Short communication

Novel weakly coordinating heterocyclic anions for use in lithium batteries

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Abstract

Ab initio calculations have been performed for a new family of lithium salts based on heterocyclic anions: $[CF_3SON_4C_{2n}]^-$ $(0 \le n \le 4)$. In total, 10 different anions and their 1:1 ion pairs with lithium ions have been studied. The lithium ion affinity globally decreases with the degree of CN-substitution to the ring. Bidentate lithium ion coordination to the sulfonyl oxygen atom and one additional atom or to two adjacent ring nitrogen atoms is strongly preferred when structurally possible. The extremely low lithium ion affinities of the anions together with an appreciable stability towards oxidation make these salts possible candidates for future lithium battery electrolytes.
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1. Introduction

New solutes for liquid, gel and dry polymer electrolytes are required to find a compromise between the poorly stable, including the formation of toxic by-products [1–3], LiPF$_6$, but non-corroding to Al current collectors and the highly conductive LiTFSI, but whose stability including that of the Al salt precludes its use above 3.8 V versus Li$^+$/Li$^\circ$ due to Al dissolution [4]. In a previous study [5], we have shown that the heterocyclic azole anions based on Hückel type stabilization and the general formula $[N_5C_{2n}]^-$ $(0 \le n \le 5)$ have very low affinities for Li$^+$, i.e. they are expected to be highly dissociated in the solvents destined to lithium batteries, the anion–cation binding enthalpy globally decreasing with the number of CN moieties. However, with the exception of 1,2,3-triazole-4,5-dicarbonitrile, TADC $(n = 2)$, such anions are difficult to synthesize. We here suggest a novel family of lithium salts based on heterocyclic anions with the general formula $[CF_3SON_4C_{2n}]^-$ $(0 \le n \le 4)$, depicted in Fig. 1 with R$^{1-4}$ = –N or –CC≡N, for which some of the pos-

sible configurations may be amenable to more facile synthesis than the former azole family. The strong electron-withdrawing character of the CF$_3$S(=O)– moieties suggests that anions with very low Li$^+$ affinities could be found and the inherent asymmetry of the anions should make the lithium salts less prone to crystallization. By *ab initio* calculations, the Li$^+$ ion coordination, type and strength, as well as the inherent anion stability versus oxidation has been investigated. Based on these calculations, we aim to suggest novel candidate lithium salts, with tailored properties for application.

2. Computational details

All 10 different anions and their corresponding 1:1 lithium ion pairs (Fig. 2a–j) have been studied by initial geometry optimization using Hartree–Fock (HF) methods employing the standard 6-31G* basis set (HF/6-31G*). Subsequently, second derivatives with respect to nuclei coordinates were calculated at this level to validate the structures obtained as energy minima. Additionally, a higher computational chemistry level model, B3LYP/6-311 + G* as implemented in Gaussian03 [6–8], was used for the anions and a selection of the most stable 1:1 ion pairs. Both the applied methods have recently been shown to

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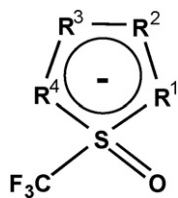*E-mail address:* patrikj@fy.chalmers.se (P. Johansson).

Fig. 1. Schematic chemical structure of the anion family; $R^{1-4} = -N$ or $-CC \equiv N$.

provide excellent agreement for the enthalpy of ion pair formation, as compared to the high-level composite G3 method [9]. In addition, the anion stability versus oxidation has been modeled as the ionization potential (IP) obtained via the vertical energy difference between the anion and its neutral radical (ΔE_v), using

VSXC/6-311 + G(2df,p), a computational scheme presented in more detail recently [10,11]. All calculations were made using the program packages Spartan'02 [12] and Gaussian03 [13].

3. Results and discussion

3.1. Lithium ion affinities

In order to compute the lithium ion affinities of the different anions, the cation–anion coordination space must be searched properly, i.e. all possible coordination sites for the lithium ion must be found and evaluated. In Fig. 3, the resulting electronic energy differences are plotted for the 1:1 ion pairs schematically depicted in Fig. 2a–j. Data are to be found in Table 1.
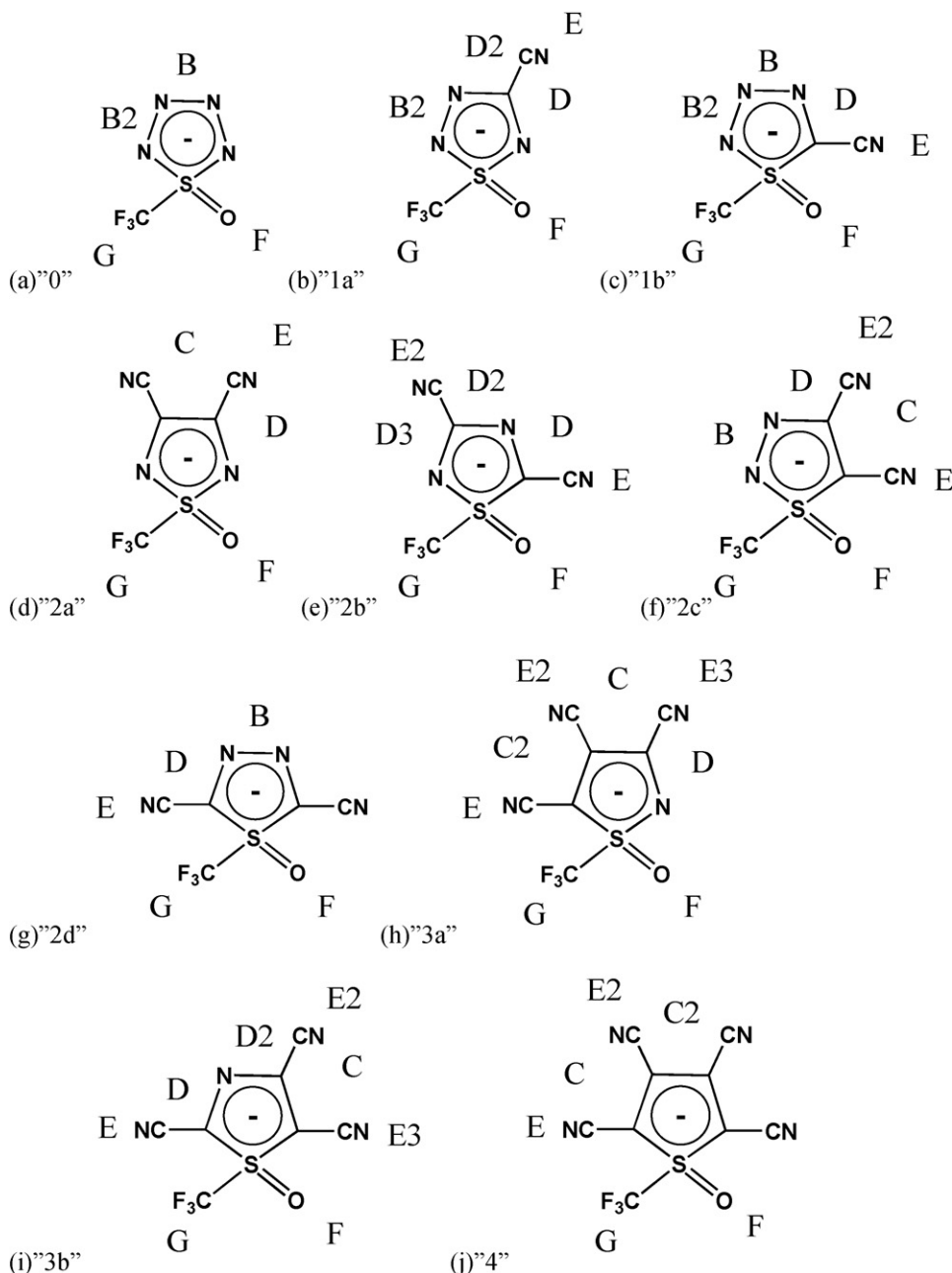

Fig. 2. Chemical structures of the anions ("0"–"4") with the 1:1 ion pairs' lithium ion sites (B–G).

Table 1
Lithium ion coordination and electronic energy differences

Anion	Site	Lithium ion coordination HF/6-31G* (atom:[Å])	ΔE_{el} HF/6-31G* [kJ mol^{-1}]	ΔE_{el} B3LYP/6-311 + G* [kJ mol^{-1}]
0	B	N2:1.9036, N3:1.9056	−546	−549
	B2	N1:1.8853, N2:1.9437	*−561*	*−553*
	F	O:1.8012, F:1.9843	−518	
1a	B2	N1:1.8771, N2:1.9407	*−554*	*−537*
	E	N$_{CN}$:1.8531	−440	
	F	O:1.9798, N1:2.0070	−552	−533
	G	N1:1.8888, F:2.1215	−533	
	G2	N4:1.9112, F: 2.0290	−513	
1b	B	N2:1.8936, N3:1.9196	−524	−527
	B2	N1:1.8963, N2:1.9274	*−539*	*−531*
	D	N3:1.9734, C$_{CN}$:2.3574	−505	
	E	N$_{CN}$:1.8349	−476	
	F	O:1.8813, N$_{CN}$:2.1037	−537	Decomposes
	G	F:1.9325	−481	
2a	C	N$_{CN}$:2.0342, N$_{CN}$:2.0343	−486	
	D	N4:1.9060	−498	
	E	N$_{CN}$:1.8488	−441	
	F	O:1.9532, N1:2.0327	*−522*	*−502*
	G	N1:1.9117, F:2.0640	−500	
2b	D	N3:1.9730, C$_{CN}$:2.3227	−494	
	D2	N3:1.9736, C$_{CN}$:2.3223	−494	
	D3	N1:1.9295	−483	
	E	N$_{CN}$:1.8334	−471	
	E2	N$_{CN}$:1.8549	−429	
	F	O:1.8930, N$_{CN}$:2.0843	*−524*	*−513*
	G	N$_{CN}$:1.9419, F:1.9472	−472	
2c	B	N1:1.9334, N2:1.8843	*−526*	*−512*
	C	N$_{CN}$:2.0763, N$_{CN}$:2.0043	−497	
	E	N$_{CN}$:1.8409	−463	
	F	O:1.9788, N1:2.0225	−519	−527
	F2	O:1.8807, N$_{CN}$:2.1011	−519	Decomposes
2d	B	N2:1.9043, N3:1.9030	−508	−512
	D	N2:1.9659	−490	
	E	N$_{CN}$:1.8419	−456	
	F	O:1.8858, N$_{CN}$:2.1059	*−512*	*−523*
3a	C	N$_{CN}$:2.0391, N$_{CN}$:2.0358	−469	
	C2	N$_{CN}$:2.0688, N$_{CN}$:2.0073	−492	−493
	D	N4:1.9341	−471	
	E	N$_{CN}$:1.8408	−457	
	E3	N$_{CN}$:1.8560	−424	
	F	O:1.8891, N$_{CN}$:2.0871	*−508*	*−494*
3b	C	N$_{CN}$:2.0594, N$_{CN}$:2.0143	−483	−491
	D	N2:1.9781, N$_{CN}$:2.4198	−472	
	E	N$_{CN}$:1.8418	−449	
	E3	N$_{CN}$:1.8491	−443	
	F	O:1.8948, N$_{CN}$:2.0903	*−501*	*−502*
4	C	N$_{CN}$:2.0141, N$_{CN}$:2.0583	−475	−478
	C2	N$_{CN}$:2.0406, N$_{CN}$:2.0403	−455	
	E2	N$_{CN}$:1.8624	−417	
	F	O:1.8922, N$_{CN}$:2.0937	*−483*	*−475*

Italics are used to note the most stable ion pair per anion and method.

The capital letters define different types of sites, most of them self-explanatory, but F being all sites with coordination to the sulfonyl oxygen atom and G being sites with coordination to any of the fluorine atoms. Only these two types of sites result in the lithium ion being out of the ring plane. The possible ion pairs of Fig. 2 not found in Table 1 or in Fig. 3 were either found significantly less stable or converged to another type of ion pair during the geometry optimization. The lithium ion affinity globally decreases with increasing −CC≡N substitution; from "0" to "4", a 14% decrease in the maximum lithium ion affinity:
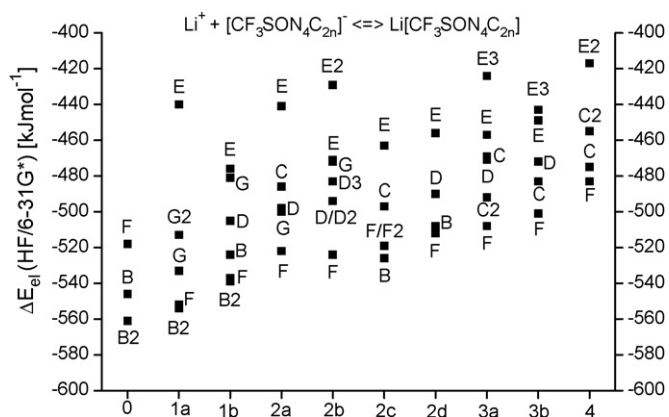
Fig. 3. Electronic energy differences (ΔE_{el}) at HF/6-31G* for the stable 1:1 ion pairs.
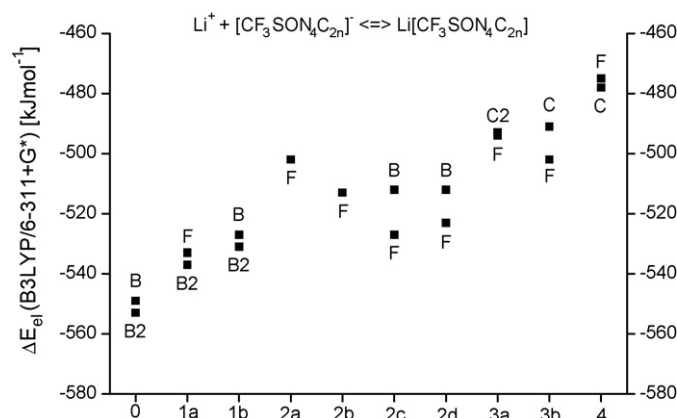

Fig. 4. Electronic energy differences (ΔE_{el}) at B3LYP/6-311 + G* for a selection of 1:1 ion pairs.

-561 to $-483\,kJmol^{-1}$. From Fig. 3, it is clear that a bidentate site at two adjacent ring nitrogen atoms, and especially B2, is preferred for "0" and "1", while F is the globally preferred site. The former is in excellent agreement with our previous study on $[N_5C_{2n}]^-$ anions [1]. Coordination to the nitrile groups, both mono- (E) and bidentately (C), is considerably less stable, but the latter becomes an appreciable site for "3" and "4". Based on this finding only selected B, C and F ion pairs, in total 20 structures, were subject to B3LYP/6-311 + G* calculations. The resulting ΔE_{el} are found in Fig. 4 and Table 1. Only minor changes are found in the relative stability of the different ion pair types, for "2c" and "4", the most stable ion pair is changed, and the global trend of decreasing lithium ion affinities with n remains. Some of the F sites are inherently different as the
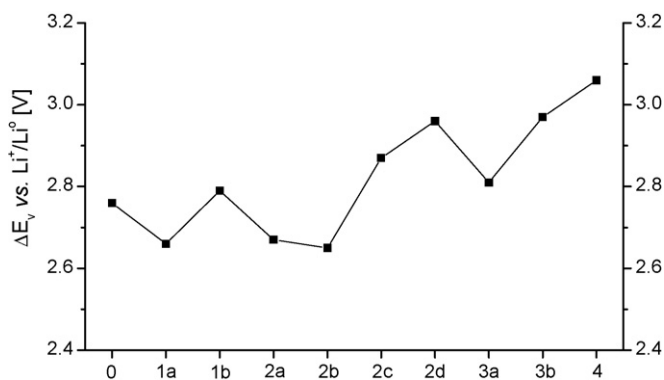

Fig. 5. ΔE_v as measure of anion stability versus oxidation.

additional coordination is either a fluorine atom (for "0") or different types of nitrogen atoms, which explains the relatively large variation in energies for 2a–d. The final range of (maximum) lithium ion affinities for the anions (-478 to -553) is to a large extent lower than for comparable anions of lithium battery interest: PF_6^- ($-567\,kJmol^{-1}$), TFSI (-592), TADC (-541) and BOB (-521) [9]. Thus the chemistry of the anions presented render excellent candidates whenever high ionic dissociation is needed.

3.2. Anion oxidative stability

Excellent dissociation into cation and anion species alone is not sufficient for a lithium salt to qualify for battery electrolyte usage. Another important aspect is the stability versus oxidation for the anion. In Fig. 5, the stability versus oxidation, as ΔE_v, is shown and overall, the stability increases somewhat with increasing n. The present anions are by this measure less stable than, e.g. the TADC anion and also considerably less stable than the small inorganic anions like PF_6^-, BF_4^-, etc. [10,11]. However, the computed data needs experimental confirmation and, furthermore, does not exclude the salts from tailored medium-voltage battery usage (e.g. LiFePO$_4$-based cathodes).

3.3. Suggested synthesis scheme

The promise of both better dissociation capability and agreeable stability versus oxidation is tempting and urges for attempts to synthesize the present anions. Therefore, we here suggest synthesis using simple precursors: di-amino-maleonitrile (DAMN) and (K) trifluoromethane sulfinate and non-intimidating conditions (Fig. 6). DAMN is commercial
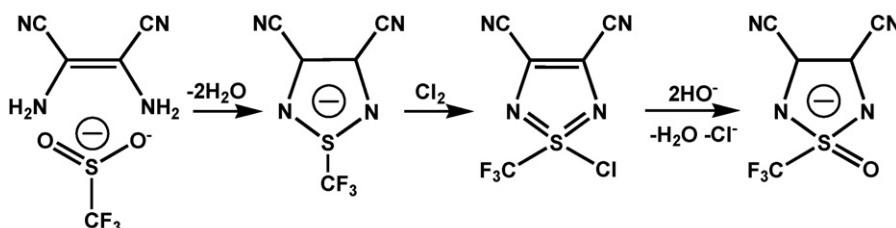

Fig. 6. Tentative scheme for synthesis of the "2a" anion.

as a starting material for dyes, while the trifluoromethane sulfinate anion is made simply by extrusion of CO_2 from trifluoroacetate ($CF_3CO_2^- + SO_2 \Leftrightarrow CF_3SO_2^- + CO_2$). The ring formation reaction is in its principle similar to the action of NO_2^- on DAMN leading to TADC.

4. Conclusions

Substituted heterocyclic anion structures with $-CC\equiv N$ groups that inhibit the possibility of bidentate coordination to two ring nitrogen atoms (i.e. structural removal of the B-sites) show very low Li^+ ion affinities. Further substitution renders anions with even lower lithium ion affinities. The extremely low lithium ion affinities of the anions, decreasing with *n*, together with an appreciable stability towards oxidation, increasing with *n*, make these lithium salts possible candidates as solutes in medium voltage battery electrolytes.

Acknowledgements

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