Effect of Bulky Anion around the Dication on the Electronic Structure and Normal Frequencies in 1,3-Bis(3-methylimidazolium-1-yl)propane Bis(trifluoromethanesulfonyl)imide Ionic Liquid

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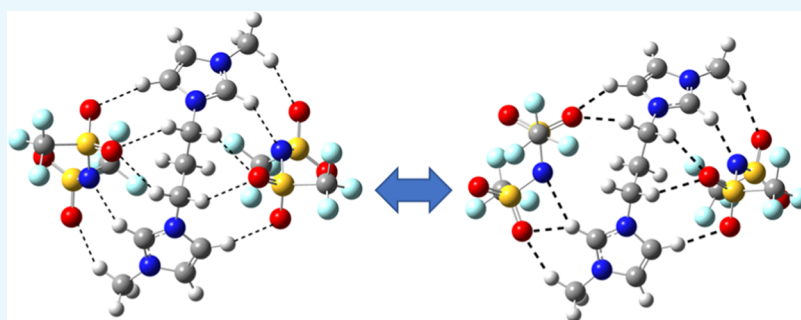
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ABSTRACT: A manifestation of hydrogen bonding between the dication and anions attributed to their relative position of the anions around the cation can influence both the conformational equilibrium and the physical properties of ionic liquids. With this view, we studied the electronic structure and normal frequencies using density functional theory calculations to analyze the hydrogen-bonding interactions in dicationic ionic liquids. The conformers are distinguished based on the hydrogen-bonding sites of the cation and anion. The weak hydrogen bonding between the dication and anions in dication ionic liquids can lead to greater conformational equilibrium compared to the monocation system. Consequences of these interactions for the vibrational spectrum are analyzed to provide an insight into the conformational equilibrium in dicationic ionic liquids at the molecular level.

INTRODUCTION

Ionic liquids (ILs) are composed of an organic cation and an organic or an inorganic anion through hydrogen bond interactions. ILs are one of the popular research areas because of their unique and interesting properties such as low melting points below 100 °C, and they possess superior physical properties such as low vapor pressure, high thermal and chemical stabilities, nonflammability, low melting point, and wide temperature range for synthesis and catalysis.[1] The advantage of ILs is the possibility of changing their properties by varying the nature of the couple cation/anion.[2,3] Similar to monocationic ILs, dicationic ILs (DILs) are popular because of their application in various fields such as replacement of traditional organic solvents, catalysts in organic reactions, and lubricants at high temperature.[4] DILs are a subclass of ILs, characterized by two cationic head groups linked to flexible aliphatic chains. The structures of the DILs can be composed of homoanionic, two identical anions, or hetroanionic, two nonidentical anions, ILs. The physical properties and their potential applications depend on the type and length of the linker between the two cations and/or on the nature of the cation. DILs can be a good candidate for an electrolyte in electrochemical devices such as lithium-ion batteries, fuel cells, dye-sensitized solar cells, and supercapacitors.[2,5,6]

In analogy with the characterization of the ILs, the factors affecting the physicochemical properties of DILs are mainly the relatively higher number of interactions between the anions and cations and the length of alkyl chains. In addition to physical properties, the intermolecular interactions, and consequently, the position of these anions around the dication play an important role in the expansion of the network structures, such as larger clusters of ion pairs in the liquid phase.[7]

Vibrational spectroscopy is an invaluable option for a deeper understanding of the interactions and structures of ILs.[8] IR and Raman spectroscopy are popular and provide information about the nature of the interactions and their consequences in the vibrational spectra. The assignment of frequencies in the experimental spectrum is relatively challenging for a reliable interpretation of vibrational spectra. A common approach is performing quantum chemical calculations to calculate vibra-

tional frequencies to be compared to experimental data.[9−12] The comparison of the vibrational frequencies calculated from quantum calculations can provide microscopic information hidden in the vibrational spectra. Thus, the presence of molecular interactions and the consequent changes in terms of frequency shifts can be revealed using vibrational spectroscopy.

In this paper, we investigate the effect of the position of the bulky Tf_2N anion around the dication on the hydrogen bonding, conformational equilibrium, and the vibrational frequencies of 1,3-bis(3-methylimidazolium-1-yl)propane bis-(trifluoromethanesulfonyl)imide ion pairs. The ILs containing inorganic bis(trifluoromethanesulfonyl)imide (Tf_2N) anion are of great interest because of their use in making hydrolytically stable, "hydrophobic" ionic liquids with low viscosity and high electrical conductivity. The Tf_2N is one of the most widely studied anions due to its unique properties such as charge diffusion and weak cation coordination. The delocalization of the negative charge around the S−N−S core of the Tf_2N anion reduces the strength of cation−anion interactions.[13] This enables the formation of low melting fluid ionic liquids with a wide range of cations such as ammonium, pyridinium, imidazolium, and pyrrolidinium cations.[14,15] The Tf_2N anion can form hydrogen bonding via SN and SO bonds with the cation. In addition to cation−anion distance, the orientation of the bulky Tf_2N anion can also affect the interaction strength. In this respect, it is important to understand the conformation analysis based on the hydrogen-bonding strength and its relevant changes in the vibrational spectrum.

We are interested in gaining insights into how the position of the bulky Tf_2N anion around the dication influences the structure and how it manifests in the vibrational spectrum. Different conformers based on different binding sites between the cation and anion will be studied, and the interaction strength will be rationalized by assignment of the stretching frequency like SO and SN of the anion. Our approach can provide insights into molecular interactions and conformational equilibrium, which can be helpful to experimental scientists.

■ RESULTS AND DISCUSSIONS

Conformation and Energetics. Optimized geometries of cations and anions are displayed in Figure 1. The electronic energy and relative stabilization energy with respect to the lowest energy conformer for all conformers, including the conformation of cation and both anions, are reported in Table 1. Optimized geometries of the first 10 conformers are shown in Figures 2 and 3. Optimized geometries of the C11−C25 conformers are shown in Figures S1−S3. The lowest energy
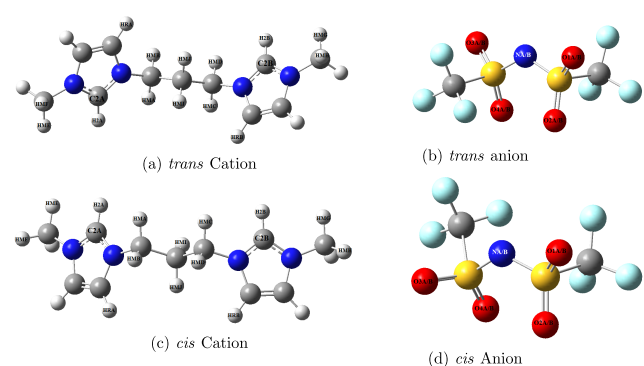
Table 1. Cation, Anion A, Anion B, SCF Electronic (AU) and Relative Stabilization Energies (kJ/mol) of Different Conformers

conformer	cation	anion A	anion B	SCF energy	relative energy
C1	trans	trans	trans	−4303.3023421	0.00
C2	trans	trans	trans	−4303.3016555	1.80
C3	trans	cis	trans	−4303.3015218	2.15
C4	trans	cis	trans	−4303.3013409	2.63
C5	trans	cis	cis	−4303.300968	3.61
C6	trans	cis	trans	−4303.3008833	3.83
C7	trans	cis	trans	−4303.3008656	3.88
C8	trans	trans	trans	−4303.2987148	9.52
C9	trans	cis	trans	−4303.2982696	10.96
C10	trans	cis	cis	−4303.2981795	10.93
C11	trans	trans	trans	−4303.2955766	17.76
C12	cis	trans	trans	−4303.295037	19.18
C13	trans	cis	trans	−4303.2949906	19.30
C14	trans	cis	cis	−4303.2947856	19.84
C15	trans	cis	cis	−4303.2947029	20.06
C16	trans	cis	cis	−4303.294646	20.21
C17	cis	trans	trans	−4303.294627	20.26
C18	trans	cis	trans	−4303.2944598	20.70
C19	cis	cis	cis	−4303.294308	21.09
C20	trans	trans	trans	−4303.2938367	22.33
C21	trans	trans	trans	−4303.2937873	22.46
C22	trans	cis	cis	−4303.29343	23.40
C23	cis	cis	cis	−4303.2903218	31.56
C24	cis	cis	cis	−4303.2899926	32.42
C25	trans	cis	trans	−4303.2890723	34.84

(a) C1

(b) C2

(c) C3

(d) C4

(e) C5

(f) C6

Figure 2. Optimized geometries of C1−C6 conformers.

(a) *trans* Cation

(b) *trans* anion

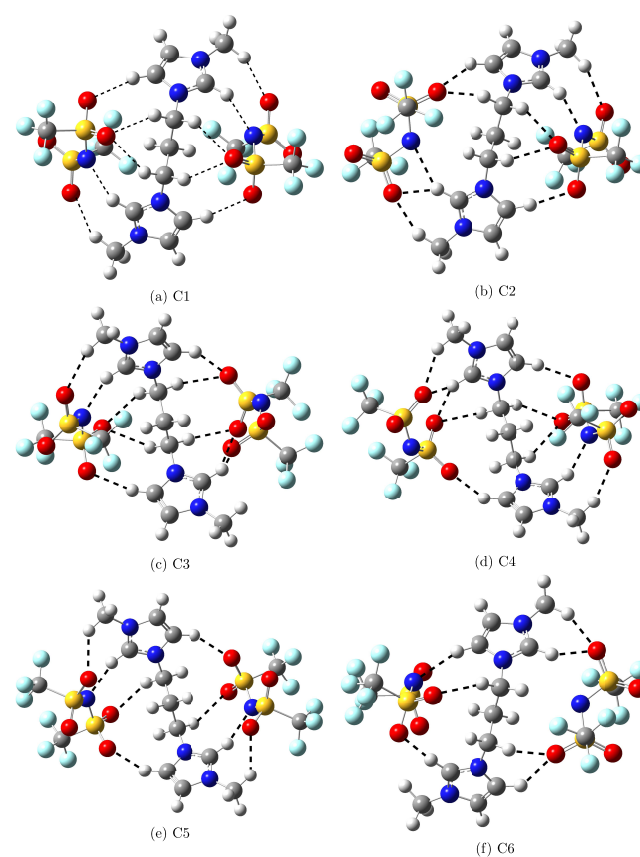(c) *cis* Cation

(d) *cis* Anion

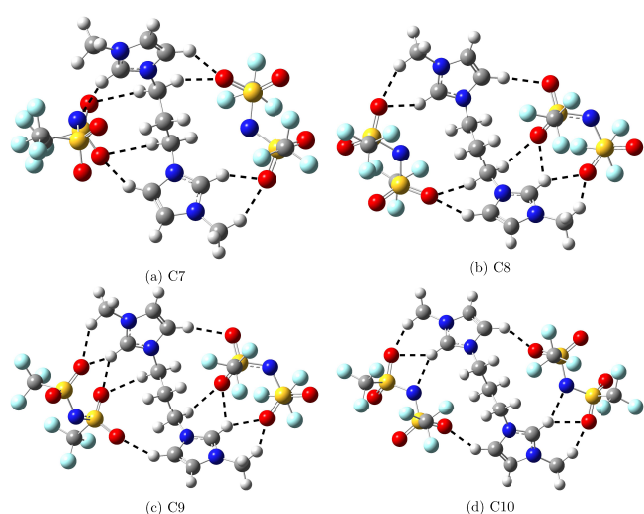**Figure 1.** Optimized geometries of cation and anion conformers.

Figure 3. Optimized geometries of C7−C10 conformers.

conformer adopted trans conformation of the cation and also trans conformation for both anions. The relatively different orientation of anions is predicted toward the cation in cis and trans conformers. Two anions are oriented in such a way as to minimize the repulsion of CF3 groups toward the cis conformer of the cation. This orientation of anions significantly affected the conformer stabilization of energy. The first 10 lowest energy conformers preferred the trans conformation of cation compared to the cis conformation. The trans conformation of the anion is relatively preferred over cis conformation in the first 10 lowest energy conformations. Conformers 1, 2, and 9 have trans conformations in the cation as well as in both anions. Thus, the orientation of the cation and anion in DILs plays an important role in the stabilization of conformation.

Hydrogen Bonding. We studied different conformers based on hydrogen-bonding sites and the orientation of ions, cation, and anion of DILs. Here, we characterized the hydrogen bonding by the distance between the hydrogen of the CH bonds and the electronegative atoms, nitrogen, and oxygen of the anion, if it is less than or equal to 2.5 Å. Hereafter, we will refer to the hydrogen atom attached to the ring carbon atom between two nitrogen atoms as C_2H. The C_2H bond is relatively polar

compared to the other CH bonds of the cation and can form a relatively stronger hydrogen bond with the anion compared to the rest of the CH bonds.[16] Here, we discussed the hydrogen-bonding analysis of the first 10 lowest energy conformers. The selected hydrogen-bonding distances of the C1−C10 conformers are compared in Tables 2 and 3. The C_2H can form a stronger hydrogen bond through nitrogen and oxygen atoms compared to the fluorine of the anion. The conformers exhibiting the $C_2H \cdots N$ interactions are lower in energy compared to the $C_2H \cdots O$ interactions. For example, the C1 and C2 conformers have two $C_2H \cdots N$ interactions, one from each anion, and the C2 conformer has an additional one $C_2H \cdots O$ interaction compared to the C1 conformer. The distance for $C_2H \cdots N$ interactions in the C1 conformer is relatively similar, whereas one $C_2H \cdots N$ interaction in the C2 conformer is relatively strong and another is relatively weak compared to those in the C1 conformer. The difference in the strength of interactions in terms of distance is due to the orientation of anions toward cations. The angle in both C-$C_2H \cdots N$ interactions in the C1 conformer is 147.5°, whereas the angles for C-$C_2H \cdots N$ are 143.1 and 153.2° in the C2 conformer. Out of the two interactions in the C2 conformer, one of the interactions is close to linearity, and the other interaction is far from linearity compared to the interactions in the C1 conformer. Thus, the conformer stabilization depends on both hydrogen-bonded interactions and the orientation of anions toward the cation. In addition to the $C_2H \cdots N$ interaction, the $C_2H \cdots O$ interaction is also predicted in the C2 conformer.

Among the first 10 conformers, stronger $C_2H \cdots O$ interactions are predicted in the C6 conformer compared to those interactions in the first two lowest energies. The hydrogen bond through C_2H is stronger compared to the hydrogen of CH2 groups. These weak interactions become important for conformer stabilization when the relative energy difference is very small. Here, the stabilization of the conformer is also governed by the hydrogen-bonding interactions through CH2 groups. In addition to stabilization, the hydrogen-bonding interactions through the CH2 group help the bulky anion-like Tf2N in stabilizing around the cation. As expected, the increase in the C_2H bond distance of the cation and SN and SO bonds of the anion participating in the interactions is observed in all of the conformers. The change in distance compared to free cation and

Table 2. Selected Hydrogen-Bonded Distance between Ring Hydrogen of the Cation and Anion (Å) in C1−C10 Conformers

		C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
H2A	NB					2.132		2.079			2.331
H2A	NA	2.179	2.483								
H2A	O1A										
H2A	O2A			2.159	2.223		2.026			2.266	
H2A	O4A			2.379	2.169					2.143	
H2A	O3A										2.175
H2A	O1B		2.076								
H2A	O3B								2.052		
H2B	NB	2.182	2.112								
H2B	NA			2.129	2.144	2.132					2.330
H2B	O1A										
H2B	O2A								2.082		
H2B	O4A								2.312		
H2B	O2B									2.320	
H2B	O4B									2.082	
H2B	O3B					2.048	2.058				2.177

Table 3. Selected Hydrogen-Bonded Distance between Alkyl Hydrogen of the Cation and Anion (Å) in C1−C10 Conformers

		C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
HMA	O2A			2.441	2.383					2.444	
HMA	O4A										
HMA	O3A					2.355		2.492			
HMA	O3B	2.382									
HMB	O3A	2.384	2.376								
HMB	O1B								2.453		
HMB	O3B			2.375	2.372						
HMC	O1A			2.477			2.327				
HMC	O4A							2.429			
HMC	O1B								2.491		
HMC	O3B	2.386	2.459								
HMD	O4A								2.465		
HMD	O3A	2.383	2.359								
HMD	O2B									2.462	
HMD	O3B			2.385	2.363	2.356					
HRB	NB						2.340				
HRB	O1A			2.227	2.206					2.250	2.143
HRB	O4A					2.168		2.279			
HRB	O1B								2.170		
HRB	O4B	2.257									
HRB	O3B		2.157								
HRA	O4A	2.257	2.200								
HRA	O3A								2.243		
HRA	O1B						2.171	2.181		2.336	2.143
HRA	O4B			2.246	2.246	2.168					
HMG	O1A	2.264	2.252								
HMG	O2A								2.304		
HMG	O1B				2.255	2.391					
HMG	O4B									2.317	
HMG	O3B						2.352	2.308			2.218
HMH	O1B			2.258							
HME	O1A					2.390					
HME	O4A				2.272					2.251	
HME	O1B		2.273								
HME	O3B								2.274		
HMF	O3A										2.219
HMF	O1B	2.264									

anion can be correlated with the strength of the interactions (Tables 4 and 5).

Vibrational Frequency Analysis. Vibrational frequency analysis can provide microscopic information about the structure and the ionic interactions of the system. The consequences of the molecular interactions manifest in the vibrational spectrum and result in the frequency shifts of the normal vibrations. The interpretation of these interactions may be a difficult task in the experimental spectrum. A good approach is to perform quantum chemical calculations to calculate the normal vibrations and compare those with the experimental spectrum. This combined approach of comparison of simulated vibration spectra with the experiment helps in assigning the vibrations of experimental spectra.[9−12,17−19]

The population of the conformers can influence the physical properties of ILs and is mainly distinguished based on the interanionic distance and orientation of the ions of the ionic liquids. These two factors influence the frequency shifts of the characteristic stretching vibrations such as C_2H of the cation or SO and SN of the anion. With this view, we discussed the selected stretching vibrations such as CH of the cation and SO and SN of the anion of the first four conformers to understand

the consequences of the molecular interactions to the vibrational spectrum. We compared these vibrations in Table 6. The intense vibrations like CF stretch, CH bending such as CH2 or CH3 rocking or wagging, etc., are not discussed in this paper. The CF bond does not play an important role in stabilization energy in the present study and can form relatively weak interaction with the CH bonds on the cation. The analysis of these vibrations does not provide insight into the conformational equilibrium in terms of the molecular interactions between the anion and cation.

The CH ring vibrations, C2B-H13 and C2A-H3, are coupled in the C1 conformer, whereas these vibrations are split in the C2−C4 conformers. As mentioned earlier, the C_2H bond makes a stronger hydrogen bonding with the anion compared to the other CH bonds, which results in a frequency shift to a lower wavenumber, red shift, compared to the corresponding vibrations in the free state. These stretching vibrations can be correlated with the strength of the interactions. A larger red shift and blue shift are predicted in the C3 conformer for C2B-H13 and C2A-H3 stretching vibrations, respectively, compared to those vibrations in the C1, C2, and C4 conformers. The overall relative strength of hydrogen bonding between the C2B-H13

Table 4. Bond Distances between Sulfur and Nitrogen of the Anion (Å) in C1−C25 Conformers

	S35NB	S36NB	S50NA	S51NA
C1	1.626	1.631	1.626	1.631
C2	1.625	1.632	1.627	1.632
C3	1.608	1.615	1.625	1.633
C4	1.603	1.620	1.626	1.632
C5	1.634	1.617	1.634	1.617
C6	1.619	1.627	1.631	1.627
C7	1.628	1.620	1.631	1.627
C8	1.597	1.627	1.631	1.628
C9	1.603	1.619	1.627	1.598
C10	1.623	1.629	1.623	1.629
C11	1.604	1.617	1.625	1.600
C12	1.604	1.631	1.614	1.610
C13	1.621	1.629	1.632	1.628
C14	1.623	1.606	1.628	1.593
C15	1.634	1.620	1.622	1.628
C16	1.616	1.614	1.618	1.613
C17	1.634	1.601	1.620	1.637
C18	1.635	1.613	1.630	1.593
C19	1.628	1.625	1.623	1.616
C20	1.597	1.627	1.615	1.605
C21	1.621	1.637	1.617	1.640
C22	1.626	1.613	1.629	1.592
C23	1.611	1.606	1.595	1.621
C24	1.614	1.603	1.596	1.623
C25	1.599	1.621	1.595	1.632

and C2A-H3 bonds is relatively small in the C1, C2, and C4 conformers compared to the C3 conformer, resulting in coupled stretching vibrations of these bonds in the C1, C2, and C4 conformers. The interaction strength based on the intermo-lecular distance between the anion and cation is relatively similar in the C2B-H13 and C2A-H3 bonds in C1, C2, and C4 conformers compared to the C3 conformer. One of the interesting properties of vibrational spectroscopy is that the manifestation of molecular interactions can be predicted by analyzing a frequency shift of the stretching vibration. The number of molecular interactions in the dication system is relatively higher than that in the monocation system. One can expect more conformation equilibrium in the dication system compared to the monocation system.

It should be mentioned here that the CH bending vibrations are intense and do not show a significant frequency shift in terms of wavenumber within a conformer. For example, the CH ring rocking vibration is predicted in the range of 1335−1328 cm^{-1}. These vibrations are intense in all of the conformers and cannot be used to distinguish the presence of conformers, in contrast to the C_2H vibrations. No significant change is predicted for the SO stretching vibrations in the present study because the $C_2H\cdots N$ interactions are predicted to be more dominating compared to the $C_2H\cdots O$ interactions. On the other hand, the doublet for the SN stretching vibration in C1 (988 and 984 cm^{-1}) and C2 (987 and 979 cm^{-1}) conformers is separated by 4 and 8 cm^{-1}, respectively, whereas this separation increases to 24 cm^{-1} in C3 and C4 conformers (1011 and 987 cm^{-1}). Thus, the assignment of molecular vibration can provide useful insight into conforma-tional equilibrium and the hydrogen bonding in dication ionic liquids.

■ CONCLUSIONS

The effect of the bulky anion around the dication on the structure and normal vibrations is studied by employing density functional and B3LYP calculations. Different conformers are simulated based on the conformers, cis and trans, of the cation

Table 5. Bond Distance between Sulfur and Oxygen of the Anion (Å) in C1−C25 Conformers

	S35O4A	S35O3A	S36O1A	S36O2A	S50O4B	S50O3B	S51O1B	S51O2B
C1	1.473	1.474	1.471	1.460	1.473	1.474	1.471	1.460
C2	1.472	1.474	1.470	1.460	1.461	1.477	1.479	1.460
C3	1.477	1.481	1.478	1.458	1.473	1.474	1.471	1.460
C4	1.477	1.480	1.480	1.458	1.472	1.474	1.471	1.460
C5	1.474	1.461	1.473	1.472	1.474	1.461	1.473	1.472
C6	1.473	1.478	1.475	1.463	1.460	1.480	1.477	1.461
C7	1.473	1.467	1.474	1.468	1.460	1.479	1.477	1.461
C8	1.482	1.469	1.458	1.482	1.460	1.480	1.476	1.460
C9	1.476	1.481	1.480	1.458	1.482	1.458	1.469	1.482
C10	1.479	1.461	1.460	1.478	1.479	1.461	1.460	1.478
C11	1.483	1.468	1.458	1.482	1.479	1.459	1.473	1.482
C12	1.476	1.476	1.477	1.462	1.484	1.460	1.460	1.482
C13	1.479	1.463	1.461	1.475	1.459	1.477	1.479	1.461
C14	1.480	1.476	1.484	1.458	1.459	1.483	1.482	1.468
C15	1.475	1.459	1.459	1.478	1.479	1.461	1.459	1.479
C16	1.473	1.478	1.474	1.469	1.479	1.481	1.477	1.464
C17	1.473	1.461	1.478	1.477	1.460	1.479	1.476	1.461
C18	1.476	1.463	1.473	1.475	1.459	1.482	1.480	1.469
C19	1.476	1.460	1.460	1.476	1.474	1.467	1.468	1.476
C20	1.483	1.468	1.457	1.483	1.482	1.458	1.459	1.482
C21	1.461	1.480	1.474	1.462	1.460	1.481	1.474	1.461
C22	1.478	1.463	1.480	1.470	1.459	1.482	1.481	1.469
C23	1.461	1.485	1.481	1.459	1.479	1.482	1.479	1.456
C24	1.460	1.484	1.482	1.460	1.480	1.480	1.479	1.457
C25	1.477	1.481	1.480	1.457	1.485	1.468	1.459	1.475

Table 6. Normal Vibration (in cm^{-1}) and Intensity of Selected Bonds in the Cation and Anion of C1–C4 Conformers

vibrations	C1	C2	C3	C4
CRB-HRB + CRA-HRA stretch	3246 (223)			
CRB-HRB stretch		3289 (120)	3272 (101)	3283 (107)
CRA-HRA stretch		3181 (202)	3247 (149)	3194 (281)
C2B-H2B + C2A-H2A Stretch	3212 (468)	3233 (422)		3239 (343)
C2B-H2B Stretch			3183 (293)	
C2A-H2A Stretch			3282 (172)	
CH ring rocking	1335 (442)	1334 (275)	1333 (356)	1333 (335)
CH ring rocking	1331 (48)	1332 (51)	1329 (48)	1330 (62)
CH ring rocking	1329 (294)	1328 (615)		
		1319 (89)		
SO$_2$ asymm stretch	1284 (191)	1282 (181)	1283 (199)	1283 (182)
SO$_2$ asymm stretch	1282 (182)			
C$_2$H ring rocking			1223 (71)	
		1213 (75)	1215 (73)	1213 (26)
	1195 (110)	1195 (66)	1196 (148)	1194 (158)
	1193 (72)	1190 (108)	1193 (85)	1193 (104)
		1189 (227)		1189 (152)
SO$_2$ symm stretch	1105 (81)	1107 (212)	1107 (101)	1107 (164)
	1104 (289)	1100 (237)	1105 (445)	1105 (511)
	1092 (47)	1093 (321)	1092 (203)	1092 (176)
	1091 (427)	1090 (95)	1092 (203)	1090 (481)
SN asymm stretch	988 (790)	987 (589)	1011 (287)	1011 (251)
	984 (244)	979 (454)	987 (504)	987 (512)
C$_2$H wag	920 (94)	927 (56)	927 (43)	921 (50)
			901 (29)	914 (24)
SN symm strech	713 (151)	716 (115)	716 (53)	716 (53)

and anion and the hydrogen-bonding sites of the cation and anion. The trans conformation of the anion, as well as the cation, are predicted in the lowest energy conformer. Our simulation results predicted a conformational equilibrium between different dication ionic liquid conformers due to weak hydrogen-bonding interactions between the cations and anions. Our theoretical studies predicted that vibrational frequencies can be used to probe the conformational equilibrium in the experiment and can also be used as a tool for the frequency assignment of the vibrational spectrum. The C$_2$H and SN stretching vibrations are important to distinguish between conformers, whereas other intense vibrations are relatively less sensitive to molecular interactions. It would be interesting to study the dynamics of hydrogen bonding in a dication system using classical molecular dynamics simulations in the future.

■ COMPUTATIONAL METHOD

Two cation conformers based on the orientation of the C$_2$H proton, namely cis and trans, are investigated in the present work. The cis conformation has the C$_2$H proton of both rings on the same side, whereas the C$_2$H protons of these rings are on the opposite side in the trans conformation. Hybrid density functional theory incorporating Becke's three-parameter exchange with the Lee, Yang, and Parr (B3LYP)[20,21] correlation functional was employed for conformer optimization using the Gaussian 16 program,[22] with the internally stored 6-31G(d,p) basis set. Stationary point geometries were characterized as the saddle points or local minima on the potential energy surface by examining the number of imaginary frequencies and the eigenvalues of the Hessian matrix. The cis cation conformer is relatively more stable by 0.27 kJ/mol than the trans conformation of the cation. Similar to the cation conformer,

we also investigated the cis and trans conformations of the anion based on CF$_3$ group orientations.[14]

We simulated different conformers based on the hydrogen-bonding sites of the cation and anion. The CH bond of C$_2$H is relatively more polar compared to the other CH bonds of the cation, which plays an important role in stronger cation–anion interactions. Like the cation, the SO and SN bonds can form relatively stronger hydrogen bonding compared to CF$_3$ groups of the anion. With this view, we considered these binding sites of the cation and anion in building the initial structure of the conformer. As stated earlier, the cation and the anion both exhibit two conformers. We considered several conformer possibilities based on the cation and anion conformation, for example, two trans anions around cis cation or two cis anions around trans cations or one cis and one trans around the cis or trans conformer of the cation. One of the motives to study different conformers is to understand a conformational equilibrium in terms of the hydrogen bonding between the cation and anion at the molecular level.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03017.

Optimized geometries of the C11–C25 conformers are shown in Figures S1–S3; optimized coordinates of C1–C25 conformers in Å (PDF)

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Notes

The authors declare no competing financial interest.

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