Gas Phase Spectroscopic Signatures of Carboxylate-Li^+ Contact Ion Pairs: New Benchmarks For Characterizing Ion Pairing in Solution

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Supporting information

1. Experimental methods

Sample preparation

In order to form (Li^+, PA^-), (Li^+, BA^-), or (Li^+, PB^-) ion pairs, the appropriate acid (phenylacetic acid, benzylacetic acid, or phenylbutyric acid respectively) and lithium hydroxide are first mixed in a solution. A slight excess of lithium hydroxide is used, which leads to a basic pH. Graphite is then added to reach a 4:1 molar ratio of the graphite:salt mixture. The mass for each reagent is calculated in order to obtain 25 mg of salt. The solution is left until complete evaporation of the solvent, leaving a solid powder which is pressed in order to form a 6 mm diameter pellet.

Gas phase methods

Samples are desorbed by a frequency-doubled Nd:YAG laser (Minilite Continuum, 10 Hz, 0.1–3 mJ/pulse). Desorption occurs at the output of a pulsed valve (1 mm diameter nozzle, repetition rate 10 Hz) generating a supersonic beam from a 30:70 Ne:He mixture at 16 bar, which cools down vaporized species and conveys them, after skimming, to the interaction region of a time-of-flight mass spectrometer.

The isolated systems are then probed by a Nd:YAG-pumped (Powerlite Continuum, 100 mJ/pulse at 355 nm) dye laser (Narrow Scan Radiant dyes, 700 µJ/pulse). UV spectra are obtained by detecting the ions generated by resonant 2-photon ionization (R2PI), and by scanning the UV wavelength. IR spectroscopy is recorded following a IR/UV double resonance technique[1]. Basically, the UV laser is tuned to the main transition of a cold conformer in order to ionize it selectively. IR beam from a Nd:YAG-pumped (Continuum Surelite, 650 mJ/pulse at 1064 nm) OPO KTP/OPA KTA Laservision (1 mJ/pulse) is sent prior to the UV beam. When the IR frequency is tuned on a vibrational transition of the species studied, the IR beam is absorbed, warming up the molecules, and leaving fewer cold molecules which eventually results in a depletion of the ion signal from the UV laser. IR spectra are then obtained from the comparison between IR-on and IR-off conditions using an experimental procedure previously described[2].

For the three ion pairs investigated, mass spectra were taken in order to monitor the possible fragmentation after photoionization of the phenyl moiety. In the case of (Li^+, BA^-) and (Li^+, PB^-), no significant fragmentation was observed, and the spectra were recorded on the parent ion channel. On the contrary, (Li^+, PA^-) fragmented in the jet

as shown in Fig. S1. From this fragmentation pattern, a reaction path from the ionized ion pair can be deduced (Fig. S2). After ionization, the resulting zwitterionic radical spontaneously fragments following a decarboxylation reaction leading to the observation of the {Benzyl, Lithium}$^+$ radical ion channel. Since this ion signal is the most intense, IR and UV spectra were carried out on this fragment.

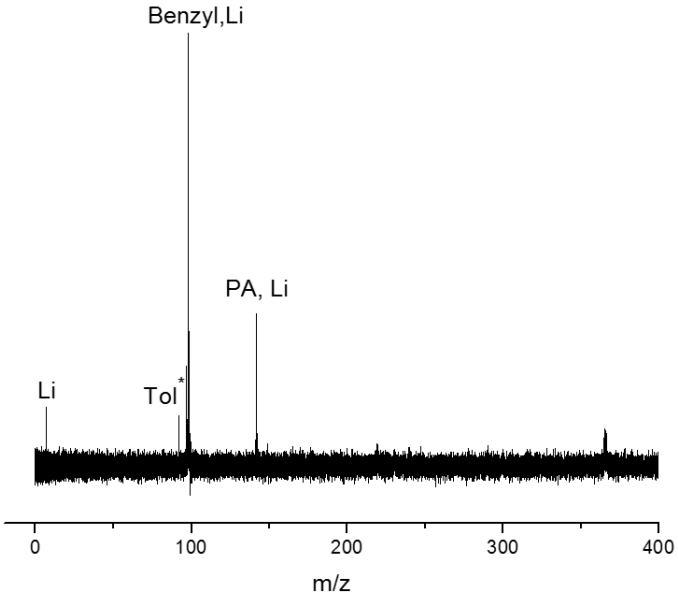


Figure S1: Differential (on-off UV resonance) mass spectrum of (Li^+, PA^-) showing the parent ion signal and its fragments. IR and UV spectroscopy were carried out by monitoring the m/z = 98 ion channel assigned to the {Benzyl, Li}$^+$ radical ion

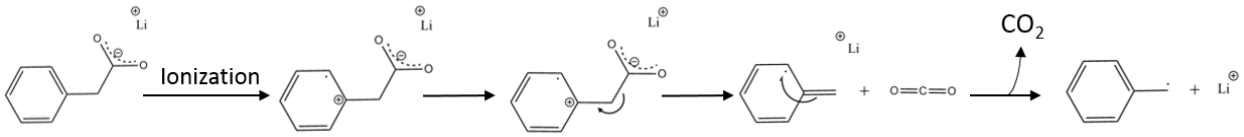


Figure S2: Possible fragmentation path for (Li^+, PA^-), consistent with the mass spectrum observed.

2. Theoretical methods

An exploration of the potential energy surfaces with the Amber 99 force field[3] using the HyperChem 7.52 package[4] was done in order to determine the conformations of the ion pairs. Geometry optimizations were then carried out on the possible structures of each ion pair at the RI-B97-D3[5]/dhf-TZVPP[6] level, using Turbomole 6.4.[7] Harmonic frequency calculations were performed at the same level, and corrected by two scaling factors for $(CO_2^-)^{anti}$ and $(CO_2^-)^{sym}$ stretches, established from published experimental values (see section 3). Theoretical spectra were built from Lorentzian functions taking into account the intensities calculated and the (scaled, if available) harmonic frequencies, and an arbitrary width of 4 cm^{-1}. Finally, the energy of each conformer was then calculated more accurately at the BSSE-corrected-Full-CCSD(T)/dhf-TZVPP//RI-B97-D3/dhf-TZVPP level (See Table 1).[8]

Atomic charges of (Li^+, PA^-), (Li^+, BA^-), and (Li^+, PB^-) were obtained from a natural bond orbital (NBO) analysis[9], carried out at the RI-B97-D3/dhf-TZVPP level.

3. CO_2^- stretches mode-dependent scaling functions

Harmonic frequencies calculated at the RI-B97-D3/dhf-TZVPP level have been corrected by mode-dependent scaling functions in order to be quantitatively compared with experiment. Relatively few IR spectra of the carboxylate group in the CO stretch region have been published, and so far, no mode-dependent correction of the harmonic frequencies has ever been applied. Two scaling functions were thus built for each CO_2^- stretch mode (symmetric and antisymmetric). For this purpose, several systems, such as the acetate anion, free or cationized amino acids or peptides, have been chosen in order to get benchmark IR values for the carboxylate group in various environments (free, or paired with singly or doubly charged cations in monodentate or bidentate conformations).[10-18] These experimental values were compared to the harmonic frequencies f_0^{th} calculated at the RI-B97-D3/dhf-TZVPP level (Fig. S3). The scaled theoretical frequency, f^{th}, are thus obtained from the following scaling functions: $\boldsymbol{f^{th}=1.00194*f_0^{th}+12.9186\ cm^{-1}}$ for the $(CO_2^-)^{anti}$ stretch (with an average error of 16 cm^{-1}), and $\boldsymbol{f^{th}=1.01975*f_0^{th}-2.075\ cm^{-1}}$ for the $(CO_2^-)^{sym}$ stretch (with an average error of 24 cm^{-1}) respectively .

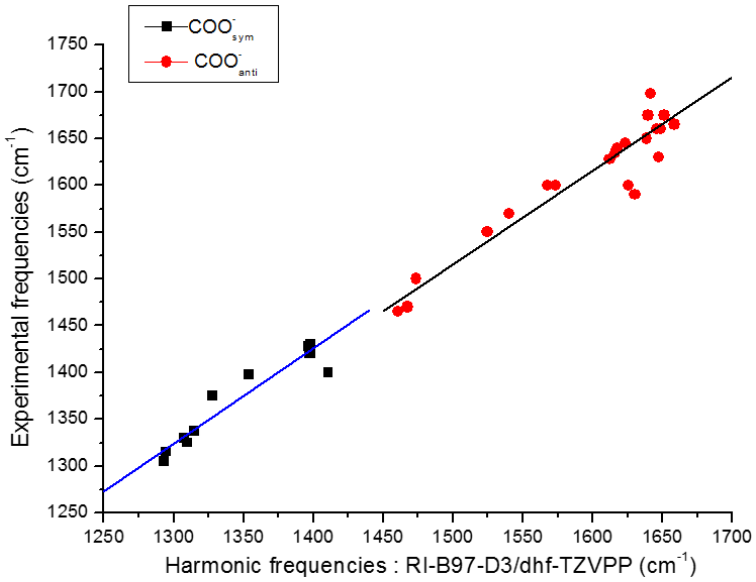


Figure S3: Correlation between experimental and theoretical harmonic frequencies on a set of carboxylate-containing systems (see text). The black line represents $(CO_2^-)^{anti}$ scaling function, and the blue line represents $(CO_2^-)^{sym}$ scaling function.

4. Theoretical results

Electronic energies with thermodynamic corrections (ΔG) of the (Li^+, AcO^-), (Li^+, PA^-), (Li^+, BA^-), and (Li^+, PB^-) ion pairs at the RI-B97-D3/dhf-TZVPP level of theory are

presented in Table S1. The comparison with the relative energies at the BSSE-corrected-Full-CCSD(T)/dhf-TZVPP//RI-B97-D3/dhf-TZVPP level (Table 1) shows no major differences between both sets of minima, suggesting that the RI-B97-D3/dhf-TZVPP level of theory is appropriate to describe the structure and energetics of these ion pairs.

Several geometrical parameters have also been reported in Table S1. An important difference can be seen here between the conformer O-π of (Li^+, PA^-) and the conformers O-O on the C-O bond length as well as the CO_2 angle, revealing the asymmetric role of the cation in the O-π conformer.

Ion pair	Conformer	ΔG (300 K) (kJ mol^{-1})	C-O bond length (pm)		CO_2 angle (°)	q(O) e		q(Li) e	D_0 (kJ mol^{-1})
(Li^+, AcO^-)	O-O	0	127.8		122	-0.80	-0.79	0.94	708
(Li^+, PA^-)	O-O	0	127.6		122	-0.79		0.94	682
	O-π	36	122.2	128.2	128	-0.90	-0.60	0.96	643
(Li^+, BA^-)	O-O (1)	0	127.9	127.5	122	-0.80		0.94	687
	O-O (2)	1	127.8	127.7	122	-0.80		0.94	682
	O-O (3)	6	127.7	127.8	122	-0.81	-0.79	0.94	-
(Li^+, PB^-)	O-O-π	0	127.3	127.5	122	-0.79	-0.77	0.92	696
	O-O (1)	8	127.7	127.8	122	-0.80	-0.79	0.94	-
	O-O (2)	9	127.7	127.9	121	-0.80	-0.79	0.94	682
	O-O (3)	10	127.8		122	-0.80		0.94	-
	O-O (4)	10	127.9	127.8	121	-0.80		0.94	-
	O-O (5)	11	127.8	127.9	122	-0.80		0.94	-

Table S1: Theoretical results for ion pairs

Atomic charges on oxygen and lithium are also indicated in Table S1. Interestingly, in these ion pairs, the atomic charge on oxygens is increased compared to the isolated anion (-0.75 e) as expected from the additional polarisation induced by the cation.

Binding energies (D_0) have been calculated for the most stable conformer of each pair (Li^+, A^-) at the level of theory based on the formula below:

$$D_0 = - E_{(Li+,\ A-)} + E_{Li+} + E_{A-}$$

$E_{(Li+,\ A-)}$ is the BSSE-corrected-Full-CCSD(T)/dhf-TZVPP//RI-B97-D3/dhf-TZVPP energy of the ion pair, Zero Point Energy calculated at the RI-B97-D3/dhf-TZVPP level included,
E_{Li+} is the Full-CCSD(T)/dhf-TZVPP energy of the lithium cation,
E_{A-} is the Full-CCSD(T)/dhf-TZVPP//RI-B97-D3/dhf-TZVPP energy of the anion in its most stable geometry (cf Table S2), Zero Point Energy calculated at the RI-B97-D3/dhf-TZVPP level included.

For this purpose, the energies of the isolated ions PA^-, BA^- and PB^- have also been calculated at the RI-B97-D3/dhf-TZVPP level of theory (Table S2). The C-O bond lengths and CO_2 angle were determined as well. For BA^- three conformers are possible. They derive from the structure adopted by the anion in the (Li^+, BA^-) ion pair, and are labeled accordingly. The same thing is found for PB^-, but we noticed that the geometry derived from the conformer O-O-π is similar to O-O^- (2) after optimization. Finally, for PA^-, the anion taken from the O-π structure is found to converge to O-O^-.

Isolated ion	Conformer	$\Delta G_{RI\text{-}B97\text{-}D3}$ (kJ mol^{-1})	$E^{el}_{RI\text{-}B97\text{-}D3}$ (kJ mol^{-1})	$E^{el}_{CCSD(T)}$ (kJ mol^{-1})	C-O bond length (pm)		CO_2 angle (°)
AcO^-	**O-O^-**	-	-	-	125.9		129
PA^-	**O-O^-**	-	-	-	125.0	125.3	131
BA^-	**O-O^- (1)**	0	0	0	125.4	126.3	129
	O-O^- (2)	0	4	8	125.8	125.6	130
	O-O^- (3)	6	10	-	125.6	126.0	130
PB^-	**O-O^- (1)**	7	15	-	125.8	125.7	130
	O-O^- (2)/ (O-O-π)$^-$	0	4	0	126.3	125.4	129
	O-O^- (3)	12	16	-	125.6	125.9	129
	O-O^- (4)	1	0	-	126.3	125.8	129
	O-O^- (5)	8	15	-	125.7	125.9	130

Table S2: Theoretical results for anions.

5. Franck-Condon active mode of the O-O-π conformer

The low frequency mode (42 cm^{-1}) which is responsible for the Franck-Condon activity observed in the (Li^+, PB^-) O-O-π conformer is represented in Figure S4. The motion can be roughly described as a relative translation of the carboxylate group and the phenyl ring in their respective plane, which mainly changes the distance of the cation to the pseudo-C_6 axis of the phenyl ring, together with, to a lesser extent, the distance of the cation to the center of the phenyl ring.

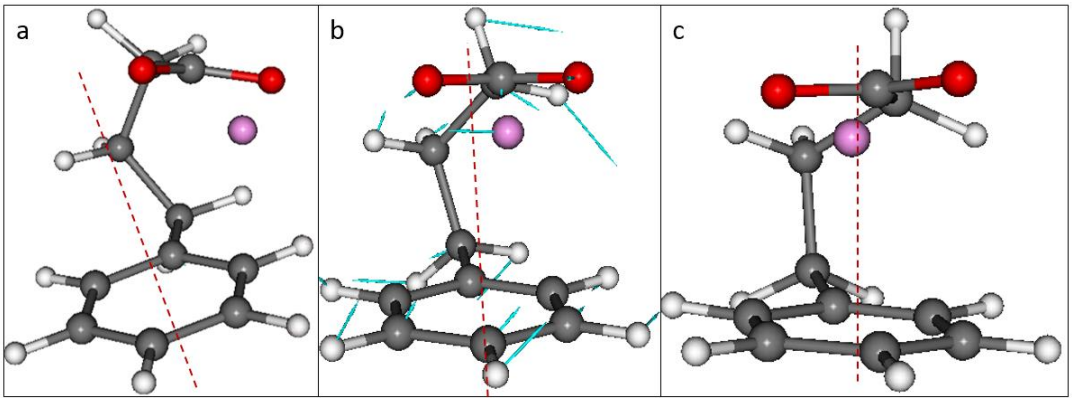
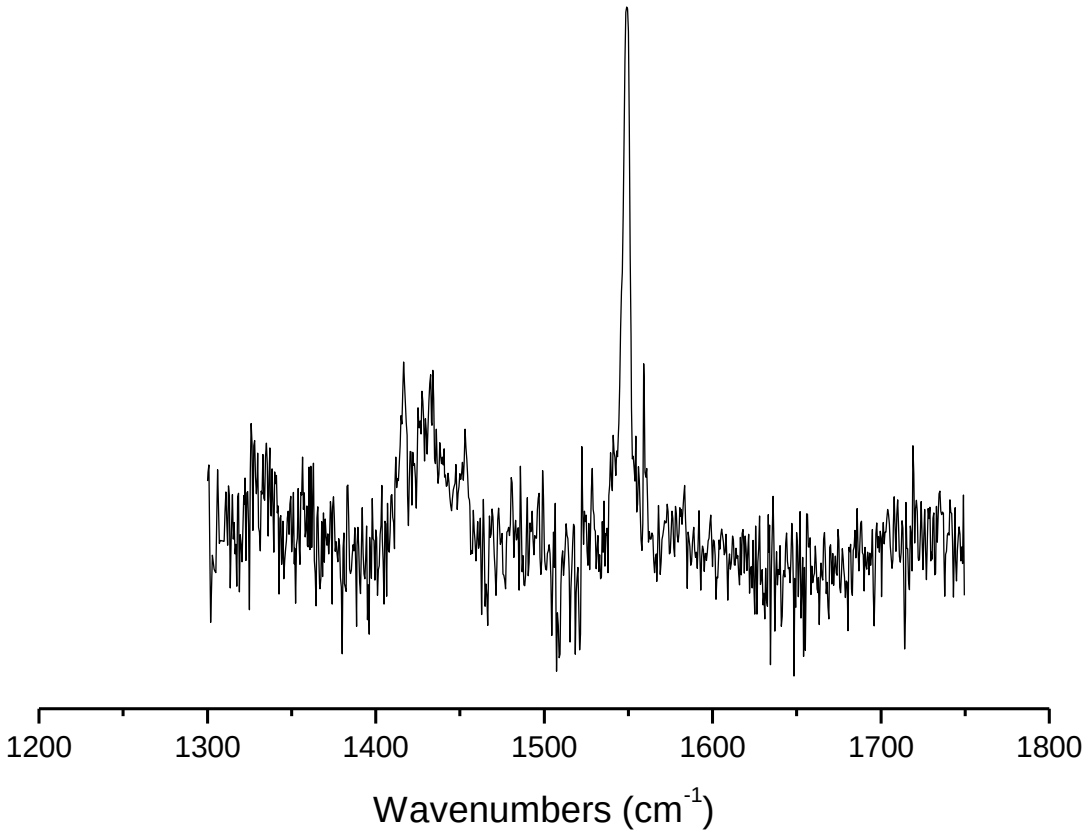


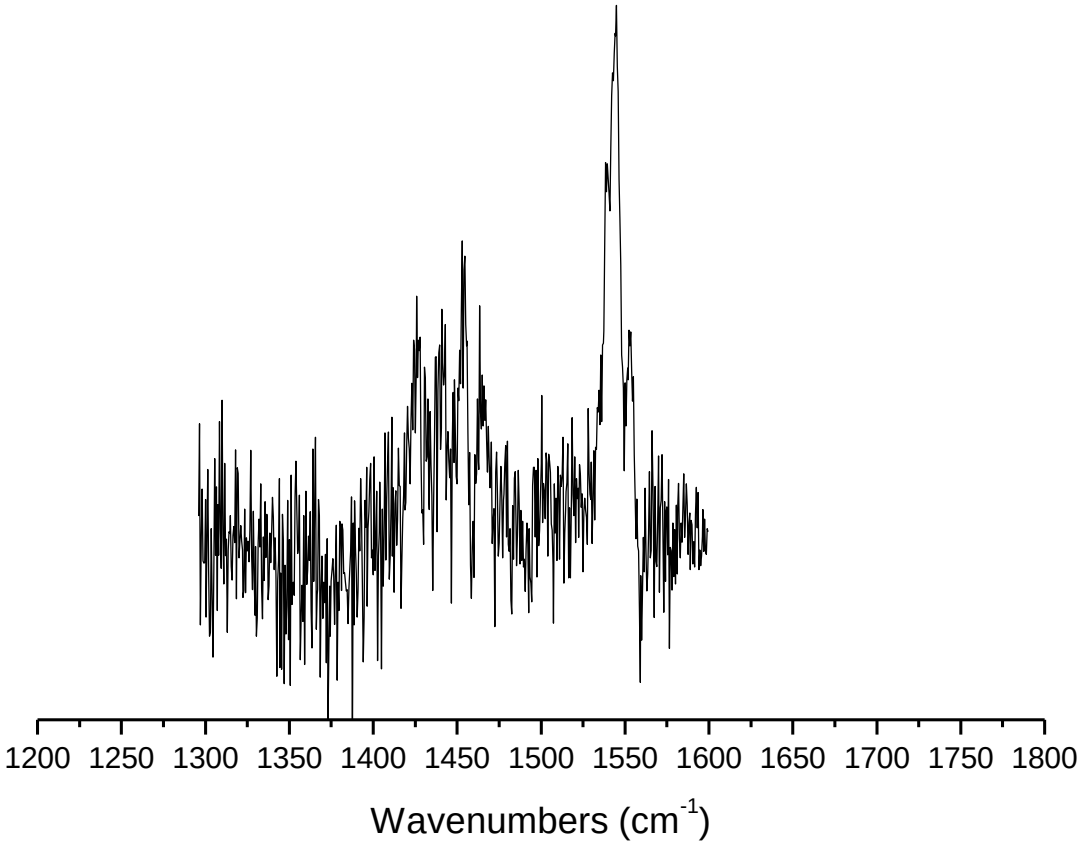
Figure S4: Representations of the low frequency normal mode (42 cm^{-1}) to which is assigned the Franck-Condon activity observed in (Li^+, PB^-) O-O-π conformer. **b** represents (Li^+, PB^-) in its equilibrium state, **a** and **c** represent arbitrary opposite displacements along this internal coordinate . The dashed red line represents the pseudo C_6 axis of the phenyl ring.

6. Enlarged IR spectra

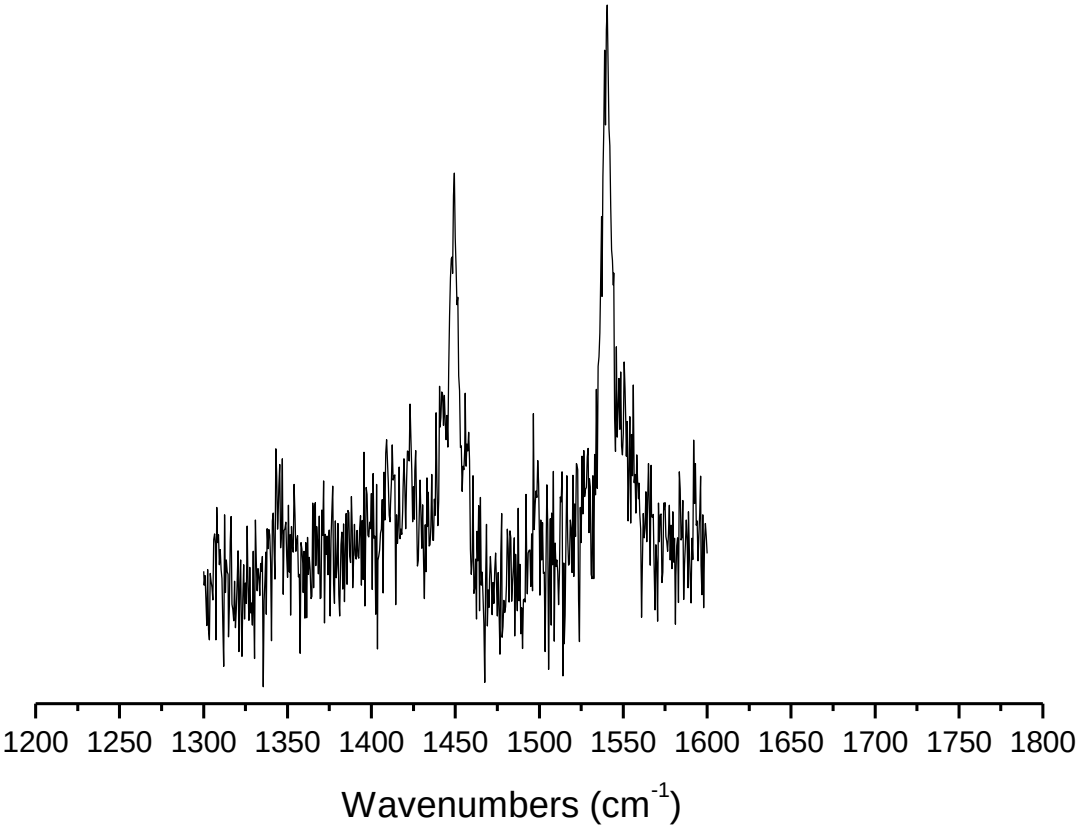
(Li^+, PA^-):



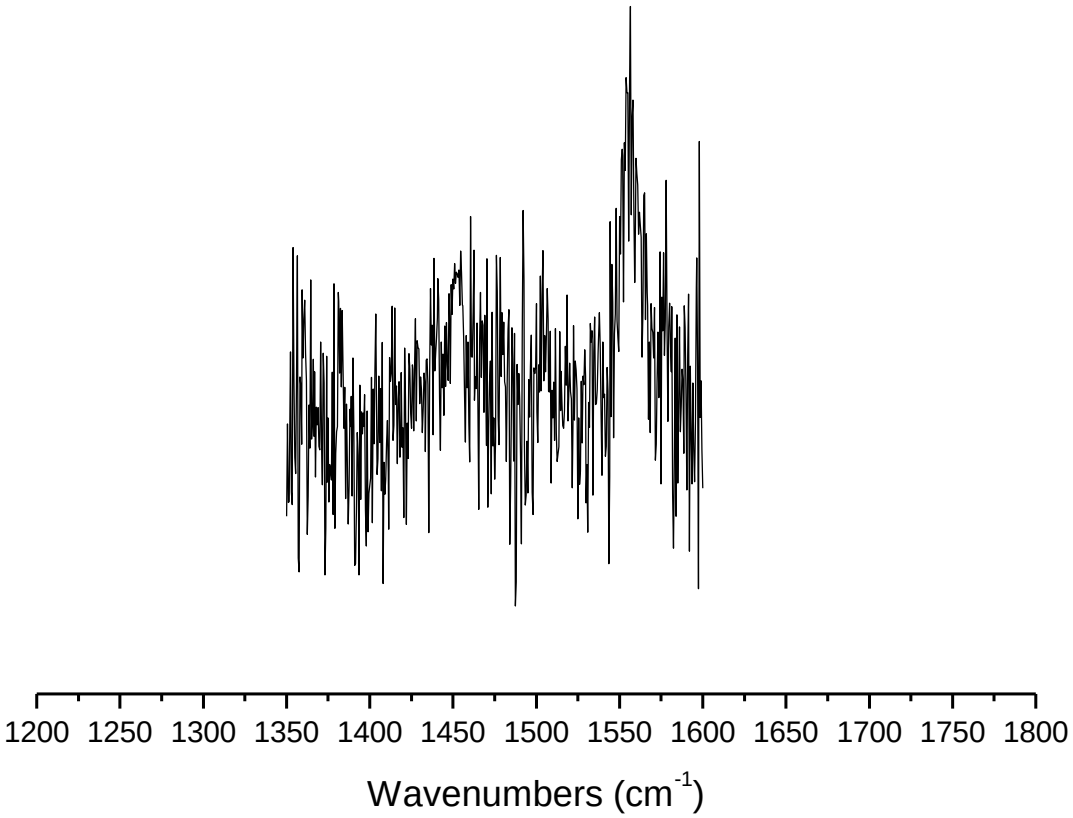
(Li^+, BA^-) Conformer A



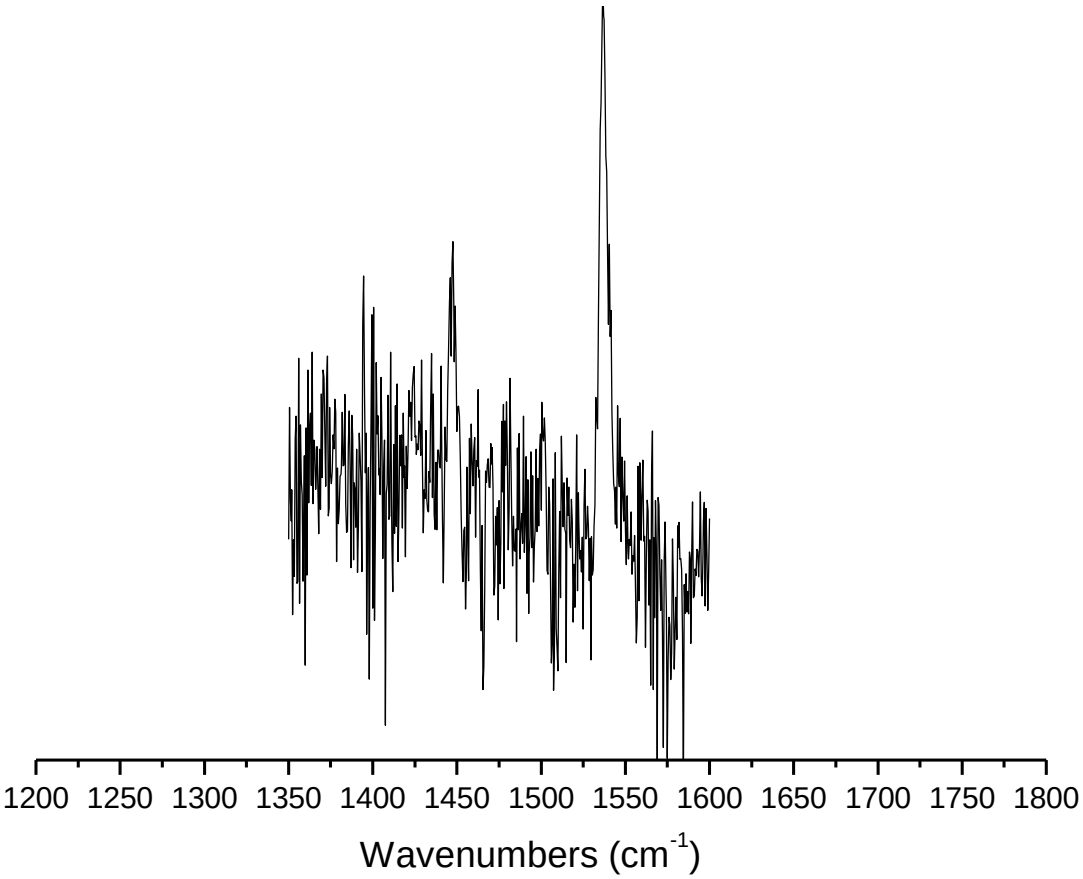
(Li^+, BA^-) Conformer B



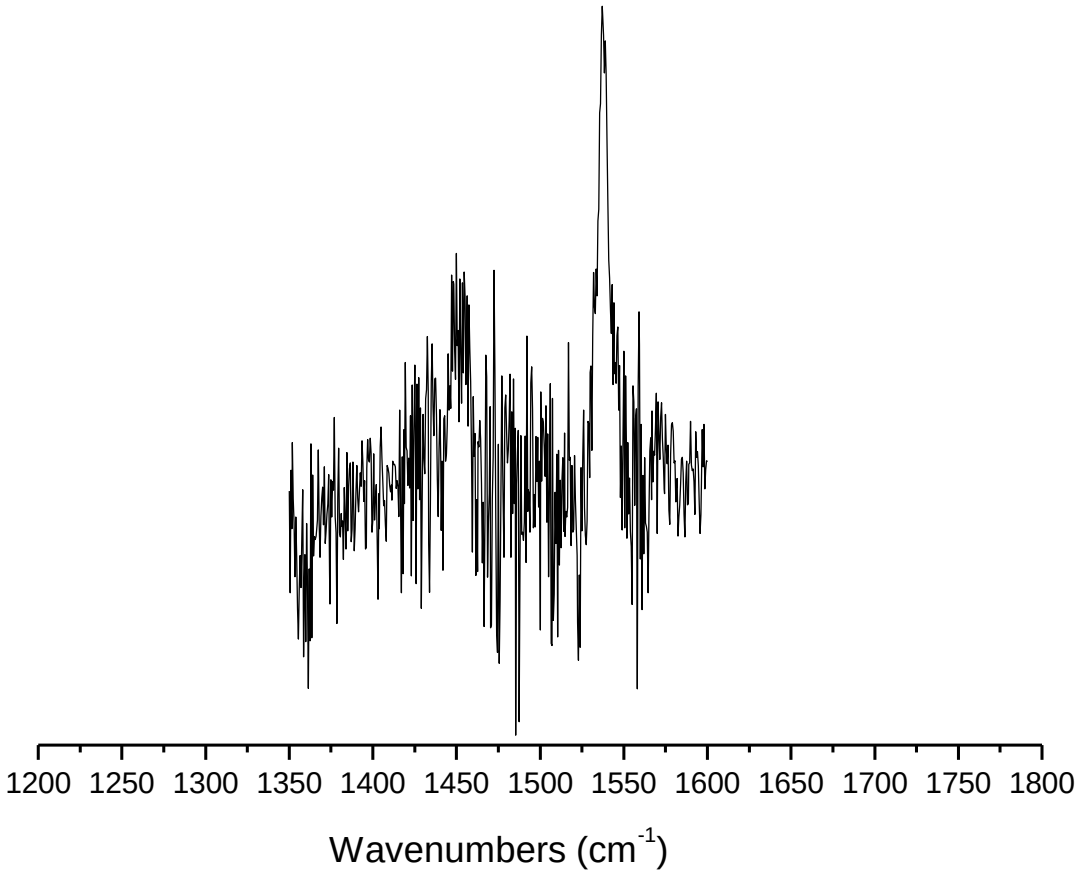
(Li^+, PB^-) Conformer A



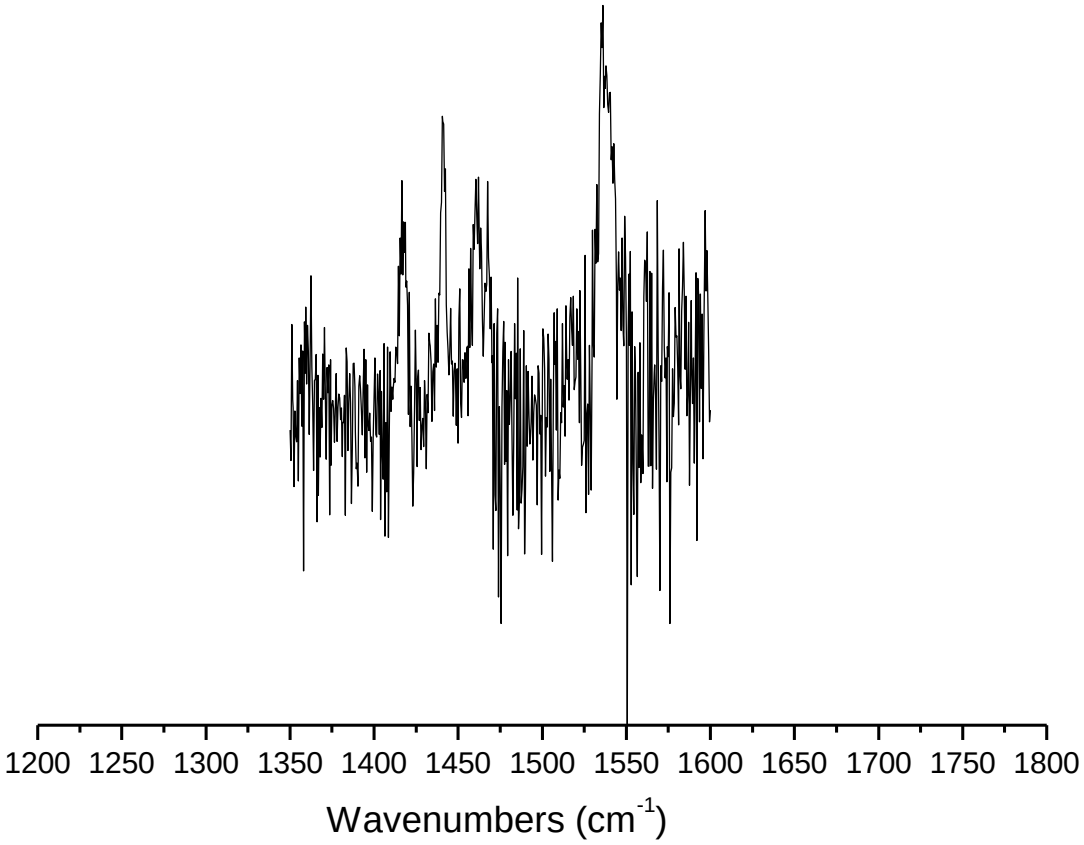
(Li^+, PB^-) Conformer B



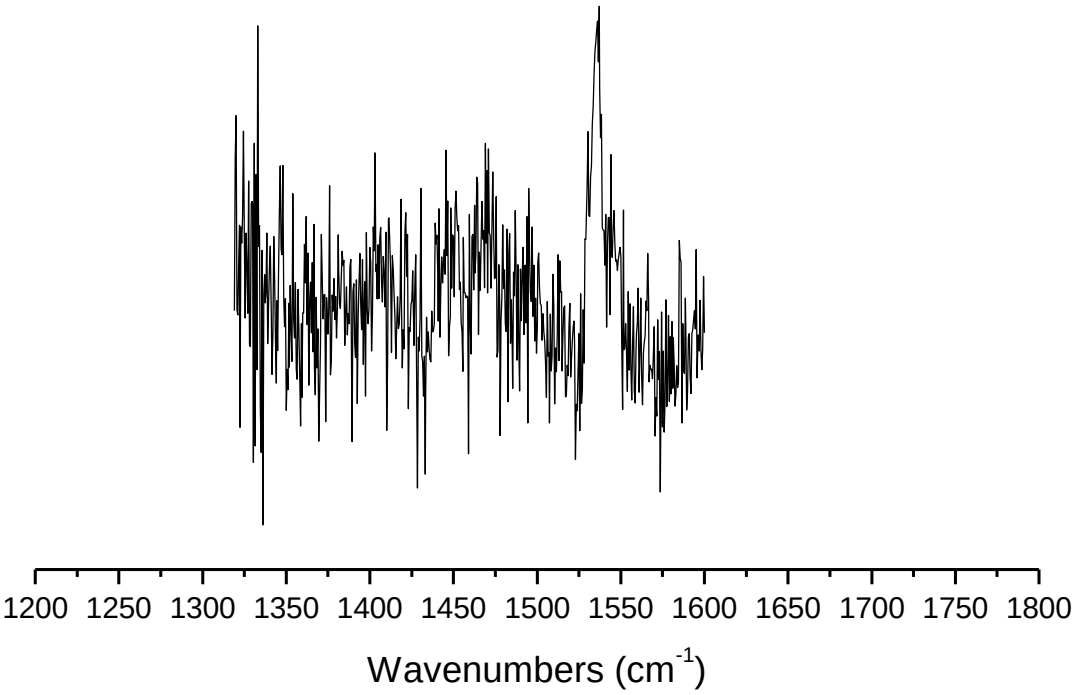
(Li^+, PB^-) Conformer C



(Li^+, PB^-) Conformer D



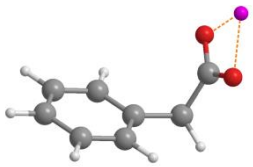
(Li^+, PB^-) Conformer E



7. Atomic coordinates (in atomic units) for each conformer discussed in the article

Coordinates of all the ion pairs optimized at the RI-B97-D3/dhf-TZVPP level of theory.

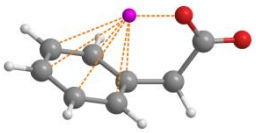
(Li$^+$, PA$^-$) O-O



(Li$^+$, PA$^-$) O-O

3.14038283912068	0.34020734246077	-1.17497170201887	c
2.61717186247511	2.90132284770074	-2.42572642390677	c
1.76094111468443	2.93869130535034	-4.67937672463218	o
2.97329158745659	4.91478733258902	-1.14858003252621	o
4.65089431479805	0.58689652256058	0.21438043572707	h
3.75054835453558	-0.98613669388731	-2.63907829350650	h
0.75713526900794	-0.61047049004443	0.09874144264162	c
-1.02322319547899	-2.02846583012519	-1.25881158547501	c
0.24706067139010	-0.01134396249795	2.62890921779183	c
-3.25513635473890	-2.84425382271732	-0.10931780264501	c
-3.74283669653513	-2.24646187725222	2.41775840405551	c
-1.98384642934249	-0.82501406991798	3.78311880195487	c
-0.65362707325053	-2.47747510045208	-3.23021492349399	h
1.60683310817048	1.10819812926481	3.68887057296671	h
-4.61245617672999	-3.95097666652719	-1.18590843910514	h
-5.47629117416549	-2.88751605843507	3.31656629814868	h
-2.34656900449906	-0.35175425417797	5.75048870165965	h
1.58972698310165	6.42976534610855	-4.04684794763625	li

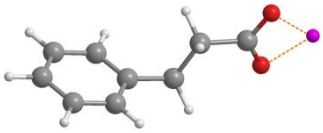
(Li$^+$, PA$^-$) O-π



(Li$^+$, PA$^-$) O-π

3.39849651671753	0.24249006448067	-1.29036672330267	c
3.10868492854158	2.94384233220213	-2.62725149712405	c
4.98832026891100	3.75282894730191	-3.69705004237113	o
0.91481035437497	3.99125678406481	-2.43709349933787	o
4.96093255989056	0.42673963437577	0.05254013844081	h
3.99715472097572	-1.07360705688659	-2.76970063053510	h
1.02697757878124	-0.62305665334392	-0.02007420116311	c
-0.86419899474336	-1.92060855634784	-1.38053679521175	c
0.45385494004255	0.12743683472379	2.47374840806064	c
-3.24044494383609	-2.39951897022808	-0.31937289994127	c
-3.79017182239934	-1.59768871274196	2.14539127505496	c
-1.91935122543096	-0.34674366410950	3.54370025391602	c
-0.46551351468785	-2.51904312871679	-3.30658545952397	h
1.88292584967367	1.12949413189767	3.56029503601821	h
-4.66257328911370	-3.40044732267710	-1.41468235168695	h
-5.63369637976528	-1.96627474235526	2.97170185565751	h
-2.30843474657138	0.25782827570676	5.46908813237580	h
-1.84777280136094	2.97507180265341	-0.95375099932603	li

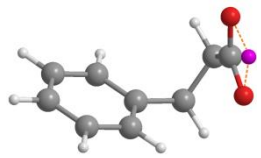
(Li^+, BA^-) O-O (1)



(Li^+, BA^-) O-O(1)

5.02167629426231	-0.26482094340009	-2.27044337407612	c
-0.64535392213635	2.85133044084359	2.65230985060735	h
-1.94589506233948	-0.07890190259675	3.42411318893130	h
2.67397547062349	0.87710100635379	-1.87577807646549	c
-1.94678846208342	0.70426084245458	-0.62279337041118	c
-2.17415784122595	1.54318278036641	2.15087650857983	c
5.30195909918040	-2.86944423615772	-1.93080142042815	c
-3.50511375874318	-0.58546012319837	-1.06262376737980	h
-2.19201204260761	2.35688815510879	-1.84595120482436	h
2.46517346773608	2.90603593563878	-2.14903295363891	h
-0.74417686961096	-4.30110191020370	-0.24314344012398	h
0.56590681277522	-0.55133998822612	-1.13940765077942	c
0.87491935422991	-3.16298099637651	-0.80703730033158	c
3.21725354161716	-4.31705153592620	-1.19815721046350	c
3.41403395257221	-6.34685770888834	-0.93828965977228	h
7.12561013404813	-3.76400463393824	-2.24208594545219	h
6.63030370409203	0.87678028731323	-2.84954670341814	h
-4.66735489124954	2.82225786226216	2.83049708738791	c
-6.41233288832275	3.03099560276817	1.17598571576630	o
-4.93776842742505	3.65547240736352	5.08091322234295	o
-8.11985766539255	4.61765865843926	3.86039650394937	li

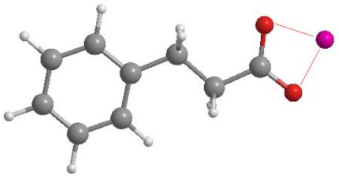
(Li^+, BA^-) O-O (2)



(Li^+, BA^-) O-O(2)

2.97681070632007	2.41609633909766	2.81095160361527	h
2.12182389819818	-1.68370690799469	-5.45466572086321	o
-1.88672014158202	-0.41256562242895	-5.10905388041856	o
0.47410861019794	-0.09636780415980	-4.69621008698113	c
1.34394460624430	2.25418729504704	-3.26938019995502	c
-0.40505381926787	2.96154169018238	-1.04392628635225	c
-0.39068596175996	0.98351025862405	1.02106789219320	c
-2.24233822654362	-0.91179897031386	1.10760422671876	c
-2.18129616493493	-2.77857350822328	2.97559411240948	c
-0.25983106651821	-2.78461700779597	4.78799568660188	c
1.37707907418650	3.81585609560058	-4.63855717173005	h
3.09724257172123	-0.89017598128779	6.12617685633135	h
-0.21397342156486	-4.23259013522942	6.24574487521375	h
-3.64156837229945	-4.22582009541410	3.02231947974104	h
1.59780938679667	-0.90711142769774	4.71997306099799	c
3.28407422035618	1.94533375975506	-2.62505264014262	h
1.52688766454690	0.95604818271522	2.85151903865737	c
-3.72185676638213	-0.91424127765000	-0.31765911852083	h
0.22050038929500	4.78044963980010	-0.26827227356098	h
-2.32416303603543	3.21124708669712	-1.77379939983644	h
-0.75279415097450	-3.48670160932343	-6.47237005411894	li

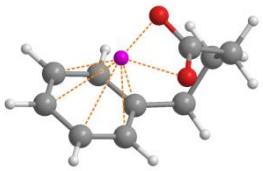
(Li^+, BA^-) O-O (3)



Li^+BA^- O-O(3)

-4.29186980763519	6.81195387335521	-1.29210633391446	o
-0.07970281658194	7.05502310244761	-1.24578844623984	o
4.90499824789218	-0.87167163765569	0.01365386703188	h
5.44868651082830	-5.43434444969103	0.88688510561594	h
1.67378765972767	-8.17979089172190	1.54024551748232	h
-2.62811824131779	-6.28846099088674	1.30517263130222	h
-3.16286737440493	-1.75133104506594	0.43559803942107	h
1.71719150203167	2.88875628589222	1.05573445409136	h
1.62679457448581	2.26020528517918	-2.16475318963658	h
-3.15325435362374	2.01927975494242	-1.99211561129613	h
1.44221553277479	-6.17440064069936	1.15605949641443	c
-2.12101538239440	5.78133427117226	-1.05586763939317	c
-2.02295276729573	2.94814456413156	-0.52267465864442	c
0.64394870930513	1.85164230120954	-0.38422056900493	c
-3.05801482980038	2.64067117273635	1.24887683677018	h
3.55862347275109	-4.63136617275497	0.78898630640631	c
3.24953694972891	-2.06144309827650	0.29705341543638	c
0.83550657663749	-0.95934645007335	0.15702727515827	c
-1.26531554637944	-2.52880145657483	0.52858213818213	c
-0.96632826167727	-5.11121184508238	1.02353207855251	c
-2.35185035505221	9.73515806741653	-1.77988071373551	li

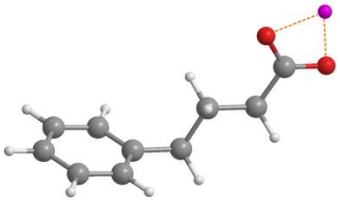
(Li^+, PB^-) O-O-π



(Li^+, PB^-) O-O-π

-0.84330834493190	1.52115444180289	2.94552005800031	c
-1.29618138640688	3.46893542825377	3.50374342012553	h
0.21934744675047	0.67823267340870	4.51417146726988	h
0.80565720121845	1.60491345828993	0.60724079708278	c
0.03452372909512	2.98422571717173	-1.52594800065705	c
-1.72874711915590	4.03786885795855	-1.45124864757913	h
3.08006243654611	0.25252913247639	0.46804707225646	c
3.69670178634508	-0.85070116426797	2.08618467388076	h
1.44737764302254	2.96869570718373	-3.75088102280351	c
0.79972513843935	4.03369348583791	-5.38412106520858	h
4.51590711569454	0.22397663570789	-1.75901421730057	c
6.28302796820357	-0.82645315848185	-1.81986526969856	h
3.69230014930858	1.56838858422931	-3.88763426193271	c
4.81119280136883	1.56660363253468	-5.61185132862899	h
-3.36532191054426	0.06956771717942	2.60187190845039	c
-4.56030946974979	0.47854831189346	4.24705410834245	h
-3.08906420092472	-2.81669012541062	2.34536365492673	c
-2.07593844495578	-3.61038303431537	3.96587255646979	h
-4.98318586750118	-3.66060438497034	2.29368025569554	h
-4.35015068002581	0.79040557757218	0.92875882791455	h
-1.71941648208368	-3.57961946006015	-0.08302525529101	c
-2.52380677538266	-2.68386769328079	-2.17030082025745	o
0.26184521944583	-4.93772464595054	0.05355453886143	o
0.88776204622409	-3.28169569476275	-3.11717344991907	li

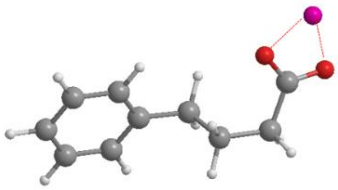
(Li^+, PB^-) O-O (1)



(Li^+, PB^-) O-O(1)

-0.11917785696758	0.84509204440340	1.85653698453126	c
-1.39023423645411	2.38537438975667	2.42522174156753	h
0.87413863431013	0.22729809600877	3.57188442926958	h
1.76825719975004	1.80655065768668	-0.05817922539889	c
4.20983432013461	0.78442124635437	-0.19186409678672	c
4.76683547091947	-0.66534243206454	1.15810070625189	h
1.09053452766595	3.67320600565677	-1.81366540041921	c
-0.79793182934494	4.48680646797036	-1.73530728155480	h
5.92872499706621	1.60297629641871	-2.02143314424906	c
7.81641862058951	0.79151112700395	-2.08741078702260	h
2.80000003621010	4.50017089780104	-3.64790471740707	c
2.23911151594829	5.95558293196307	-4.98701705441192	h
5.22825735323058	3.46575634462322	-3.75838426051060	c
6.56448721235219	4.11026057299055	-5.18030069343679	h
-1.71118014471836	-1.36745601988426	0.82489873742938	c
-2.71134756708173	-0.76627193051719	-0.88578814201335	h
-3.60848183691972	-2.34238777345894	2.77302650471999	c
-2.64941247028482	-2.98664390783497	4.49691683101378	h
-4.87638739240843	-0.81792330659115	3.39257657315077	h
-0.45511650290703	-2.90671900695033	0.23658173717863	h
-5.29084361652819	-4.50661197141178	1.87688263504054	c
-6.79240144284421	-5.51634775497265	3.47767512049280	o
-5.18703742838141	-5.25185769339677	-0.41591760041860	o
-7.69704756333657	-7.50744528155482	0.69287040298335	li

(Li^+, PB^-) O-O (2)

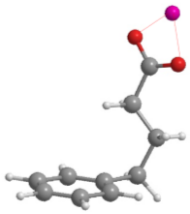


Li^+PB^- O-O(2)

-1.55897855061464	0.17974790521470	-0.08792819488247	c
-2.02448975710810	-0.94875201459046	-1.76287511667863	h
-3.24049765168743	1.29662929233666	0.39487421444215	h
0.63086901608799	1.91360648960232	-0.67632474935863	c
0.71635854325360	4.39435139285596	0.24830075873422	c
-0.86298445662924	5.10935783625387	1.35714156720402	h
2.68577853621253	1.03051067519875	-2.10286185277185	c
2.64371569469638	-0.89580314867592	-2.82408464944117	h
2.79032908075693	5.95733962646266	-0.23925399320907	c
2.81661002339136	7.87935435039064	0.48992864844345	h
4.76219283763106	2.58230197701636	-2.59576507073536	c
6.33381052945966	1.86523530254846	-3.71061972495377	h
4.82196476381283	5.05534348978214	-1.66408800124879	c
6.43557132378089	6.26811631541539	-2.04978112612143	h
-0.96117472761537	-1.64859221411617	2.10218372565571	c
0.75040478920341	-2.71375102557206	1.63405554347738	h
-3.12223554086362	-3.49840066336130	2.63152115919977	c
-2.72905158481772	-4.58926277197303	4.35522420669457	h
-4.90966607121372	-2.50952599771027	2.97974919556772	h

-0.55369362122000	-0.54640257064335	3.81212425946595	h
-3.59040635132176	-5.44405125352874	0.55048237687819	c
-5.72464809526366	-6.56900569423851	0.48691795870436	o
-1.84374077813334	-5.94461782767696	-1.04301267926018	o
-4.26603795179802	-8.22372947099122	-2.28590845580596	li

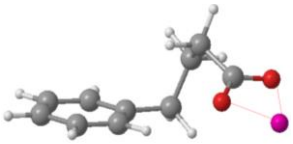
(Li^+, PB^-) O-O (3)



Li^+PB^- O-O(3)

-1.04997669203683	2.05939866986491	-2.14675032676278	c
-0.65387516499184	1.48751389024045	-4.10205578565416	h
-1.72320154815698	4.02093899719821	-2.21793069850210	h
1.35425181600898	1.94119203332078	-0.60454419336994	c
3.42633402635138	0.48599714353101	-1.38323187168422	c
3.32336470075311	-0.53262584234078	-3.16731091329099	h
1.52571388107397	3.23293171353106	1.70560822369587	c
-0.06794478331023	4.36987392163302	2.33936063571271	h
5.60943704053599	0.32324995230860	0.09614169131338	c
7.19572940952387	-0.81640227001771	-0.54465555903116	h
3.70054519214213	3.08013847636252	3.19141599584099	c
3.79758163092953	4.10306313153859	4.97197391149825	h
5.75358845965849	1.62067213289316	2.39065561244842	c
7.45056483754417	1.50097806598782	3.54342658513323	h
-3.18134521157193	0.38243276054143	-1.06287085743919	c
-3.57566831360758	0.93385235771340	0.89282717524456	h
-2.54062991901694	-2.43479402205339	-1.14484598110805	c
-2.17977339921857	-3.07390674305791	-3.08371531401965	h
-0.78228817476686	-2.80008315683894	-0.10197486940981	h
-4.92567783718621	0.72531253599495	-2.12998626333595	h
-4.54172540234870	-4.16730035051583	-0.00905814526647	c
-4.44219072106792	-6.52540723185827	-0.52589447459176	o
-6.23542304648883	-3.25881092223092	1.45372225625711	o
-7.23739078075216	-6.65821524374624	1.63969316632185	li

(Li^+, PB^-) O-O (4)

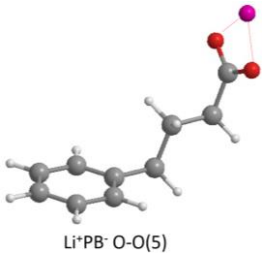


Li^+PB^- O-O(4)

-2.49330723397071	1.03979439346450	-0.12126928365527	c
-3.07663390158041	0.16095358252494	-1.90793401667975	h
-3.73746976331950	2.67193328564051	0.17784789087237	h
0.21424853415931	1.93445221952580	-0.32269339202594	c
1.98353884513133	0.62259476553864	-1.80046795089891	c
1.38376383657506	-1.05268107514128	-2.83049540918163	h
1.03234802654906	4.05756385541805	1.03828899324791	c
-0.32039197901421	5.09623795343717	2.19064280138997	h
4.49938986020311	1.41866433105946	-1.91494843271652	c
5.84510801235958	0.37595032499769	-3.06763729970577	h
3.54515536317465	4.86003755277319	0.92679715812936	c
4.13908853262862	6.51727728004100	1.98867746009948	h
5.28983437007201	3.54039286964972	-0.55440393712101	c
7.24637148601365	4.16258712202512	-0.64880688301448	h
-2.92798766464228	-0.86229443549061	2.05561189127192	c
-2.28410197349493	-0.00805113689371	3.83288503300149	h

-1.55951981150103	-3.40369755015943	1.67813511846202	c
0.47944830302279	-3.12767332768624	1.49684839744963	h
-1.92075595250216	-4.61005941912587	3.32488707182496	h
-4.95870802411774	-1.22894945383988	2.23403576506723	h
-2.53329134036135	-4.79376963777786	-0.64833082223589	c
-4.86063910423573	-5.43638026349861	-0.72600269104533	o
-1.03181351384541	-5.25553515990611	-2.48658884775567	o
-3.95367490730372	-6.67934807657616	-3.91507861478030	li

(Li$^+$, PB$^-$) O-O (5)



1.05504051313094	-1.08153695019336	1.49416685577861	c
1.05638014499425	-0.69003032059250	3.53221611336513	h
2.17239063431956	-2.80708376682308	1.20983888554958	h
2.24927142641618	1.09480248609840	0.08357767610445	c
3.52762723455609	0.69186603920645	-2.20302964508456	c
3.72560055196620	-1.22732190208169	-2.91852117111084	h
2.01594690618278	3.58068214051972	0.97300577454656	c
1.02926904504795	3.92455350678869	2.74563168119113	h
4.54951108666427	2.71123514782101	-3.56276589770201	c
5.54169708667204	2.35809009287551	-5.32818304479426	h
3.03383749208337	5.60812748218323	-0.37767336467265	c
2.84044684087935	7.52142629060131	0.34881159707773	h
4.30492149714009	5.17934506587458	-2.65334945618767	c
5.10405300981061	6.75370491165882	-3.70482301666197	h
-1.68338087540159	-1.57552889205469	0.62877332539339	c
-2.81098373851862	0.14039126709686	0.91675877896613	h
-2.91090669033404	-3.79360348688383	2.06040898604784	c
-1.81622202938870	-5.52118756073382	1.73971868302474	h
-2.94896613965104	-3.37395136563380	4.08771969642207	h
-1.69286203976588	-1.97579626210472	-1.40592509710280	h
-5.60394767537697	-4.20667444057071	1.14081108677661	c
-5.99821189220430	-5.73014576274975	-0.69242375704174	o
-7.39704522413457	-2.95181072588580	2.16459966784607	o
-9.34346716508813	-4.62955299441689	-0.27934435773158	li

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