Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for

The Addition of CO_2 to four Superbase Ionic Liquids: a DFT study

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Table S1 NAO charges for the anion alone $\mathbf{x}^-$ and in the ionic pair **x** before or after CO_2 addition x_{Ny} in respect to the notation of scheme 2. (a) $[P_{3333}]$[Benzim], (b) $[P_{3333}]$[124Triz], (c) $[P_{3333}]$[123Triz] and (d) $[P_{3333}]$[Bentriz]

	N1	N2	C2	H2	C4	C5	C6	C7	C8	C9	H6	H7	H8	H9	C*	O1	O2
a^-	-0.62	-0.62	0.21	0.14	0.09	0.09	-0.23	-0.27	-0.27	-0.23	0.18	0.17	0.17	0.18			
a^-N1	-0.52	-0.57	0.29	0.2	0.11	0.15	-0.22	-0.24	-0.24	-0.22	0.24	0.19	0.18	0.19	0.96	-0.75	-0.75
a	-0.63	-0.63	0.21	0.16	0.08	0.08	-0.24	-0.26	-0.26	-0.24	0.20	0.19	0.20	0.20			
aN1	-0.52	-0.52	0.28	0.21	0.11	0.13	-0.24	-0.21	-0.23	-0.20	0.23	0.20	0.20	0.21	0.94	-0.78	-0.75
a*N1	-0.68	-0.60	0.20	0.16	0.08	0.08	-0.24	-0.24	-0.25	-0.22	0.20	0.19	0.19	0.20	1.06	-0.54	-0.54

	N1	N2	N4	C1	C2	H1	H2	C*	O1	O2
b^-	-0.43	-0.43	-0.64	0.11	0.11	0.14	0.14			
b^-N1	-0.32	-0.31	-0.58	0.22	0.15	0.20	0.16	0.96	-0.75	-0.75
b	-0.51	-0.45	-0.58	0.14	0.15	0.16	0.17			
bN1	-0.33	-0.34	-0.54	0.25	0.19	0.21	0.18	0.95	-0.78	-0.72
b*N1	-0.48	-0.48	-0.59	0.14	0.13	0.17	0.16	1.05	-0.55	-0.50

	N1	N2	N3	C4	C5	H4	H5	C*	O1	O2
c^-	-0.39	-0.20	-0.39	-0.17	-0.17	0.16	0.16			
c^-N1	-0.30	-0.08	-0.33	-0.07	-0.13	0.22	0.18	0.96	-0.75	-0.70
c	-0.37	-0.29	-0.38	-0.11	-0.11	0.19	0.19			
cN1	-0.30	-0.16	-0.30	-0.10	-0.03	0.20	0.24	0.97	-0.79	-0.68
c*N1	-0.37	-0.28	-0.41	-0.11	-0.11	0.20	0.19	1.06	-0.56	-0.51

	N1	N2	N3	C4	C5	C6	C7	C8	C9	H6	H7	H8	H9	C*	O1	O2
d^-	-0.39	-0.12	-0.39	0.06	0.06	-0.22	-0.26	-0.26	-0.22	0.19	0.18	0.18	0.19			
d^-N1	-0.32	-0.02	-0.32	0.07	0.13	-0.21	-0.23	-0.24	-0.20	0.24	0.19	0.19	0.20	0.98	-0.75	-0.70
d	-0.39	-0.21	-0.39	0.07	0.07	-0.21	-0.23	-0.23	-0.21	0.20	0.20	0.20	0.20			
dN1	-0.31	-0.10	-0.29	0.08	0.14	-0.21	-0.2	-0.22	-0.19	0.25	0.20	0.20	0.21	0.97	-0.80	-0.69
d*N2	-0.39	-0.22	-0.39	0.06	0.07	-0.21	-0.23	-0.23	-0.20	0.20	0.20	0.20	0.20	1.05	-0.55	-0.50

Table S2 Second Order interaction Threshold 1 kcal.mol^{-1}. (a) [P_{3333}][Benzim], (b) [P_{3333}][124Triz], (c) [P_{3333}][123Triz] and (d) [P_{3333}][Bentriz]

a	17	BD (2) C 7 - N 8	/666.	BD*(1) C 19 - H 36	1.46
	86	LP (1) N 8	/666.	BD*(1) C 19 - H 36	1.57
	87	LP (1) N 9	/657.	BD*(1) C 16 - H 29	1.55
	88	LP (2) N 9	/657.	BD*(1) C 16 - H 29	3.12
b	72	LP (1) N 2	/548.	BD*(1) P 8 - C 18	5.63
	73	LP (1) N 3	/569.	BD*(1) C 15 - H 36	5.14
c	72	LP (1) N 3	/560.	BD*(1) C 12 - H 29	1.5
	73	LP (1) N 4	/171.	RY*(1) P 8	1.04
	73	LP (1) N 4	/545.	BD*(1) P 8 - C 9	1.26
	73	LP (1) N 4	/546.	BD*(1) P 8 - C 12	1.4
	73	LP (1) N 4	/547.	BD*(1) P 8 - C 15	9.77
	73	LP (1) N 4	/548.	BD*(1) P 8 - C 18	1.45
	73	LP (1) N 4	/577.	BD*(1) C 18 - H 42	1.16
	74	LP (2) N 4	/547.	BD*(1) P 8 - C 15	1.03
	75	LP (1) N 5	/578.	BD*(1) C 18 - H 43	2.3
d	15	BD (2) C 5 - N 7	/677.	BD*(1) C 24 - H 48	1.51
	86	LP (1) N 8	/668.	BD*(1) C 21 - H 41	3.34
	87	LP (1) N 9	/646.	BD*(1) P 14 - C 18	3.08
	87	LP (1) N 9	/650.	BD*(1) C 15 - H 27	1.44
	88	LP (2) N 9	/646.	BD*(1) P 14 - C 18	1.19

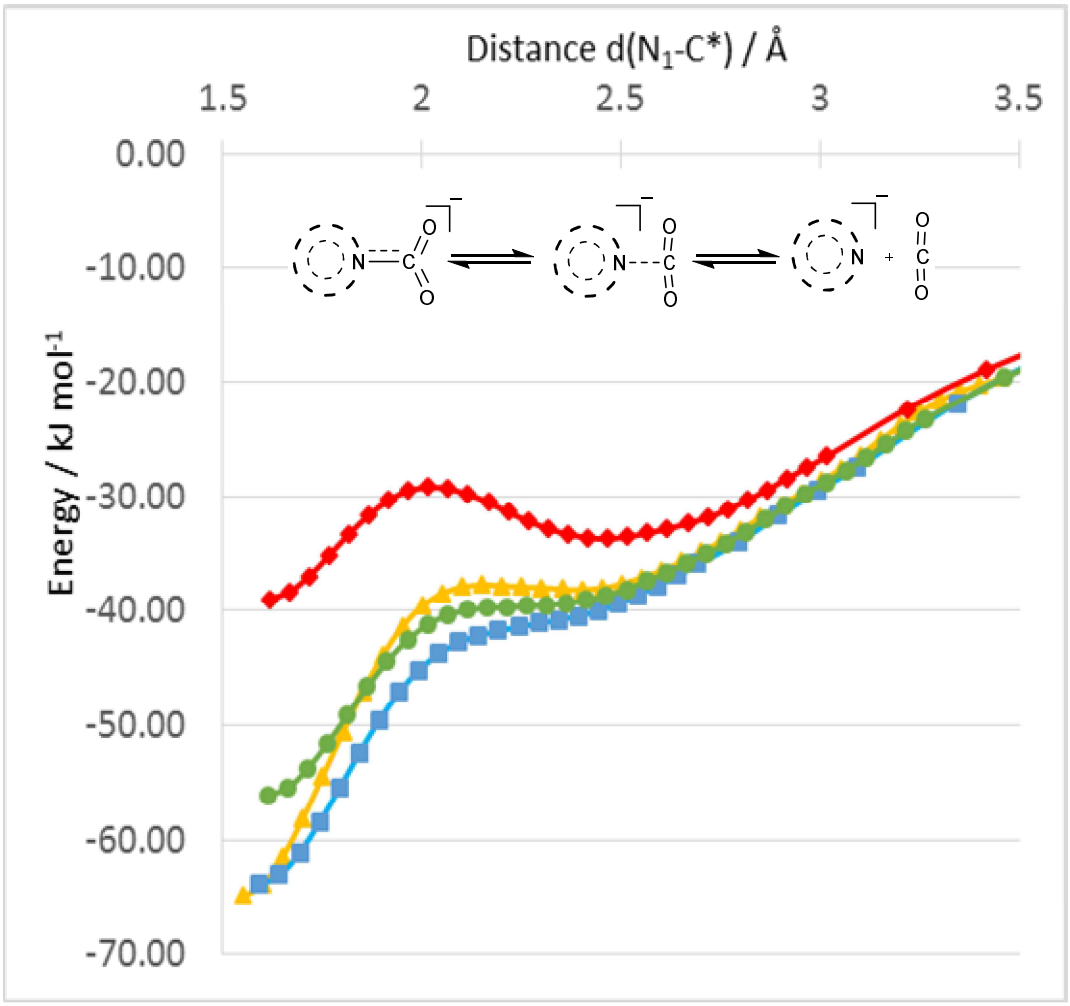

Figure S1. Relative energy profiles (without ZPE) for carbamate anion-CO_2 dissociation along the coordinate of d(Nx-C*). Colour code: $[Benzim]^-$ = Yellow triangle, $[124Triz]^-$ = blue square, $[123Triz]^-$ = green circle, $[Bentriz]^-$ = red square

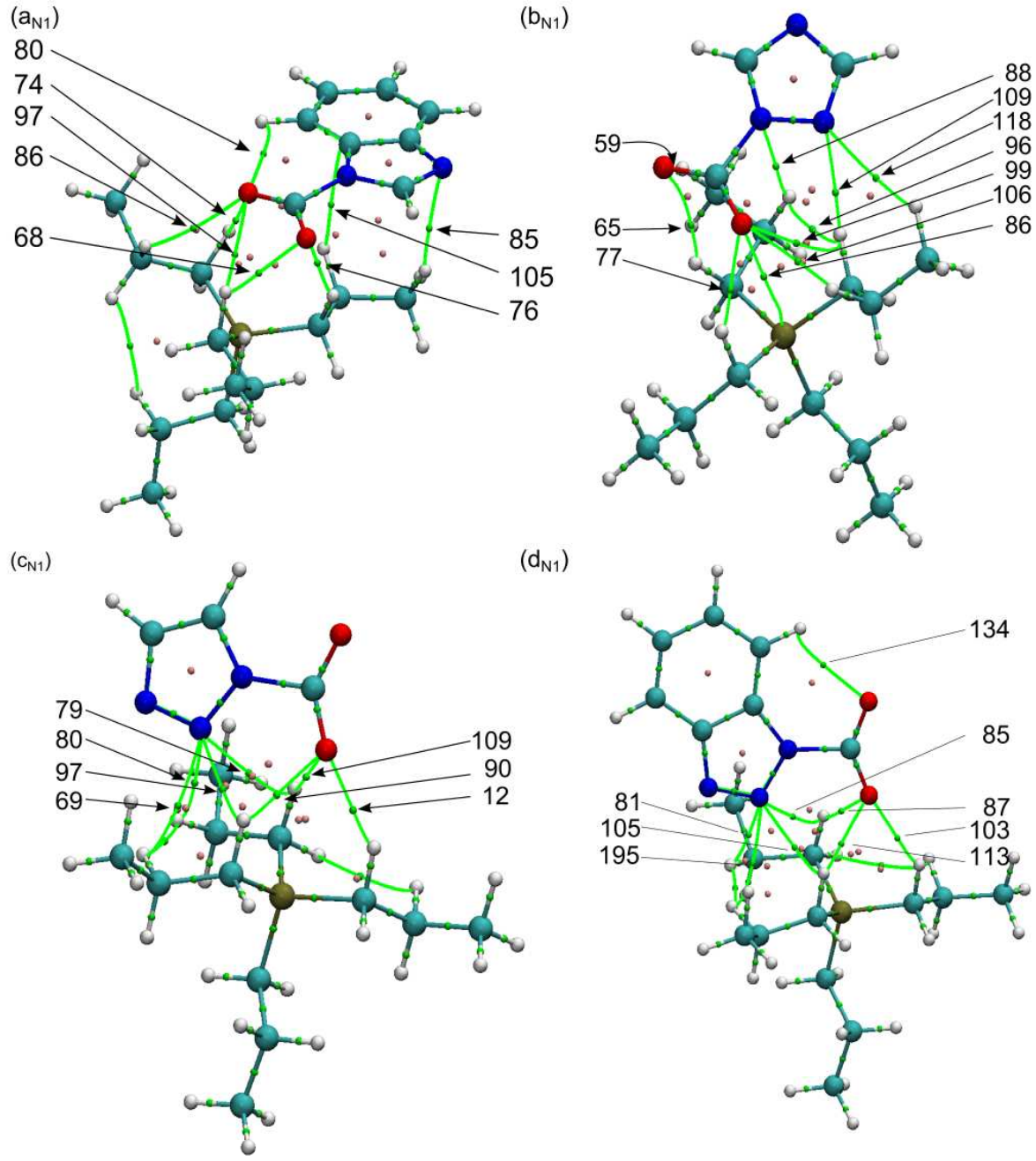

Figure. S2. AIM analysis of the most stable carbamate ionic pairs **x:** (a) [P_{3333}][Benzim], (b) [P_{3333}][124Triz], (c) [P_{3333}][123Triz] and (d) [P_{3333}][Bentriz]. Atoms are coloured N=blue, C=cyan, P=Brown, H=white, O=red. Small dots are critical points with bcp (-3,+1) = green, rcp (+3,+1) = pink. Green lines are the paths connecting atoms to bcp. Numbers are the cp labels.

Table S3. Intermolecular critical point properties from atoms in molecules (AIM) analysis for the most stable carbamate ionic pair product: electron density ρ(r), laplacian of the electron density $\nabla^2\rho(r)$ and ellipticity ε and E_{HB} Force HB. at critical point (CP). The critical point are numbering according to figure S2

	Critical Point	Nb	ρ(r) / a.u.	∇2ρ(r)/a.u.	ε	V(r) / au
a_{N1}	rcp – 5m	69	0.5769131531E-01	0.3923384533E+00	-1.298910	-0.8910353670E-01
	rcp – 6m	90	0.2221195443E-01	0.1607585231E+00	-1.208664	-0.2555020138E-01
	bcp N-HC3	85	0.7671787260E-02	0.2167028008E-01	0.570218	-0.4048629827E-02
	bcp O1-HC1	68	0.1477515045E-01	0.4995357081E-01	0.142608	-0.9219103406E-02
	bcp O1-HC1	76*	0.1136910478E-01	0.3987419439E-01	1.028569	-0.6888203143E-02
	bcp O2-HC1	74	0.1358110351E-01	0.4526221966E-01	0.259732	-0.8550180526E-02
	bcp O2-HC1	97	0.1621547356E-01	0.5775561246E-01	0.271804	-0.1061454447E-01
	bcp O2-HC2	86	0.7446079100E-02	0.2789408870E-01	2.437077	-0.4984654837E-02
	bcp O2-H6(intra)	80	0.1300263861E-01	0.4506549599E-01	0.314263	-0.8593114333E-02
b_{N1}	rcp	101	0.6490020173E-01	0.4680411130E+00	-1.309845	-0.1065052448E+00
	bcp N-HC1	109	0.1485815513E-01	0.4693568505E-01	0.049839	-0.7814222022E-02
	bcp N-HC2	88	0.8433412991E-02	0.2520033231E-01	0.396340	-0.4975139458E-02
	bcp N-HC3	118	0.5311274108E-02	0.1544133866E-01	0.346281	-0.2778193757E-02
	bcp O-HC1	77	0.1772936385E-01	0.6463921732E-01	0.217021	-0.1163633377E-01
	bcp O-HC1	99	0.1390096853E-01	0.4994604580E-01	0.811661	-0.9614981225E-02
	bcp O-HC2	106	0.9461743245E-02	0.3465599488E-01	0.569491	-0.6287087313E-02
	bcp O-P	86	0.1305160854E-01	0.3970097727E-01	0.966064	-0.9161750600E-02
	bcp O-HC1	65	0.1401811695E-01	0.5127784193E-01	1.559793	-0.8740365988E-02
	bcp O-HC3	59	0.5589204797E-02	0.1707586787E-01	0.189750	-0.3318644440E-02
c_{N1}	rcp	96	0.6025459148E-01	0.4742570636E+00	-1.286937	-0.1007236391E+00
	bcp N-HC1	79	0.1313295970E-01	0.4294443510E-01	0.162308	-0.7495674870E-02
	bcp N-HC1	97	0.9944940109E-02	0.3304146719E-01	0.412163	-0.5918918391E-02
	bcp N-HC2	69	0.7787450795E-02	0.2733590427E-01	1.271840	-0.4778911368E-02
	bcp N-HC2	80	0.1048717028E-01	0.3487613290E-01	0.169694	-0.6239077416E-02
	bcp O-HC1	90	0.1489747336E-01	0.4948018122E-01	0.066081	-0.9306566019E-02
	bcp O-HC1	112	0.1649501782E-01	0.6593464768E-01	0.125651	-0.1102290521E-01
	bcp O-HC1	109	0.1536019771E-01	0.4976760394E-01	0.084414	-0.9585948331E-02
d_{N1}	rcp – 5m	114	0.5775239775E-01	0.4525391310E+00	-1.276557	-0.9504467832E-01
	rcp – 6m	129	0.2229615702E-01	0.1621018824E+00	-1.218966	-0.2565939343E-01
	bcp N…HC1	85	0.1290532894E-01	0.4252559577E-01	0.177619	-0.7407314246E-02
	bcp N…HC2	81	0.8763037960E-02	0.3007795070E-01	0.488581	-0.5323685025E-02
	bcp N…HC1	105	0.9507537454E-02	0.3182698659E-01	0.410661	-0.5665044491E-02
	bcp N…HC2	95	0.9154775324E-02	0.3046931380E-01	0.211243	-0.5450891189E-02
	bcp O…HC1	103	0.1699677596E-01	0.6847989418E-01	0.129078	-0.1148670169E-01
	bcp O…HC1	113	0.1733129966E-01	0.5804294354E-01	0.081649	-0.1108193247E-01
	bcp O…HC1	87	0.1540817989E-01	0.5146745216E-01	0.071072	-0.9708786149E-02
	bcp O2-H6(intra)	134	0.1222149096E-01	0.4359527884E-01	0.387033	-0.8015938907E-02

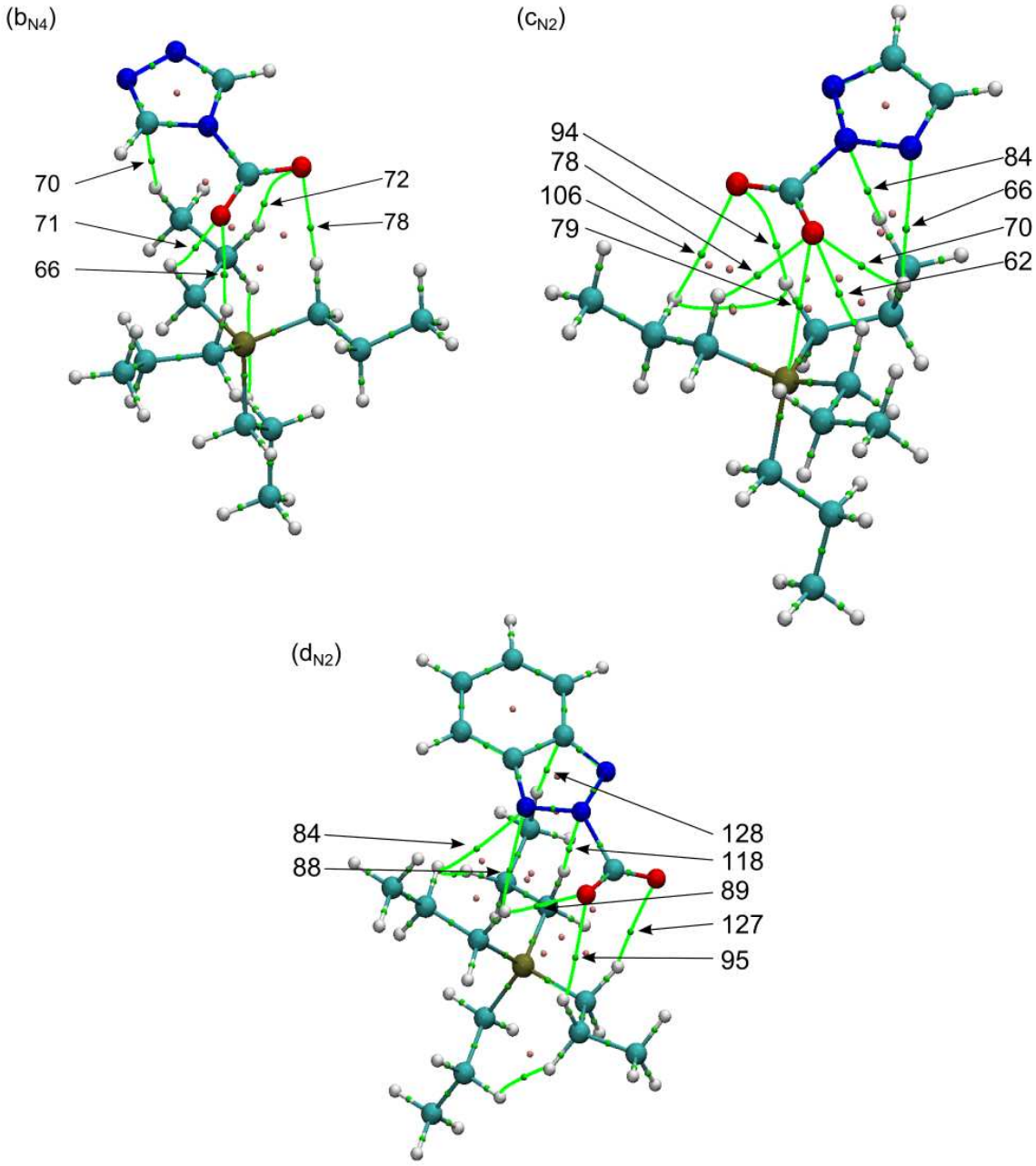

Figure S3. AIM analysis of the secondary carbamate ionic pairs **x:** (b) [P_{3333}][124Triz], (c) [P_{3333}][123Triz] and (d) [P_{3333}][Bentriz]. Atoms are coloured N=blue, C=cyan, P=Brown, H=white, O=red. Small dots are critical points with bcp (-3,+1) = green, rcp (+3,+1) = pink. Green lines are the paths connecting atoms to bcp. Numbers are the cp labels.

Table S4. Intermolecular critical points properties from atoms in molecules (AIM) analysis for the secondary carbamate ionic pair product: electron density ρ(r), laplacian of the electron density $\nabla^2\rho(r)$ and ellipticity ε and E_{HB} Force HB. at critical point (CP). The critical points are numbered according to figure S3

	Critical Point	Nb	ρ(r) / a.u.	∇2ρ(r)/a.u.	ε	V(r) / au
b_{N4}	rcp	57	0.6171964201E-01	0.4592387069E+00	-1.287914	-0.1006191071E+00
	bcp C_1-H_{C3}	70	0.6360140294E-02	0.1861514132E-01	0.959046	-0.3378634598E-02
	bcp O-H_{C1}	66	0.1778879340E-01	0.6882242870E-01	0.199864	-0.1202362853E-01
	bcp O-H_{C1}	71	0.1504427167E-01	0.4970055133E-01	0.310986	-0.9689724433E-02
	bcp O-H_{C1}	72	0.2113916836E-01	0.7327496628E-01	0.021638	-0.1355680216E-01
	bcp O-H_{C2}	78	0.8327670501E-02	0.2673723056E-01	1.265322	-0.4780673756E-02
c_{N2}	rcp	64	0.6244681267E-01	0.4725391769E+00	-1.292135	-0.1033305830E+00
	bcp N-H_{C3}	84	0.6292572455E-02	0.1984323170E-01	0.526376	-0.3905290625E-02
	bcp N-H_{C2}	66	0.8383303124E-02	0.2534321382E-01	0.067804	-0.4556891585E-02
	bcp O-P	79	0.1260350700E-01	0.3858155879E-01	1.095299	-0.8871475034E-02
	bcp O-H_{C1}	62	0.1878262890E-01	0.7659130719E-01	0.218056	-0.1308718879E-01
	bcp O-H_{C1}	78	0.1757885365E-01	0.5838959613E-01	0.214279	-0.1123955109E-01
	bcp O-H_{C1}	94	0.1309524342E-01	0.4610329665E-01	1.653763	-0.7891305529E-02
	bcp O-H_{C2}	106	0.8211272154E-02	0.2642495941E-01	0.213722	-0.5111242403E-02
d_{N2}	rcp – 5m	123	0.6129123652E-01	0.4602024925E+00	-1.311625	-0.1006103672E+00
	rcp – 6m	121	0.2209302619E-01	0.1579079834E+00	-1.223502	-0.2511390456E-01
	bcp N···H_{C1}	88	0.1218330794E-01	0.3897508940E-01	0.202707	-0.6756929098E-02
	bcp N···H_{C2}	84	0.7530861371E-02	0.2339793346E-01	0.690272	-0.4335630987E-02
	bcp N···H_{C1}	118	0.1302542933E-01	0.4395134216E-01	0.163573	-0.7727862472E-02
	bcp C···H_{C3}	128	0.6780770362E-02	0.1805055882E-01	0.486596	-0.3225198509E-02
	bcp O···H_{C1}	127	0.1445214621E-01	0.4844651995E-01	0.216896	-0.8528875299E-02
	bcp O···H_{C1}	89	0.1802472498E-01	0.6365793723E-01	0.075404	-0.1150592270E-01
	bcp O···H_{C2}	95	0.1128534757E-01	0.3685398211E-01	0.040984	-0.7025989348E-02

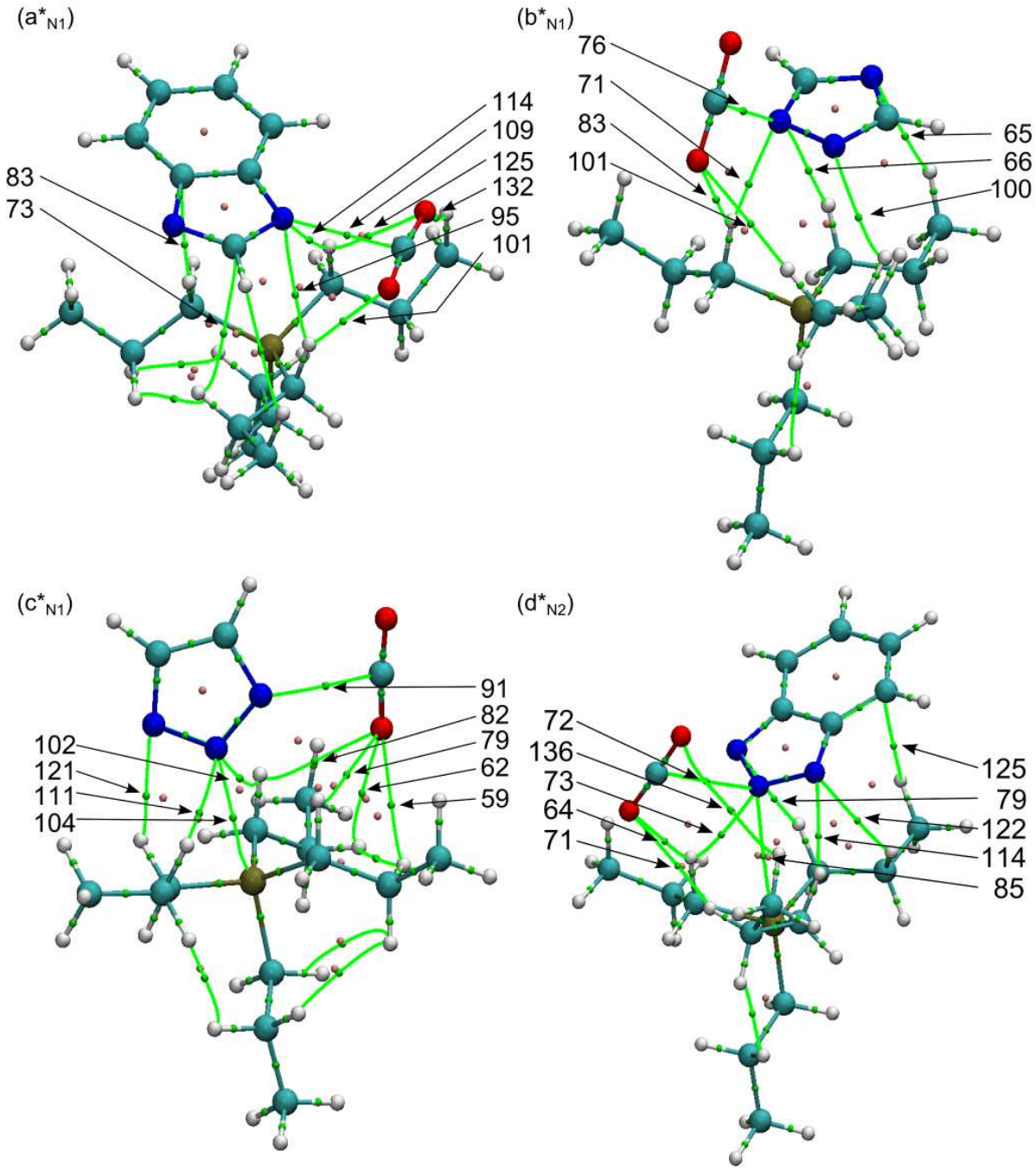

Figure S4. AIM analysis of the most stable CO_2 - ionic pair adducts **x*:** (a) [P_{3333}][Benzim], (b) [P_{3333}][124Triz], (c) [P_{3333}][123Triz] and (d) [P_{3333}][Bentriz]. Atoms are coloured N=blue, C=cyan, P=Brown, H=white, O=red. Small dots are critical points with bcp (-3,+1) = green, rcp (+3,+1) = pink. Green lines are the paths connecting atoms to bcp. Numbers are the cp labels.

Table S5. Intermolecular critical points properties from atoms in molecules (AIM) analysis for the most stable CO_2 - ionic pair adducts: electron density ρ(r), laplacian of the electron density $\nabla^2\rho(r)$ and ellipticity ε and E_{HB} Force HB. at critical point (CP). The critical points are numbered according to figure S4

	Critical Point	Nb	ρ(r) / a.u.	∇2ρ(r)/a.u.	ε	V(r) / au
$\mathbf{a}_{N1*}$	rcp – 5m	86	0.6093487220E-01	0.3957770349E+00	-1.320398	-0.9404457990E-01
	rcp – 6m	102	0.2193869818E-01	0.1574479387E+00	-1.207800	-0.2502159607E-01
	bcp N-H_{C1}	95	0.1113967791E-01	0.3022989015E-01	0.345795	-0.5809632053E-02
	bcp N-H_{C1}	114	0.1260324677E-01	0.3732610732E-01	0.227019	-0.6746264929E-02
	bcp N-C*	109	0.2027453257E-01	0.6338325762E-01	0.500004	-0.1361734743E-01
	bcp O-H_{C1}	101	0.7249507943E-02	0.2344266952E-01	0.217097	-0.4250462445E-02
	bcp O-H_{C1}	125	0.5065025096E-02	0.1726858176E-01	1.538805	-0.3129129902E-02
	bcp O-H_{C3}	132	0.7550380105E-02	0.2634821766E-01	0.034203	-0.4721232808E-02
	bcp C_2-H_{C2}	73	0.4794196705E-02	0.1524998801E-01	0.237173	-0.2415951502E-02
	bcp C_4-H_{C1}	83	0.1546932581E-01	0.5300923230E-01	3.071210	-0.9243655815E-02
$\mathbf{b}^*_{N1}$	rcp	72	0.6472595804E-01	0.4630427838E+00	-1.306227	-0.1057646870E+00
	bcp N-H_{C1}	71	0.2022953934E-01	0.6855552754E-01	0.091620	-0.1233118987E-01
	bcp N-H_{C1}	66	0.1221542389E-01	0.4283955540E-01	2.314756	-0.7199301420E-02
	bcp N-H_{C1}	100	0.1475339428E-01	0.4506105119E-01	0.041858	-0.8106661066E-02
	bcp N-H_{C3}	65	0.5472242924E-02	0.1454747211E-01	0.161518	-0.2759566499E-02
	bcp N-C*	76	0.1257837473E-01	0.4521207881E-01	0.930778	-0.8312627141E-02
	bcp O-H_{C1}	83	0.8921259310E-02	0.3174343320E-01	0.192642	-0.5560060521E-02
	bcp O-H_{C3}	101	0.4742374126E-02	0.1620906517E-01	0.095321	-0.2904902737E-02
$\mathbf{c}^*_{N1}$	rcp	113	0.6032963708E-01	0.4731719015E+00	-1.270664	-0.1007081409E+00
	bcp N···H_{C1}	121	0.1507531611E-01	0.5671364074E-01	0.419118	-0.9456877609E-02
	bcp N···H_{C1}	102	0.1677788568E-01	0.5964965239E-01	2.078819	-0.1075236145E-01
	bcp N···H_{C2}	111	0.1034695399E-01	0.3498324853E-01	1.365437	-0.6404915601E-02
	bcp N···P	104	0.2377192352E-01	0.5295431220E-01	0.215460	-0.1448848221E-01
	bcp N···C*	91	0.1627450235E-01	0.5323787992E-01	0.611640	-0.1063005570E-01
	bcp O···H_{C1}	82	0.7368098555E-02	0.2570117036E-01	0.217920	-0.4748842905E-02
	bcp O···H_{C2}	62	0.6743951429E-02	0.2624720583E-01	0.225958	-0.4501628337E-02
	bcp O···H_{C1}	79	0.5853891190E-02	0.2042310094E-01	0.664442	-0.3771605559E-02
	bcp O···H_{C2}	59	0.6340273979E-02	0.2263149480E-01	0.141531	-0.4098067184E-02
$\mathbf{d}^*_{N2}$	rcp – 5m	81	0.5890055381E-01	0.4563020395E+00	-1.285178	-0.9737571966E-01
	rcp – 6m	91	0.2227031567E-01	0.1586406312E+00	-1.219921	-0.2532093278E-01
	bcp N···H_{C1}	79	0.1200889198E-01	0.4021294171E-01	1.333201	-0.7112940947E-02
	bcp N···H_{C1}	114	0.1874644078E-01	0.6450657937E-01	0.178979	-0.1127647759E-01
	bcp N···H_{C2}	122	0.8048151265E-02	0.2251067904E-01	0.168931	-0.4423065407E-02
	bcp N···H_{C1}	73	0.1622971416E-01	0.5520779682E-01	0.069346	-0.9798200854E-02
	bcp N···P	85	0.1070135940E-01	0.3286762156E-01	5.782675	-0.6841335002E-02
	bcp C···H_{C3}	125	0.5153762887E-02	0.1364713563E-01	1.047250	-0.2462734773E-02
	bcp O···H_{C1}	64	0.8419431634E-02	0.2964362679E-01	0.071271	-0.5162610801E-02
	bcp O···H_{C2}	71	0.5172485516E-02	0.1671537787E-01	0.048408	-0.3145547695E-02
	bcp O···H_{C3}	136	0.1582497605E-02	0.6799119231E-02	0.817743	-0.8188864642E-03