy (kJ/mol) of diethylenetriamine relative to most stable conformer (C_s #6).

	HF/6-31G*	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
C_s #1	10.11	9.24	14.86	15.90
C_s #2	9.84	7.87	17.96	15.72
C_s #3	9.15	8.02	17.16	15.90
C_s #4	12.73	11.76	12.22	12.77
C_s #5	6.88	5.05	6.21	3.71
C_s #7	2.00	3.48	0.16	4.34
C_s #8	2.88	28.19	31.44	
C_s #9	2.29	2.05	2.05	1.57

Reaction of diethylenetriamine with carbon dioxide in the gas phase can give one of two possible carbamic acids. For end substitution, we examined four possible structures varying in the placement and orientation of the carboxyl group. The C_1 #2 structure was the most stable of the four. For middle substitution, neither of the two C_s structures was a minimum, and upon relaxing symmetry a major conformational change took place to give the C_1 structure.

Table S7: Energy (kJ/mol) of diethylenetriamine+CO₂ products relative to most stable conformer (end- C_1 #2).

DETA + CO ₂		HF/6-31G*	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
NHEtNH ₂ EtNHCOOH	C_1 #1	6.51	6.55	5.29	5.20
NHEtNH ₂ EtNHCOOH	C_1 #2*	-17.98	-18.64	-10.98	-18.38
NHEtNH ₂ EtNHCOOH	C_1 #3	10.26	10.39	10.80	11.09
NHEtNH ₂ EtNHCOOH	C_1 #4	5.18	5.59	5.92	6.68
NCOOH(EtNH ₂) ₂	C_s #1	96.63	99.68	75.88	75.73
NCOOH(EtNH ₂) ₂	C_s #2	88.74	92.05	67.67	68.72
NCOOH(EtNH ₂) ₂	C_1 #1	20.08	20.60	5.20	4.43

*relative to DETA + CO₂

We also tried calculations on three zwitterionic forms of the carbamic acid (labeled $\text{NHEtNH}_3^+\text{NHCOO}^-$ (ZW1), $\text{NH}_2\text{EtNH}_2^+\text{EtNHCOO}^-$ (ZW2), and $\text{NCOO}^-\text{EtNH}_2\text{EtNH}_3^+$ (ZW3). ZW1 and ZW3 were not stable at the three lowest levels of theory, undergoing either a proton transfer from N to O, or a proton transfer from N to N(COO) with elimination of CO_2 . ZW2 also underwent elimination at HF/STO-3G and proton transfer at the MP2 levels, but was stabilized enough at the other HF levels by hydrogen bonding to remain zwitterionic. The natural amino acids are also neutral in the gas-phase, becoming zwitterionic only in the solution or solid state.

Attempts to optimize the zwitterionic forms in solution were plagued by geometry convergence difficulties and by unexplained job terminations.

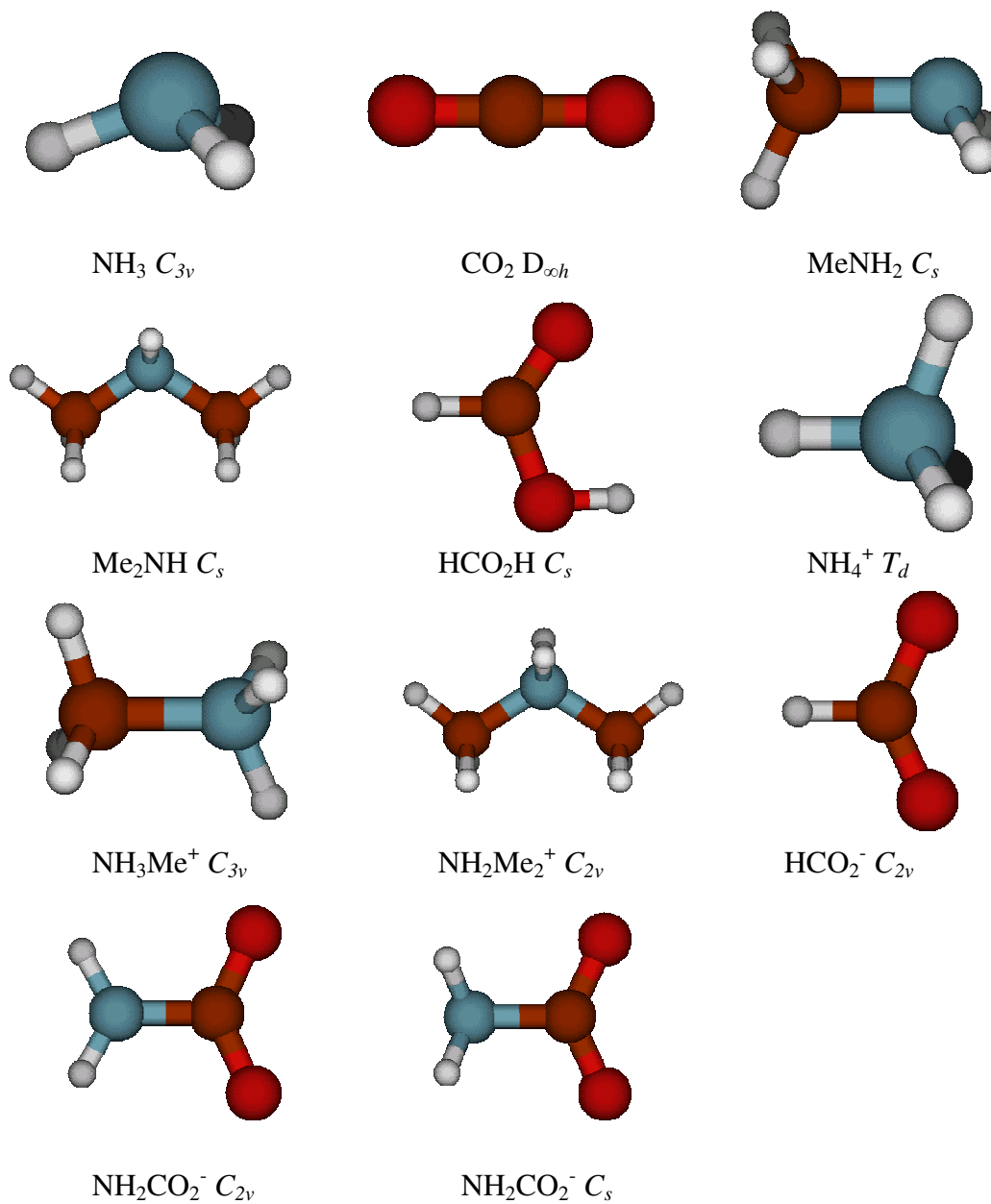


Figure S78: Structures of some model systems.

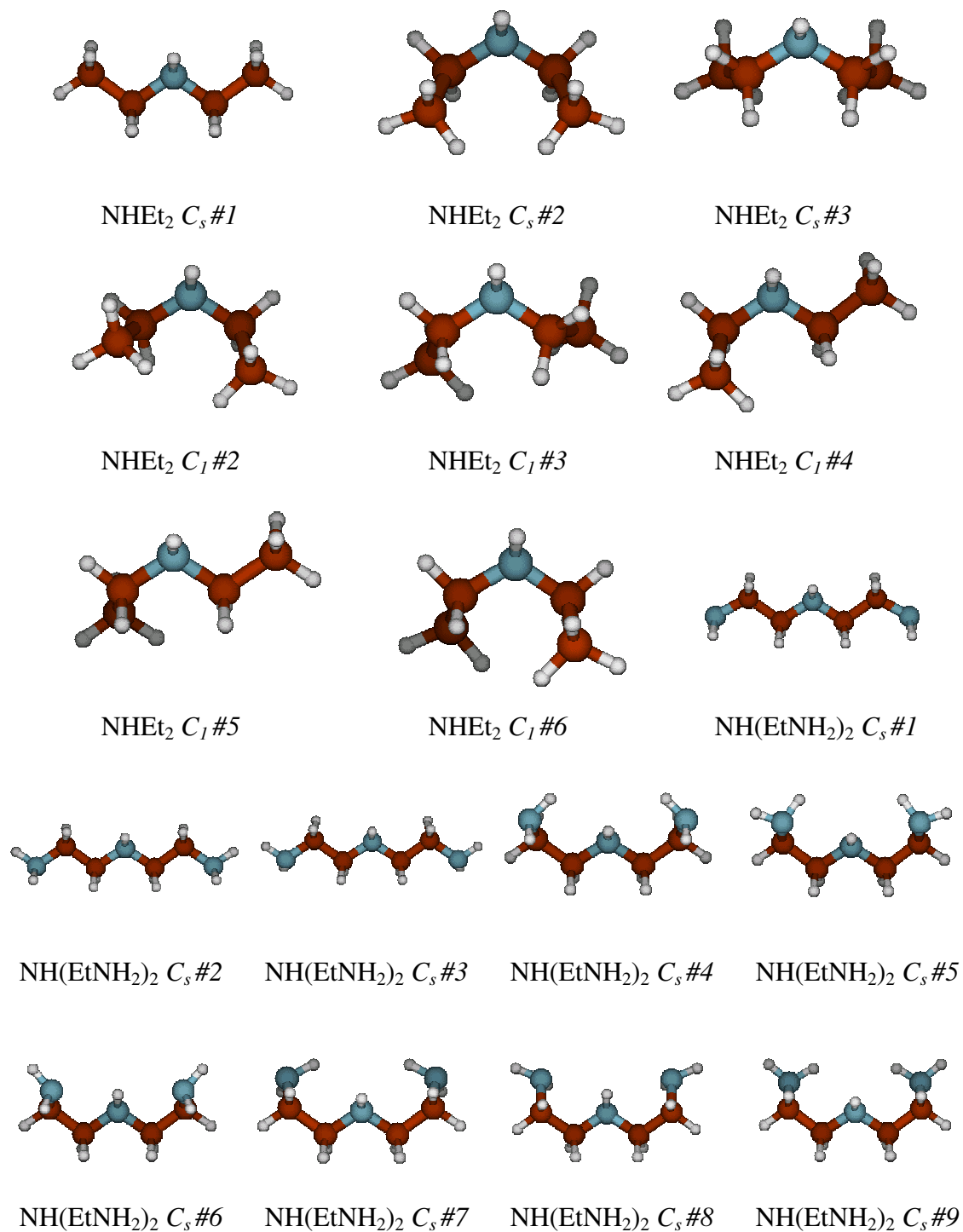


Figure S79: Structures of some model systems (continued).

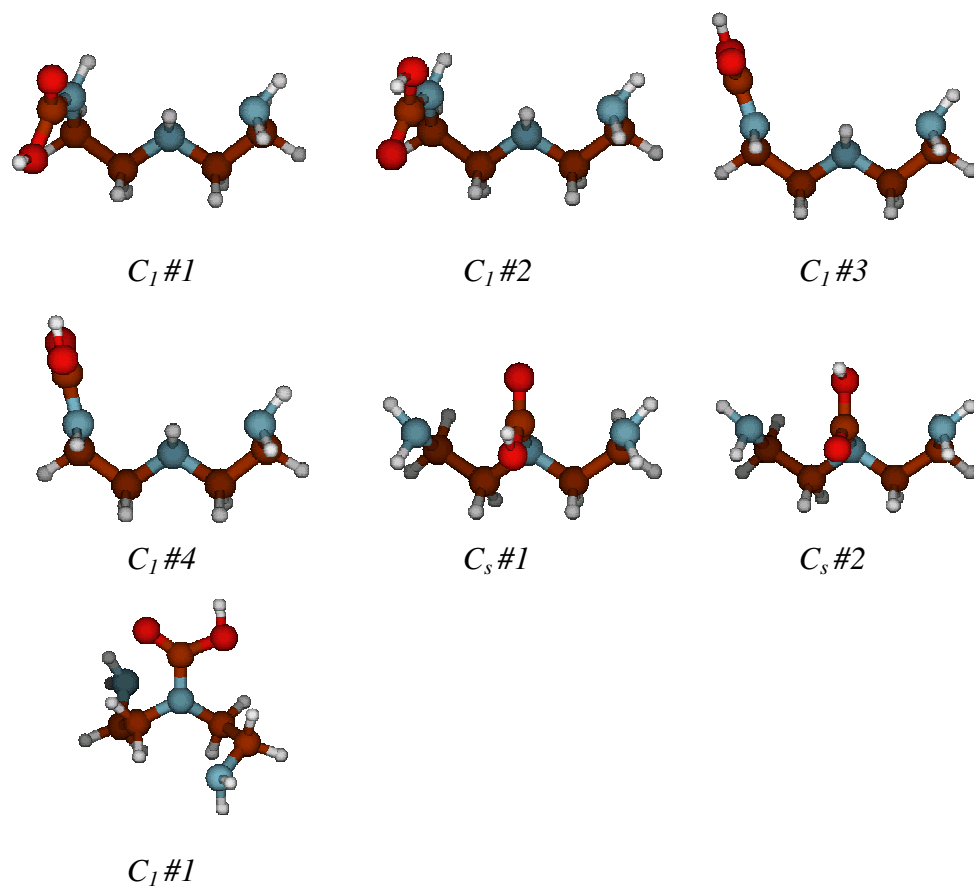


Figure S80: Structures of some products.

Table S8: Energies of simple model systems.

Species	Symmetry	HF/STO-3G	HF/3-21G	HF/6-31G*
NH ₃	C _{3v}	-55.4554198	-55.8722035	-56.1843563
CO ₂	D _{∞h}	-185.0683996	-186.5612575	-187.6341762
NH ₂ CH ₃	C _s	-94.0328628	-94.6816559	-95.2098286
NH(CH ₃) ₂	C _s	-132.6122008	-133.4948470	-134.2388500
HCO ₂ H cis	C _s	-186.2178842	-187.7001993	-188.7623096
NH ₄ ⁺	T _d	-55.8688455	-56.2338557	-56.5307714
NH ₃ CH ₃ ⁺	C _{3v}	-94.4606320	-95.0593420	-95.5734914
NH ₂ (CH ₃) ₂ ⁺	C _{2v}	-133.0500244	-133.8829448	-134.6135310
HCO ₂ ⁻	C _{2v}	-185.4562771	-187.1046323	-188.1826260
NH ₂ CO ₂ ⁻	C _{2v}	-239.7916370	-241.8553137	-243.2322591
NH ₂ CO ₂ ⁻	C _s	-239.8053450	-241.8555686	-243.2363952
NH(CH ₂ CH ₃) ₂	C _s #1	-209.7767143	-211.1382267	-212.3140471
NH(CH ₂ CH ₃) ₂	C _s #2	-209.7708747	-211.1342638	-212.3070360
NH(CH ₂ CH ₃) ₂	C _s #3	-209.7703631	-211.1329784	-212.3076244
NH(CH ₂ CH ₃) ₂	C ₁ #2	-209.7711688	-211.1342657	-212.3072899
NH(CH ₂ CH ₃) ₂	C ₁ #3	-209.7706830	C ₁ #5	-212.3081764
NH(CH ₂ CH ₃) ₂	C ₁ #4	-209.7752334	-211.1373279	-212.3117335
NH(CH ₂ CH ₃) ₂	C ₁ #5	-209.7748884	-211.1368035	-212.3120787
NH(CH ₂ CH ₃) ₂	C ₁ #6	-209.7732739	-211.1357705	-212.3095883

Species	Symmetry	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
NH ₃	C _{3v}	-56.1894994	-56.3542116	-56.3631970
CO ₂	D _{∞h}	-187.6387868	-188.1077474	-188.1179592
NH ₂ CH ₃	C _s	-95.2141732	-95.5065308	-95.5157013
NH(CH ₃) ₂	C _s	-134.2426411	-134.6652981	-143.6748241
HCO ₂ H cis	C _s	-188.7691846	-189.2417803	-189.2567555
NH ₄ ⁺	T _d	-56.5312766	-56.7002940	-56.7011658
NH ₃ CH ₃ ⁺	C _{3v}	-95.5741592	-95.8682030	-95.8700818
NH ₂ (CH ₃) ₂ ⁺	C _{2v}	-134.6142656	-135.0366835	-135.0397809
HCO ₂ ⁻	C _{2v}	-188.2081943	-188.6679746	-188.7113798
NH ₂ CO ₂ ⁻	C _{2v}	-243.2605079	-243.8730120	-243.9231848
NH ₂ CO ₂ ⁻	C _s	-243.2635263	-243.8792646	-243.9277683
NH(CH ₂ CH ₃) ₂	C _s #1	-212.3183927	-213.0027802	-213.0154753
NH(CH ₂ CH ₃) ₂	C _s #2	-212.3110114	-212.9966054	-213.0084698
NH(CH ₂ CH ₃) ₂	C _s #3	-212.3121330	-212.9973706	-213.0101959
NH(CH ₂ CH ₃) ₂	C ₁ #2	-212.3113533	-212.9969977	-213.0091133
NH(CH ₂ CH ₃) ₂	C ₁ #3	-212.3126628	-212.9980028	-213.0109630
NH(CH ₂ CH ₃) ₂	C ₁ #4	-212.3159128	-213.0010461	-213.0133737
NH(CH ₂ CH ₃) ₂	C ₁ #5	-212.3165216	-213.0013443	-213.0142008
NH(CH ₂ CH ₃) ₂	C ₁ #6	-212.3138323	-212.9995475	-213.0121873

Table S9: Energies of reactants and products.

Species	Symmetry	HF/STO-3G	HF/3-21G	HF/6-31G*
NH(EtNH ₂) ₂	C _s #1	-318.3944807	-320.5598431	-322.3510424
NH(EtNH ₂) ₂	C _s #2	-318.3933275	-320.5590610	-322.3511459
NH(EtNH ₂) ₂	C _s #3	-318.3946421	-320.5594011	-322.3514084
NH(EtNH ₂) ₂	C _s #4	-318.3923002	-320.5593075	-322.3500419
NH(EtNH ₂) ₂	C _s #5	-318.3940012	C _s #6	-322.3522727
NH(EtNH ₂) ₂	C _s #6	-318.3959597	-320.5648457	-322.3548922
NH(EtNH ₂) ₂	C _s #7	-318.3991270	-320.5633690	-322.3541313
NH(EtNH ₂) ₂	C _s #8	-318.3874401	C _s #6	-322.3537944
NH(EtNH ₂) ₂	C _s #9	-318.3957963	-320.5633743	-322.3540211
NHEtNH ₂ EtNHCOOH	C ₁ #1	-503.4949483	-507.1557246	-509.9934364
NHEtNH ₂ EtNHCOOH	C ₁ #2	-503.4965926	-507.1575571	-509.9959150
NHEtNH ₂ EtNHCOOH	C ₁ #3	-503.4954064	-507.1534047	-509.9920084
NHEtNH ₂ EtNHCOOH	C ₁ #4	-503.4968635	-507.1553270	-509.9939428
NCOOH(EtNH ₂) ₂	C _s #1	-503.4819310	-507.1258108	-509.9591089
NCOOH(EtNH ₂) ₂	C _s #2	-503.4817066	-507.1248183	-509.9621149
NCOOH(EtNH ₂) ₂	C ₁ #1	-503.4820314	-507.1548382	-509.9882668

Species	Symmetry	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
NH(EtNH ₂) ₂	C _s #1	-322.3626131	-323.3631784	-323.3903256
NH(EtNH ₂) ₂	C _s #2	-322.3631319	-323.3619949	-323.3903958
NH(EtNH ₂) ₂	C _s #3	-322.3630780	-323.3622998	-323.3903253
NH(EtNH ₂) ₂	C _s #4	-322.3616504	-323.3641841	-323.3915201
NH(EtNH ₂) ₂	C _s #5	-322.3642089	-323.3664703	-323.3949696
NH(EtNH ₂) ₂	C _s #6	-322.3661308	-323.3688372	-323.3963824
NH(EtNH ₂) ₂	C _s #7	-322.3648041	-323.3687763	-323.3947286

$\text{NH}(\text{EtNH}_2)_2$	C_s #8	-322.3553929	-323.3568623	C_s #7
$\text{NH}(\text{EtNH}_2)_2$	C_s #9	-322.3653485	-323.3680578	-323.3957826
$\text{NHEtNH}_2\text{EtNHCOOH}$	C_1 #1	-510.0095213	-511.4787499	-511.5193597
$\text{NHEtNH}_2\text{EtNHCOOH}$	C_1 #2	-510.0120156	-511.4807655	-511.5213416
$\text{NHEtNH}_2\text{EtNHCOOH}$	C_1 #3	-510.0080599	-511.4766516	-511.5171182
$\text{NHEtNH}_2\text{EtNHCOOH}$	C_1 #4	-510.0098854	-511.4785112	-511.5187989
$\text{NCOOH}(\text{EtNH}_2)_2$	C_s #1	-509.9740488	-511.4518659	-511.4924982
$\text{NCOOH}(\text{EtNH}_2)_2$	C_s #2	-509.9769541	-511.4549916	-511.4951691
$\text{NCOOH}(\text{EtNH}_2)_2$	C_1 #1	-510.0041704	-511.4787867	-511.5196560

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