

Spectroscopic and *ab initio* characterization of the conformational states of the bis(perfluoroethanesulfonyl)imide anion (BETI[−])

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Ab initio calculations were combined with infrared and Raman studies to spectroscopically distinguish the two conformers of the BETI[−] or bis(perfluoroethanesulfonyl)imide anion, [N(SO₂C₂F₅)₂][−], as was previously done for [N(SO₂CF₃)₂][−], the TFSI[−] anion. BETI[−] is predicted to exist, as does TFSI[−], in two conformational states of C₂ and C₁ symmetries, the former being more stable by about 6 kJ mol^{−1}. This conformational isomerism produces weak Raman splittings that can be resolved only at low temperatures. Thus, solutions of LiBETI with glymes cooled down to 113 K exhibit a very intense Raman doublet at ~745–740 cm^{−1} characteristic of a quenched conformational equilibrium between the C₂ and C₁ conformers. Annealing of the (G3)₂:LiBETI solvate, where G3 is triglyme, leads to an ordered crystalline phase with all the anions in the C₂ conformation, as in the reference salt Me₄NBETI. This conclusion cannot be extended to all the systems in which the BETI[−] anion interacts weakly with the cation, however, since the diglyme solvate, (G2)₂:LiBETI, contains both C₁ and C₂ anion conformers (in 2:1 ratio) at low temperatures independent of the sample's thermal history. The conformational splittings are larger in infrared, as illustrated by two absorption bands at 601 and 615 cm^{−1} associated with the C₂ and C₁ anion conformers, respectively. It is possible to follow the relative intensities of these bands in a LiBETI solution with diglyme above room temperature up to 387 K. The C₂ conformer is found to be more stable than C₁ by 4.7 ± 0.7 kJ mol^{−1}. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: vibrational spectroscopy; *ab initio* calculations; conformation; bis(perfluoroethanesulfonyl)imide

INTRODUCTION

The [N(SO₂C₂F₅)₂][−] anion, abbreviated as BETI[−] for bis(perfluoroethanesulfonyl)imide, has properties very similar to the parent TFSI[−] or [N(SO₂CF₃)₂][−] anion, i.e. high conformational flexibility and strong delocalization of the negative charge. A study of these properties using *ab initio* calculations and vibrational spectroscopy has recently been reported¹ on TFSI[−]. A similar study is presented here on BETI[−].

The BETI[−] anion is a relatively recent addition to the salts used in electrochemistry. The lithium salt, LiBETI, is easily dissociated in polar solvents or polymers to give lithium-conducting electrolytes^{2–5} and the bulky BETI[−] anion can also be one of the constituents of ionic liquids.^{6,7} Johansson

*et al.*⁸ have already predicted the existence of two conformers of C₂ and C₁ symmetry for BETI[−] (Fig. 1); the former is reported to be more stable by only 5.4–7.3 kJ mol^{−1}. Johansson *et al.*⁸ also measured IR spectra for the LiBETI salt in poly(ethylene oxide) and reported a computed vibrational assignment based on a potential energy distribution (PED) calculation together with IR and Raman intensities for the C₂ conformer and for the corresponding acid HBETI.⁸ Later Capiglia *et al.* proposed a qualitative vibrational assignment of this anion,⁹ but the two conformers have never been identified spectroscopically. In addition, as previously emphasized for TFSI[−], it is very important to distinguish spectral perturbations induced by ionic association from those due to conformational equilibrium.¹ Very few crystalline structures with the BETI[−] anion have as yet been isolated and studied by X-ray diffraction techniques.¹⁰ To the best of our knowledge, the tetramethylammonium salt, Me₄NBETI, is the only

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example of a reference compound in which the uncoordinated 'free' anion is known to be in a C_2 conformation (Fig. 1(c) and Table 1).¹¹

We have undertaken a classical approach to the $BETI^-$ conformational isomerism consisting of a combination of *ab initio* calculations of the 'free' conformers along with infrared (IR) and Raman spectroscopy of the reference salt Me_4NBETI , and of dilute solutions of $LiBETI$ as a function of temperature. Dilution of $LiBETI$ in an adequate solvent is expected to produce only solvent-separated ion-pairs (SSIPs) for this weakly associating salt. The respective fraction of the two uncoordinated anion conformers may then be examined as a function of temperature provided the anion conformers have well-separated IR or Raman components.

EXPERIMENTAL

Using starting structures from the previous work,⁸ geometry optimizations as well as subsequent numerical wavenumber calculations for the C_2 and C_1 conformers were made using Becke's three-parameter hybrid method with the Lee–Yang–Parr correlation functional (B3LYP).^{12–14} The Pople-type basis set 6–31G** was chosen, as the

Table 1. Selected bond lengths $R(\text{\AA})$, bond angles $A(\text{degrees})$ and dihedral angles $D(\text{degrees})$ for the $BETI^-$ anion. The atoms are numbered as shown in Fig. 1. The calculated energies and enthalpy difference between the two conformers are also reported

	Calculated values		Exp. values
	C_1	C_2	Me_4NBETI
$R\ N(1)S(2)$	1.612	1.618	1.578
$R\ N(1)S(3)$	1.619	1.618	1.584
$R\ S(2)O(4)$	1.466	1.466	1.424
$R\ S(2)O(6)$	1.469	1.470	1.431
$R\ S(2)C(5)$	1.887	1.888	1.840
$R\ S(3)C(9)$	1.888	1.888	1.848
$R\ C(5)C(12)$	1.545	1.544	1.528
$R\ C(5)F(13)$	1.353	1.352	1.340
$A\ S(3)N(1)S(2)$	125.4	124.2	124.0
$A\ N(1)S(2)C(5)$	104.8	101.6	102.3
$A\ N(1)S(3)C(9)$	98.8	101.6	102.0
$A\ O(4)S(2)O(6)$	119.2	119.0	118.5
$A\ S(2)C(5)C(12)$	115.0	114.7	115.6
$A\ F(21)C(5)F(13)$	108.7	108.7	108.3
$D\ S(3)N(1)S(2)C(5)$	82.4	91.5	–91.0
$D\ S(2)N(1)S(3)C(9)$	–123.3	91.5	–95.1
$D\ N(1)S(2)C(5)C(12)$	–177.0	–167.2	–179.6
$D\ N(1)S(3)C(9)C(11)$	168.9	–167.2	177.1
Energy (au)	–2302.767596	–2302.769894	–
$\Delta H\ (\text{kJ mol}^{-1})$	+5.95	0	–

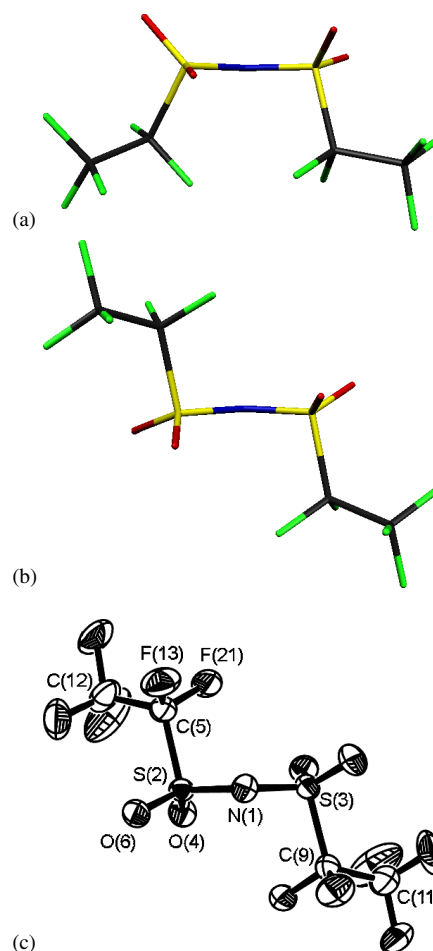


Figure 1. Calculated $BETI^-$ structures for the C_1 (a) and C_2 (b) conformers, and experimental $BETI^-$ C_2 conformer in the Me_4NBETI crystal (c). Some geometrical parameters are reported in Table 1.

B3LYP/6–31G** combination was shown to provide realistic molecular geometries and vibrational wavenumbers for the parent $TFSI^-$ anion.¹ The calculations were done using the Gaussian03 program package.¹⁵ In order to quantify the contributions to the observed vibrational modes, the PED matrix was computed for both C_1 and C_2 conformers, using the same set of internal coordinates. These calculations were made using GAMESS¹⁶, with the minimum energy structures differing somewhat owing to a different implementation of the B3LYP functional. However, this should not be crucial to the PED matrices.

The $LiBETI$ salt was generously provided by 3M. The Me_4NBETI salt was synthesized by a metathesis reaction between Me_4NCl and $LiBETI$ in water and purified by recrystallizing three times in hot deionized water. Both the $LiBETI$ and Me_4NBETI salts were dried by heating under vacuum overnight before use. The structure of the Me_4NBETI crystal was determined by Victor G. Young, Jr. from the X-ray Crystallographic Laboratory at the

University of Minnesota.¹¹ The solvents were purchased from Sigma-Aldrich and kept over 4 Å molecular sieves. Glymes $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ are denoted G2 and G3 for $n = 2$ and 3, respectively. All products were stored and handled in an argon-filled dry box. Solutions of LiBETI in G2 or G3 were also prepared inside the dry box.

The IR experiments were performed using a Nicolet Nexus spectrometer with a resolution of 4 cm^{-1} and accumulation times of about 420 s. The samples were hermetically contained between two cesium iodide windows either as a liquid film or as a nujol or fluorolube mull for the solids. Reference spectra of the pure solvent, nujol or fluorolube, were also recorded to enable subtraction of their contribution. The Raman spectra were recorded, as previously described for TFSI[−], with a Labram HR800 Jobin-Yvon spectrometer equipped with a krypton ion laser (752.45 nm), an air-cooled CCD detector (ANDOR) and a 600 grooves/mm grating.¹ The laser power was generally 20 mW at the sample and the spectral resolution was 2 cm^{-1} . The samples were contained in glass tubes, and accumulation times were between 200–600 s. This experimental setup allowed the reported spectra to be acquired with a minimum of fluorescence. The spectra below room temperature were recorded with a Dilor cryostat flushed with a stream of gaseous nitrogen.

RESULTS AND DISCUSSION

Theoretical predictions

Selected geometrical parameters of the two conformers of the BETI[−] anion are reported in Table 1 and compared to the corresponding Me₄NBETI experimental values determined by X-ray diffraction at 173 K. As shown in the projections of Fig. 1, the C₁ and C₂ conformers differ essentially by the position of the CF₂–CF₃ groups with respect to the SNS plane: the S(3)N(1)S(2)C(5) and S(2)N(1)S(3)C(9) torsional angles are 82.4 and -123.3° for C₁, respectively; they are both equal to 91.5° for C₂. In Me₄NBETI they are 91 and 95° , respectively (Table 1). Thus, Me₄NBETI can be considered as a reference compound for the C₂ conformation when the anion has only a weak interaction with cations. We also note in Table 1 the excellent agreement between the experimental and calculated S–N–S angle for the C₂ conformation, a parameter highly sensitive to the computational level applied.^{8,17}

If we consider that a *trans* (t) conformation is associated with torsion angles of $180 \pm 45^\circ$, a *cis* (c) conformation with $0 \pm 45^\circ$ and a *gauche* (g⁺) or *gauche* minus (g[−]) conformation with the remaining angular range, the C₁ conformer can adopt the tg⁺g[−]t or tg[−]g⁺t forms and the C₂ conformer the tg⁺g⁺t or tg[−]g[−]t forms. Therefore, both conformers have a multiplicity of 2 and the observed IR or Raman intensities are simply proportional to the populations and to the absorption (IR) or scattering cross sections (Raman) of the considered vibration for a given conformer. All the calculated wavenumbers and IR and Raman intensities, for both conformers, are reported in Table 2. The present

results mostly agree with the previously reported ones,⁸ but the latter did not include the C₁ data, and the effect of conformational isomerism on the vibrational spectra was not addressed.

Raman spectra of Me₄NBETI

The calculated Raman spectra are first compared to the experimental spectra of Me₄NBETI. The crystal structure of this salt was determined at 173 K, and no information is yet available about the eventual conformational changes as a function of the temperature, driven for example by order–disorder phase transitions. Therefore, Raman spectra have been recorded in the 298–113 K temperature interval. It is found that the spectra are quite reproducible at a given temperature, independent of the thermal history of the sample. In addition, all the spectral features vary smoothly as a function of temperature; they do not exhibit any discontinuity that could be associated with a phase transition. This agrees with the DSC data that indicates phase transitions at 343 and 387 K before the salt melts at 405 K.¹¹ A comparison between the calculated and experimental Raman spectra is performed in two spectral ranges (Figs 2 and 3). Let us first consider the most intense Raman line at about 740 cm^{-1} (Fig. 2). This line, due to an expansion/contraction of the entire anion,^{1,8} is calculated at 705.5 and 712 cm^{-1} for the C₁ and C₂ conformers, respectively. In an earlier calculation,⁸ this band was obtained at as high as 810 cm^{-1} for the C₂ conformer, probably owing to the modest HF/6–31G* level used. Between 298 K and 113 K, the Me₄NBETI salt exhibits a relatively narrow line, the position and FWHM of which move continuously and reversibly from 741 to 743 cm^{-1} and from 7.4 to 3.5 cm^{-1} , respectively (Fig. 2). One can conclude that the BETI[−] anion adopts the C₂ conformation over the temperature range examined. The other observed line in this region, at 754 cm^{-1} , is produced by the symmetric stretching vibration $\nu_s(\text{C}_4\text{N})$ of the Me₄N⁺ cation.

The same kind of comparison can be made in the $1200\text{--}1120\text{ cm}^{-1}$ spectral range (Fig. 3). Indeed, another intense doublet is calculated at $1130.4/1124.2\text{ cm}^{-1}$ for the C₁/C₂ conformers, respectively (Table 2). According to the PED matrices, these modes are due to almost pure SO₂ symmetric stretching (C₁: 1130 cm^{-1} 70%, C₂: 1124 cm^{-1} 70%). Rather distinct features for the two conformers also occur at about $1180\text{--}1190\text{ cm}^{-1}$ (associated with almost pure CF₂ stretchings (>80% for both conformers) (Table 2 and Fig. 3). The narrow lines observed at 1137 and 1189 cm^{-1} for Me₄NBETI can be associated with the calculated C₂ components at 1124 and 1176 cm^{-1} , respectively. Note that in Figs 2 and 3 the calculated wavenumbers have been multiplied by an arbitrary factor for a more convenient comparison with the experimental spectra.

Raman spectra of LiBETI in glymes

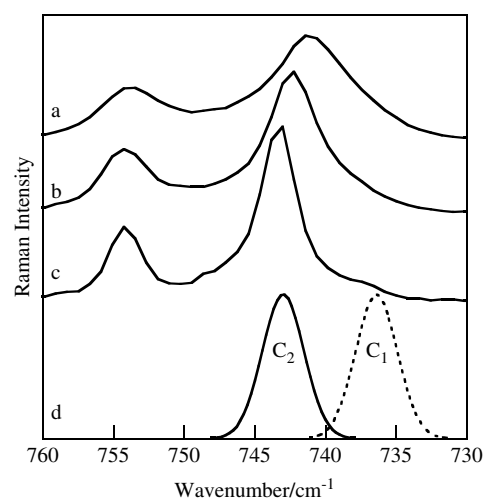
Situations in which the BETI[−] anions are in a relatively 'free' state are provided by LiBETI solvates, where the

Table 2. Calculated wavenumbers and intensities (km mol^{-1} for IR and $\text{\AA}^4 \text{amu}^{-1}$ for Raman)

C ₁ Conformer				C ₂ Conformer			
ν (cm^{-1})	IR	Raman	Sym.	ν (cm^{-1})	IR	Raman	Sym.
13.8	0.3	0.0	A	21.3	0.6	0.0	A
19.9	0.2	0.1	A	31.8	0.9	0.0	A
39.5	0.2	0.0	A	33.0	0.9	0.1	B
47.2	0.1	0.1	A	33.4	0.4	0.0	B
59.1	0.1	0.0	A	57.3	0.2	0.0	A
72.9	0.1	0.2	A	63.5	0.4	0.0	B
104.2	0.1	0.5	A	101.3	0.0	1.7	A
122.5	0.8	0.7	A	128.6	0.9	0.7	A
158.4	0.5	0.3	A	142.5	1.6	0.0	B
172.4	1.0	1.0	A	171.3	0.1	0.4	A
194.9	1.5	0.3	A	198.7	2.1	0.2	A
201.5	0.0	2.9	A	202.7	1.8	0.1	B
203.8	1.4	1.0	A	223.5	0.5	0.0	A
219.5	0.5	0.0	A	223.8	0.6	0.3	B
223.4	0.5	0.1	A	256.5	10.3	0.5	B
262.0	1.8	3.0	A	263.3	0.0	9.5	A
262.5	2.4	6.1	A	272.6	1.6	2.6	B
285.5	0.5	4.8	A	289.1	0.1	6.0	A
308.4	0.9	3.5	A	303.8	11.7	0.2	B
312.4	1.1	2.5	A	316.5	1.9	0.5	B
316.0	0.2	1.4	A	317.5	0.0	1.2	A
361.3	0.3	1.3	A	359.3	1.8	4.3	A
362.5	0.4	1.4	A	362.1	2.7	0.1	B
368.5	4.4	2.6	A	366.0	2.6	1.9	A
393.1	5.8	0.6	A	369.5	1.7	4.0	B
449.6	2.2	1.6	A	444.9	0.0	1.8	A
464.6	1.6	1.3	A	461.4	0.2	1.3	B
494.1	168.6	1.6	A	498.9	137.4	1.2	B
521.3	6.0	1.8	A	520.3	0.0	3.1	A
523.0	17.2	2.0	A	524.5	24.2	0.2	B
543.7	29.6	0.2	A	555.0	0.2	4.1	A
576.8	113.4	1.8	A	579.6	0.7	3.4	A
588.4	10.9	2.2	A	588.9	5.1	0.8	B
589.6	9.2	1.7	A	599.0	335.9	0.1	B
624.0	39.2	0.5	A	609.1	0.2	4.7	A
626.2	80.8	3.4	A	629.6	16.6	0.7	A
637.8	31.2	1.9	A	633.3	7.0	0.8	B
705.5	72.0	24.3	A	711.8	42.8	24.3	A
746.5	11.6	0.4	A	746.9	8.0	0.2	B
754.0	8.7	4.0	A	754.4	0.0	3.8	A
967.7	221.7	0.7	A	966.1	414.4	0.1	B
988.5	61.7	0.7	A	987.9	15.3	2.5	A
1027.5	144.9	1.3	A	1022.3	215.1	0.2	B
1115.2	443.3	3.5	A	1116.0	387.1	0.5	B
1130.4	196.2	15.7	A	1124.2	37.6	15.7	A
1171.0	259.6	3.5	A	1172.3	185.0	0.4	B
1177.3	78.7	3.4	A	1175.7	78.1	7.2	A
1193.3	142.1	0.4	A	1196.7	69.9	1.5	A
1200.0	70.5	1.1	A	1199.7	192.8	0.2	B

Table 2. (Continued)

C ₁ Conformer				C ₂ Conformer			
ν (cm^{-1})	IR	Raman	Sym.	ν (cm^{-1})	IR	Raman	Sym.
1220.8	85.8	6.2	A	1220.1	481.6	0.3	B
1223.0	451.2	3.0	A	1220.9	31.9	11.9	A
1258.4	133.3	0.2	A	1259.3	188.0	0.3	B
1259.7	131.3	0.5	A	1260.0	112.2	0.8	A
1304.5	196.7	6.4	A	1303.6	139.4	5.7	B
1322.8	410.0	6.9	A	1325.7	430.1	5.2	A
1339.6	138.2	1.9	A	1340.7	183.7	0.2	B
1346.3	117.0	8.3	A	1349.7	103.1	9.7	A

**Figure 2.** Comparison of the experimental Raman spectra of Me_4NBETI at 298 K (a), 208 K (b) and 113 K (c) with the calculated spectra of the C_1 (dotted line) and C_2 (solid line) BETI^- conformers (d). The calculated wavenumbers have been arbitrarily multiplied by a scaling factor of 1.044 for a better comparison with the experimental data, and the calculated bands have been given a Gaussian profile of 3.3 cm^{-1} FWHM. The line at 756 cm^{-1} corresponds to the $\nu_s(\text{C}_4\text{N})$ vibration of the Me_4N^+ cation.

Li^+ cation is fully coordinated by organic ligands leaving uncoordinated BETI^- anions as SSIPs. LiBETI solutions in G2 or G3 were studied as a function of the temperature. According to DSC measurements, a crystalline $(\text{G}3)_2\text{LiBETI}$ solvate melts at 271 K and undergoes a solid–solid phase transition at 267 K.¹⁰ The structure of the $(\text{G}3)_2\text{LiBETI}$ solvate is unknown, but the cation is presumably fully solvated by glyme oxygens to make a SSIP with the anion.¹⁰ The phase diagram of $[\text{G}2]/[\text{LiBETI}]$ mixtures also indicates the formation of a crystalline phase with a $(\text{G}2)_2\text{LiBETI}$ composition. This compound melts at 365 K and undergoes a solid–solid phase transition at 244 K.¹⁰ Attempts to elucidate the $(\text{G}2)_2\text{LiBETI}$ crystal structure failed, presumably because

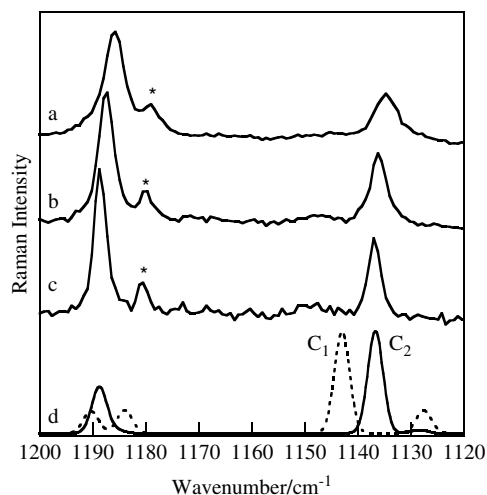


Figure 3. Same as Fig. 2 but in a different spectral range and with a scaling factor of 1.011. The asterisks indicate a line due to the cation. All other experimental and calculated lines come from the BETI^- anion.

the room-temperature, disordered phase was frozen in the quenched crystals at 173 K.¹⁰

Let us first consider the $(\text{G3})_2\text{:LiBETI}$ system. The melted state is characterized by a broad and asymmetric band (Fig. 4(a)). A first cooling, down to 113 K, reveals two main components at ~ 745 and 741 cm^{-1} (Fig. 4(b)). The former is at about the same position as in Me_4NTFSI and can be associated to a C_2 conformational state. The latter, situated at lower wavenumbers by $\sim 4\text{ cm}^{-1}$, can be associated to the C_1 conformational state, in reasonable agreement with the calculated splitting represented in Fig. 4(d). The relative intensities of these two components vary slightly depending upon the cooling rate. Slow cooling ($\sim 20\text{ K min}^{-1}$) produces a slightly larger amount of C_2 conformations than fast cooling (Fig. 4(b)). It appears that comparable quantities of the two conformers have been quenched at low temperature into a metastable amorphous phase. Indeed, annealing up to 223 K and cooling again down to 113 K produce a unique narrow line at 744 cm^{-1} (Fig. 4(c)). Thus, the annealing process has produced a low-temperature, ordered, crystalline phase containing only the C_2 conformation of BETI^- . Note in addition that the profile of the amorphous phase cannot be fully reproduced using only the two main components at ~ 741 and 745 cm^{-1} . At least two additional components at 747 and 737 cm^{-1} are needed (Fig. 5). By analogy with the observations¹ made for TFSI^- , the higher wavenumber component at 747 cm^{-1} might correspond to frozen contact ion-pair (CIP) interactions between BETI^- and Li^+ . For the lower wavenumber component at 737 cm^{-1} , one can simply infer that conformational states other than C_1 and C_2 can exist at high temperature and are quenched at low temperature. The spectra of the melt at 296 and 398 K (Fig. 4(a)) cannot be decomposed in the same way because the components have merged into a broad and featureless profile. More generally,

the conformational splittings in the Raman spectra ($\leq 6\text{ cm}^{-1}$) are sufficient to allow a conformational analysis in the solid phases, but too small to be distinguished in the broader features of the melt.

The same kind of study was performed on the $(\text{G2})_2\text{:LiBETI}$ solvate. At room temperature, a broad band with a maximum at about 744 cm^{-1} is observed (Fig. 6(a)). Its asymmetry suggests a higher population of C_2 than C_1 conformers. At 168 K, the C_2 and C_1 contributions can be distinguished by eye, with a slightly higher intensity for the former (Fig. 6(b)). At 153 K, the two components have

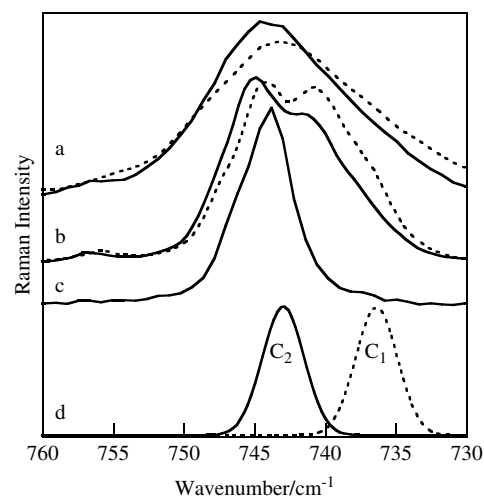


Figure 4. Raman spectra of melted $(\text{G3})_2\text{:LiBETI}$ at 296 K (solid line) and at 398 K (broken line) (a), compared to the amorphous solid phase at 113 K obtained after a first slow cooling ($\sim 1\text{ K min}^{-1}$, solid line) or a first fast cooling ($\sim 20\text{ K min}^{-1}$, broken line) (b) and to the ordered solid phase at 113 K (c). The calculated bands of the two conformers are again reported for a convenient comparison.

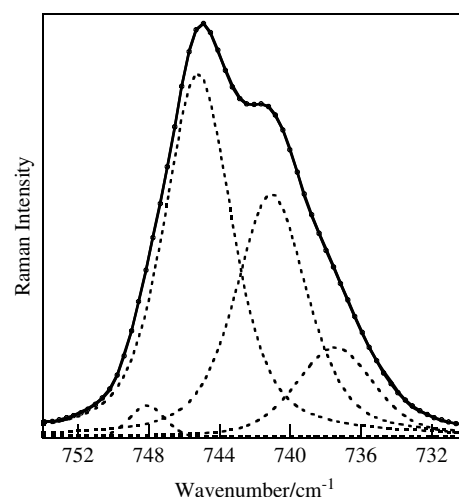


Figure 5. Raman spectrum of the $(\text{G3})_2\text{:LiBETI}$ amorphous phase at 113 K (slow cooling) fitted by four components.

about the same intensity (Fig. 6(c)) and at 113 K, the C_1 component has nearly twice the intensity as C_2 (Fig. 6(d)). Many cooling/heating cycles have been performed with annealing temperatures between 220 and 170 K, but the evolution reported in Fig. 6 is essentially maintained with only small variations in the relative intensities of the two components. At 113 K, the C_1 component is always the more intense one. This is quite an unexpected behavior since the low-temperature phase of $(G3)_2$:LiBETI has been shown to contain only C_2 conformers, in agreement with the theoretical prediction of a lower energy for C_2 than for C_1 . However, this prediction is for the gas state and it is possible that in some systems such as $(G2)_2$:LiBETI intermolecular forces favor the C_1 conformation. It is also possible that we have simply not succeeded in stabilizing the low-temperature ordered phase of $(G2)_2$:LiBETI.

Note that the 1200–1120 cm^{-1} region, where the C_1 and C_2 conformers give distinct Raman signatures (Fig. 3), is not reported for the $(G2)_2$:LiBETI and $(G3)_2$:LiBETI solvates because the glyme molecules exhibit interfering lines in this region. Therefore, we prefer to concentrate on the complementary IR spectroscopy to resolve the remaining issues.

Infrared spectra

According to our calculations, the IR spectra should permit the two conformers to be more easily distinguished, particularly in the 550–650 cm^{-1} region where neither the glymes nor the Me_4N^+ cation absorb. The BETI $^-$ modes are primarily due to F–C–F bending (from either the CF_3 or the CF_2 groups), and additionally to N–S–O bending. In Fig. 7, the calculated and experimental spectra in this

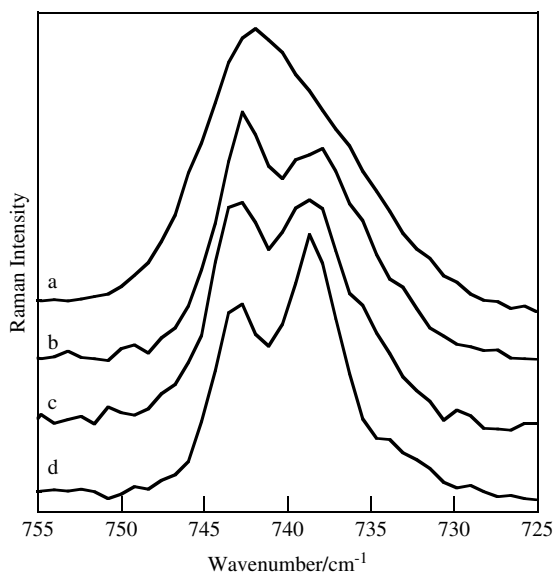


Figure 6. Raman spectra of $(G2)_2$:LiBETI at 298 K (a), 168 K (b), 153 K (c) and 113 K (d).

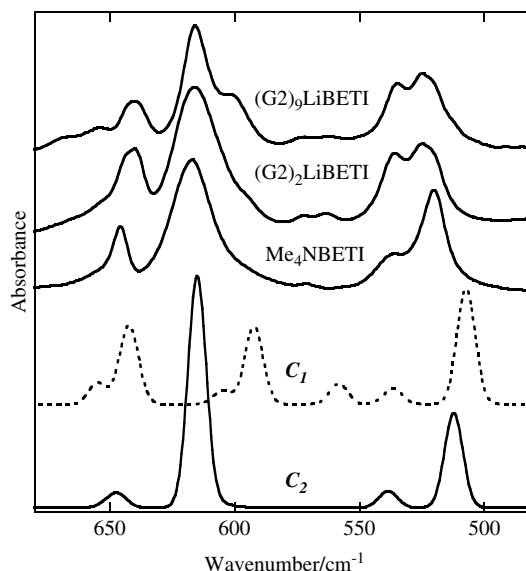


Figure 7. Comparison of the calculated IR spectra of the C_1 and C_2 BETI $^-$ conformers with the experimental IR spectra of the $(G2)_2$:LiBETI and Me_4NBETI salts and of a $[G2]/[\text{LiBETI}] = 9$ solution at room temperature. The calculated wavenumbers have been multiplied by a scaling factor of 1.0267 for a better comparison with the experimental data and the calculated bands have been given a Gaussian profile of 8.5 cm^{-1} FWHM.

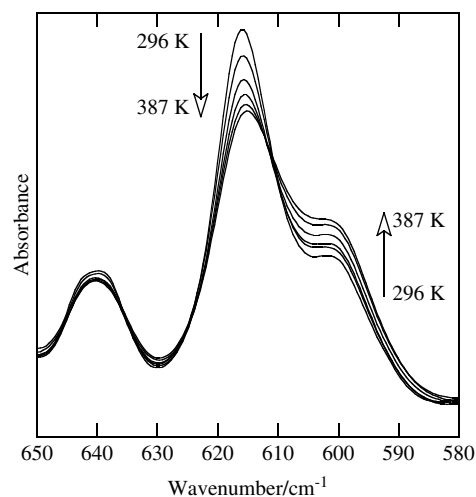


Figure 8. IR spectra of a $[G2]/[\text{LiBETI}] = 9$ solution as a function of temperature.

region are compared. The spectrum of the Me_4NBETI reference compound is in good agreement with the C_2 calculated spectrum. The other samples exhibit some additional or more intense features arising from the C_1 conformer contribution. A more direct illustration of the conformational equilibrium in solution is provided by the thermal dependence of the $[G2]/[\text{LiBETI}] = 9$ spectrum between 296 and 387 K (Fig. 8). For a convenient comparison, the region of the methylene and methyl stretching vibrations, between 3100

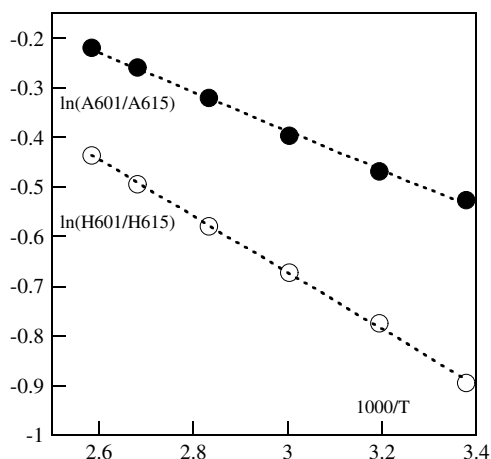


Figure 9. Arrhenius plot from the relative areas (black circles) or heights (open circles) of the 601 and 615 cm^{-1} fitted components in Fig. 8.

and 2650 cm^{-1} , has been normalized. The quantitative study of the temperature effect is based on a fitting of the profile by three Gaussian components. In the investigated temperature range, the fitted components remain centered at 640 ± 0.1 , 615.5 ± 0.3 and 601.4 ± 0.3 cm^{-1} and their FWHMs are also rather constant at around 10, 11 and 15 cm^{-1} , respectively. The 640 cm^{-1} component is a mixed band due to contributions from both conformers and has a weak temperature dependence, as expected from the computed wavenumbers and IR intensities, with one band from the C_2 conformer at 629.6 cm^{-1} (16.6 kJ mol^{-1}) and three from the C_1 conformer at 637.8 (31.2), 626.2 (80.8), and 624.0 cm^{-1} (39.2). The central very strong 615.5 cm^{-1} component, essentially due to the C_2 conformer, is calculated to be a single very intense band, 335.9 kJ mol^{-1} at 599.0 cm^{-1} , arising mainly from the central $\text{O}_2\text{S}-\text{N}-\text{SO}_2$ part (>55% according to the PED), and its relative intensity also decreases by heating, as expected. Finally, the relative intensity of the 601.4 cm^{-1} component increases on heating, as expected for a peak with mainly C_1 contribution. The calculations reveal two C_1 contributions at 589.6 and 588.4 cm^{-1} and one C_2 contribution at 588.9 cm^{-1} . Each of the C_1 contributions has double the intensity of the C_2 contribution, and therefore this band is treated as a pure C_1 . The relative integrated intensities and heights of two of the three fitted components are reported in the Arrhenius plot of Fig. 9. The data points are well aligned in both cases, but the slopes are rather different and lead to energies differences between the C_2 and C_1 conformers of 3.3 kJ mol^{-1} from the areas and 4.7 kJ mol^{-1} from the heights. We believe that the determination from the heights is somewhat more accurate than from the areas because a small imprecision on the base line affects the latter more. We retain finally the experimental value of 4.7 ± 0.7 kJ mol^{-1} , which is comparable to, but smaller than, the calculated value of 6 kJ mol^{-1} . Such an increase is generally observed for a given conformational equilibrium when going from the liquid to gas state.

CONCLUSIONS

The similarities between the BETI^- and TFSI^- anions are striking: they can both exist under two conformational states of C_2 and C_1 symmetry, the former being more stable by about 4–6 kJ mol^{-1} for BETI^- and by 2–3 kJ mol^{-1} for TFSI^- depending on the solvent used and the method of determination. These anions present very similar IR features in the 580–650 cm^{-1} region with unique absorption bands for the C_2 and C_1 conformers, in very good agreement with the calculated IR spectra. The distinction is less easy with Raman spectroscopy, as predicted by smaller calculated conformational splittings. From this study, it is confirmed that BETI^- adopts the C_2 conformational state in the Me_4NBETI crystalline phase. The $(\text{G}3)_2\text{:LiBETI}$ solvate is easily quenched at low temperature into a metastable state with comparable quantities of the two BETI^- conformers, before being crystallized by annealing into an ordered phases with BETI^- in the C_2 conformational state. The preliminary results obtained with the $(\text{G}2)_2\text{:LiBETI}$ solvate show, however, that the C_2 conformational state is not systematically obtained at low temperature owing presumably to intermolecular forces being of the same order of magnitude as the energy difference between the C_1 and C_2 conformers in the gas state.

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