

Theoretical Study of Electronic Substituent Effect in Fluorine-Containing Sydnone

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Abstract: Calculation of several sydnone derivatives were performed with density functional theory (DFT) at the B3LYP levels to understand the substituent effects that had been introduced to sydnone ring. Sydnone ring can be introduced two substituents that are R¹ on nitrogen and R² on carbon. Sydnone derivatives that had alkyl groups as both of R¹ and R² were studied as electrolyte of lithium rechargeable batteries and expected to improve the properties by changing the combination of R¹ and R². Potential window and resistance against oxidation that are important electrolyte properties can be estimated from Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy levels; and then DFT calculations of sydnone derivatives having several combination of R¹ and R² were performed. Although, the substituent effects of sydnone were still partial understanding, we proposed three types of R¹ and R² combination, such as R¹ = CH₃ and R² = CF₃, R¹ = (CH₃)₃Si and R² = CH₃, and R¹ = (CH₃)₃Si and R² = CF₃, for the improved sydnone derivatives.

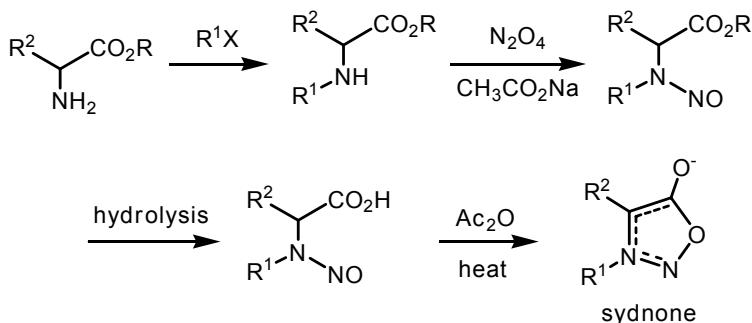
Introduction

Lithium rechargeable battery is expected as useful power source in the next generation and one of the important technical breakthroughs toward the practical use is finding out of the good electrolyte. The electrolyte is required to have wide electrical potential window, resistance to oxidation, good solubility of electrolyte salt, low-viscosity, and good electric constant. Sydnone derivatives, which is a room-temperature ionic liquid, was investigated as a candidate of electrolyte and Sasaki *et al* reported that sydnones have good properties and potentials for electrolyte [1]. General synthetic scheme of sydnones is shown in Scheme 1 and substituent R¹ and R² can be altered to suit required electrolyte properties by the selection of the amino acid and the amine moieties. Among the required electrolyte properties, the electrical potential window and resistance against oxidation can be estimated from the calculated energy levels of HOMO and LUMO by computational chemistry. According to Koopman's theorem, a correlation is expected between the HOMO energy level and the oxidation potential, because the negatives of the orbital energies in the ground state are equal to the ionization potentials [2]. The electron affinity of the electrolyte is also correlated to the LUMO energy level; therefore, the electrical potential window can be estimated from the energy gap (Eg) between HOMO and LUMO energy level. In this paper, we report the analyses of the substituent effects between the electrical potential window and the combination of substituent R¹ and R² by means of the density functional theory (DFT) calculations.

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Scheme 1

Computational Methods

All geometry optimizations, population analyses, and energy calculations were carried out with density functional theory (DFT)[3] at Becke's three parameters (B3) exchange functional along with the Lee-Yang-Parr (LYP) non-local correlation functional (B3LYP) level [4, 5] with 6-311+G(d, p) basis set [6] and verified to be either minima or transition states from their Hessian matrices for all reactions: minima for all positive eigenvalues. Natural population analysis and natural charge analysis were performed at the same level using natural bond orbital (NBO) program [7]. The DFT and the NBO calculations were performed using the Gaussian98 program package [8].

Results and Discussions

The sydnone derivatives that non-substituted at N position ($R^1 = \text{H}$) are expected too reactive for electrolyte usage then we selected **1** ($R^1 = \text{CH}_3$, $R^2 = \text{H}$) as a reference compound. Sydnone **1** was also used in experimental studies and the target of our computational study was to explore sydnone derivatives that have good properties than **1**. The calculation of geometry optimization for **1** was performed and optimized structure was shown in Figure 1. The five atoms, O1, N2, N3, C4, and C5, were coplanar and these atoms constructed a distorted five membered ring because of O1-N2 and C4-C5 lengths were slightly longer than other three bonds. The energy levels of LUMO, HOMO, and Eg (energy gap) of **1** were obtained by the population analyses as -2.01 eV, -6.54 eV, and 4.53 eV, respectively. The Eg is corresponding to the range of electrical potential window and we explored the compound that has lower HOMO level as well as

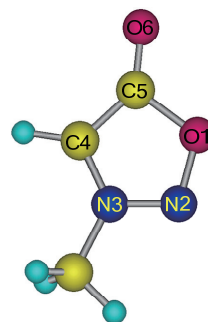


Figure 1: Selected bond lengths(Å) and angles($^{\circ}$) of **1** were as follows; O1-N2 = 1.4539, N2-N3 = 1.3030, N3-C4 = 1.3458, C4-C5 = 1.4187, C5-O6 = 1.1999, C5-O1-N2 = 111.33, O1-N2-N3 = 105.00, N2-N3-C4 = 115.14, N3-C4-C5 = 106.89, C4-C5-O1 = 101.64, O1-C5-O6 = 121.34, C4-C5-O6 = 137.03.

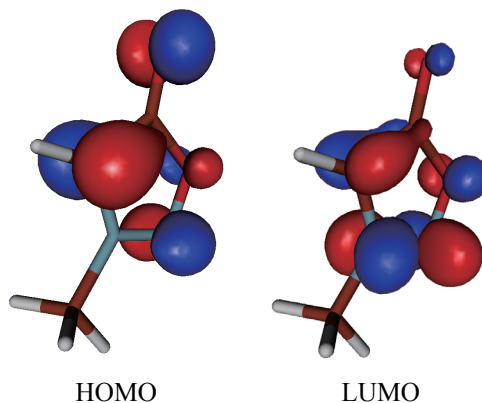


Figure 2: The shapes of HOMO and LUMO of **1**

higher LUMO level by changing the combination of R^1 and R^2 .

It is expected that the substituent R^1 and R^2 have a direct electronic influence on N3 and C4, respectively. The shapes of HOMO and LUMO of **1** obtained by the population analyses were shown in Figure 2. Focus on N3 and C4 atoms, large HOMO coefficient and middle LUMO coefficient were found on C4. On the other hand, there was no HOMO coefficient on N3 and middle LUMO coefficient was found on N3. From above, it was expected that substituent R^2 to make an effect on both of HOMO and LUMO and R^1 make an effect on LUMO.

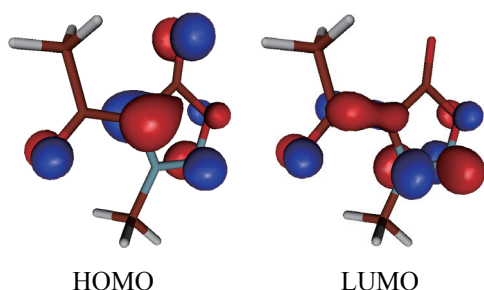


Figure 3: The shapes of HOMO and LUMO of **10**

The substituent R^1 was fixed to CH_3 by way of experiment and geometry optimizations and population analyses were performed for several kinds of R^2 as shown in Table 1. The energy levels of HOMO and LUMO were increased by introducing alkyl (CH_3 , ^iPr , ^tBu) or trimethylsilyl ($(\text{CH}_3)_3\text{Si}$) groups that have electron-donating property as R^2 . By introducing halogens (F, Cl, Br, I) that have electron-withdrawing property as R^2 , both of HOMO and LUMO levels were lowered. The reduced value of the HOMO levels were proportional to electronegativity of halogen atoms, the

HOMO levels of fluorine substituted **6** was lowest and of iodide substituted **9** was highest among halogen substituted sydnones **6-9**. The HOMO levels were greatly lowered by acetyl (**10**) and methoxycarbonyl (**11**) substituents that have strong electron-withdrawing property. Unfortunately, the LUMO levels of **10** and **11** also lowered about the same value of that of HOMO, electrical potential windows (Eg) had not expanded. The carbonyl moieties of acetyl and methoxycarbonyl groups were located on the same plane as sydnone structure and these geometries were made available to resonance stabilization. As shown in Figure 3, both of HOMO and LUMO have expanded to R^2 substituent, which contributed to stabilize molecule by delocalization. However, the aromatic groups such as phenyl (**12**) and 2-pyridyl (**13**) substituents were also electron-withdrawing group, LUMO energy were increased as well as no enough effect for decreasing HOMO energy. Especially about **12**, the phenyl and sydnone rings of the optimized structure were not coplanar. For this reason, there was no resonance stabilization and both of HOMO and LUMO energy level were raised. From the results described above, introducing electron-withdrawing group can be expected desired effects. Then, the combination $R^1 = \text{CH}_3$ and $R^2 = \text{CF}_3$ was calculated and the sydnone derivative **14** gave low HOMO level (-7.28 eV) and large Eg (4.56 eV) as we had expected.

Table 1: HOMO and LUMO energy levels and Eg of the substituted sydnones having CH_3 group as R^1 .

Sydnone	1	2	3	4	5	6	7	8	9	10	11	12	13	14
R^1	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3
R^2	H	CH_3	^iPr	^tBu	$(\text{CH}_3)_3\text{Si}$	F	Cl	Br	I	$-\text{COCH}_3$	$-\text{CO}_2\text{CH}_3$	$-\text{C}_6\text{H}_5$	$-\text{2-Py}$	CF_3
LUMO [eV]	-2.01	-1.80	-1.79	-1.71	-1.88	-2.22	-2.22	-2.21	-2.11	-2.73	-2.56	-2.11	-2.32	-2.72
HOMO [eV]	-6.54	-6.20	-6.16	-6.13	-6.28	-6.62	-6.58	-6.55	-6.43	-6.96	-6.98	-6.05	-6.25	-7.28
Eg [eV]	4.53	4.40	4.37	4.42	4.40	4.40	4.36	4.34	4.32	4.23	4.42	3.94	3.93	4.56

For the screening of R^1 , the substituent R^2 was fixed as CH_3 , then geometry optimization and population analyses were performed. The results that the energy levels of HOMO and LUMO and E_g of sydnone **15-27** were shown in Table 2. Introducing electron-donating groups as R^1 , the HOMO energy levels of sydnone **15** and **18** were lower than that of **16** and **17**. It was notable that the LUMO level of **18** was not lowered, therefore **18** gave largest E_g (4.80 eV) among all calculations. Sydnone **19-22** had halogen group elements as R^1 and the E_g of these sydnone became reduced as increasing atomic number. The HOMO energy levels were increased gradually as well as the LUMO energy levels were decreased considerably in **19-22**. The shapes of HOMO of **19-22** were similar to that of **1**, however, the LUMO were spread around the halogen atoms except **19**. As an example, the shapes of HOMO and LUMO of **22** were shown in Figure 4. The LUMOs of **20**, **21**, and **22** were corresponding with the anti-bond orbital between nitrogen and halogen atoms. The energy levels of σ^* orbital were calculated using NBO program to give -0.81 (N-Cl σ^* bond of **20**), -2.29 (N-Br σ^* bond of **21**), and -2.35 (N-I σ^* bond of **22**) eV, respectively, and these order of energy levels was the same the order of LUMO levels of **20** (-2.95 eV), **21** (-3.73 eV), and **22** (-4.06 eV). By introducing electron-withdrawing groups, the LUMO energy levels of **23-27** were reduced and E_g also became lower.

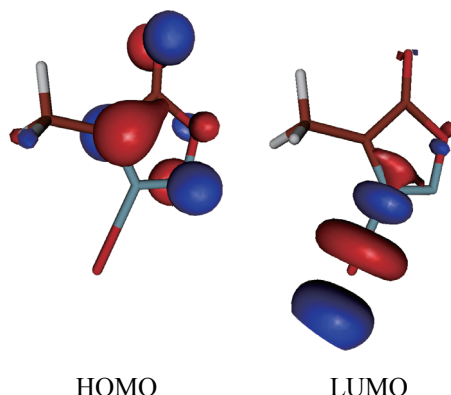


Figure 4: The shapes of HOMO and LUMO of **22**

Table 2: HOMO and LUMO energy levels and E_g of the substituted sydnone having CH_3 group as R^2 .

Sydnone	15	16	17	18	19	20	21	22	23	24	25	26	27
R^1	H	^iPr	^tBu	$(\text{CH}_3)_3\text{Si}$	F	Cl	Br	I	$-\text{COCH}_3$	$-\text{CO}_2\text{CH}_3$	$-\text{C}_6\text{H}_5$	-2-Py	CF_3
R^2	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3
LUMO [eV]	-2.08	-1.68	-1.60	-1.64	-2.37	-2.95	-3.73	-4.06	-2.78	-2.84	-2.10	-2.53	-2.78
HOMO [eV]	-6.39	-6.06	-6.01	-6.44	-6.95	-6.68	-6.59	-6.41	-6.45	-6.38	-6.08	-6.08	-6.80
E_g [eV]	4.31	4.38	4.41	4.80	4.59	3.73	2.86	2.35	3.67	3.54	3.98	3.54	4.02

For the detail analyses of substituent effect, several natural charges were calculated by NBO program and sum of natural charge of R^1 , R^2 , and sydnone rings moieties were shown in Table 3. Make a comparison between **2**, **10**, and **14**, all the natural charges of sydnone ring were about -0.3 and $\text{CH}_3(R^1)$ group of **2** was almost neutral. Introducing electron-withdrawing group to R^2 , the natural charges of $\text{CH}_3(R^1)$ groups of **10** and **14** were changed to *ca* +0.3.

Table 3: Sum of Natural Charge of R¹, R², and sydnone ring moieties.

Sydnone	1	2	6	10	14	17	18
R ¹	+0.308 (CH ₃)	+0.060 (CH ₃)	+0.318 (CH ₃)	+0.335 (CH ₃)	+0.327 (CH ₃)	+0.337 (^t Bu)	+0.653 ((CH ₃) ₃ Si)
R ²	-0.233 (H)	-0.304 (CH ₃)	-0.306 (F)	+0.027 (-COCH ₃)	+0.007 (CF ₃)	+0.056 (CH ₃)	+0.051 (CH ₃)
Sydnone ring	-0.542	-0.364	-0.012	-0.308	-0.334	-0.393	-0.704

Most of the lost electrons from R¹ were on carbon atom that mainly belonging to 2p_x and 2p_y atomic orbitals. The energy levels of all atomic orbitals of carbon and hydrogen atoms of **14** were decreased than that of **2**. By the population analyses, there were no HOMO and LUMO coefficients on carbon and hydrogens in CH₃ group. It was considered that these energy decreases of atomic orbitals not induced ether decreasing HOMO or LUMO energy levels but stabilizing whole molecule **14**. Therefore, the energy levels of HOMO and LUMO showed parallel change to give similar Eg.

Table 4: Natural Charge, Electronic Population and Energy levels of AO on CH₃ (R²)group.

Sydnone	2		14	
	Natural Charge	Electronic Population (Energy Level of AO [eV])	Natural Charge	Electronic Population (Energy Level of AO [eV])
C	-0.614	2s: 1.086 (-7.59) 2p _x : 1.243 (-3.61) 2p _y : 1.064 (-3.33) 2p _z : 1.211 (-3.49)	-0.369	2s: 1.093 (-9.06) 2p _x : 1.184 (-4.86) 2p _y : 0.853 (-4.17) 2p _z : 1.225 (-4.93)
H ^a	+0.225	1s: 0.774 (+0.30)	+0.232	1s: 0.766 (-0.76)

^a Natural Charge, Population, and Energy level of AO were average of three hydrogen atoms.

Table 5: Natural Charge, Electronic Population and Energy levels of AO on the nitrogen that was substituted R¹.

Sydnone	17		18	
	Natural Charge	Electronic Population (Energy Level of AO [eV])	Natural Charge	Electronic Population (Energy Level of AO [eV])
N	-0.144	2s: 1.185 (-15.30) 2p _x : 1.344 (-8.73) 2p _y : 1.195 (-8.09) 2p _z : 1.392 (-8.34)	-0.435	2s: 1.293 (-16.64) 2p _x : 1.530 (-9.71) 2p _y : 1.183 (-7.60) 2p _z : 1.394 (-8.13)

atom that was substituted by R² was raised. The donated electrons were belonged 2s and 2p_x atomic orbitals and the energy levels of these electronic population increased atomic orbital were decreased as shown in Table 5.

Then the natural charges of each atoms in CH₃(R¹) group of **2** and **14**, electronic populations and energy levels of valence atomic orbital were shown in Table 4 for the analyses of detail electron configuration. By changing R² from CH₃ to CF₃, the electron density on CH₃(R¹) was lowered.

Compare ^tBu group with (CH₃)₃Si group using **17** and **18** in Table 3, (CH₃)₃Si group had large electron-donating ability than ^tBu group. The electron density of sydnone ring of **18** has risen and it may be caused lowering HOMO level. Among the sydnone ring, the electron density of nitrogen

Table 6: Natural Charge, Electronic Population and Energy levels of AO on the carbon that was substituted R².

Syndnone	1	6
	Natural Charge Electronic Population (Energy Level of AO [eV])	Natural Charge Electronic Population (Energy Level of AO [eV])
C	2s: 0.955 (-6.15) 2p _x : 0.925 (-2.77) 2p _y : 1.114 (-2.81) 2p _z : 1.192 (-4.69) -0.208	2s: 0.789 (-5.81) 2p _x : 0.949 (-3.39) 2p _y : 0.654 (-2.62) 2p _z : 1.152 (-5.45) 0.424

strong electron-donating ability; and then the electron density of syndnone ring of **1** was raised to -0.542. In contrast, fluorine has strong electron-withdrawing ability and the electron density of syndnone ring of **6** was considerably less than that of **1**. Contrary to expectation, there were not so much the difference of HOMO and LUMO levels between **1** and **6**. Among the syndnone ring, electron densities of the carbon that was substituted R² were changed significantly, then natural charges, electronic population and energy levels of AO on the carbon of **1** and **6** were collected up in Table 6. Compare **6** with **1**, the energy levels of 2p_x and 2p_z were decreased but the populations of these atomic orbitals were similar. The populations of 2s and 2p_y were decreased but the energy levels of these atomic orbitals were similar. By the reason of these behaviors as above, the electronic perturbation that caused by changing R² were denied.

Although, the substituent effects of syndnone were still partial understanding, we had designed syndnone **19** that has (CH₃)₃Si as R¹ and CF₃ as R². All calculations were performed to **19** and following results, HOMO energy level = -6.89 eV, LUMO energy level = -2.39 eV, and Eg = 4.50 eV, were obtained.

Conclusion

In our computational study, we can propose some syndnone derivatives that were expected to have good properties than **1**. Syndnone **14** and **19** had lower HOMO level and similar Eg than **1**. So **14** and **19** were expected to have excellent oxidation resistance and similar electrical potential window with **1**. Syndnone **18** can be expected good oxidation resistance and wide potential window than **1**, because HOMO level and Eg of **18** were suitable for the desired properties than that of **1**. The study of the substituent effects was not enough but we got some clue as to design the desired molecules. We have planned to synthesize the proposed syndnone derivatives, then measuring the properties of them in the further investigation.

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Similar analyses were performed for syndnone **1** and **6**. Syndnone **1** had CH₃ group as R¹ and hydrogen as R². On the other hand, **6** had fluorine as R² instead of hydrogen. In this case, the electronic perturbation by R² was much influenced to the electronic density of syndnone ring as shown in Table 3. Generally, hydrogen has

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