Experimental and Theoretical Investigation of the Geometry and Vibrational Frequencies of 1,2,3-Triazole, 1,2,4-Triazole, and Tetrazole Anions

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Optimized geometries, vibrational frequencies, scale factors, and IR absorption intensities were calculated for the 1,2,3-triazole anion (**1**) at the B3LYP, LDA, BLYP, BVWN, HF, and MP2 levels of theory using the 6-31G** (BS1), 6-31++G** (BS2), cc-pVDZ (BS3) and aug-cc-pVDZ (BS4) basis sets and for 1,2,4-triazole (**2**) and tetrazole (**3**) anions at the same lavels of theory using the BS1 and BS2 basis sets only. The calculations were also carried out at the AM1, PM3 and MNDO semiempirical levels. For comparison with the calculated results, the IR and Raman spectra of **2** and **3** were measured, while for **1** the experimental assignment reported in the literature was used. Measurement of the spectra of **2** and **3** resulted in a complete assignment of the fundamental vibrations of both anions except for few bands corresponding only to the C−H stretching and out-of-plane modes. The force fields were scaled with respect to the experimental frequencies using one-scale-factor (1SF) scaling. The agreement between the calculated and experimental frequencies was excellent, especially with the B3LYP method, scaled and unscaled. The agreement between the experimental and calculated IR absorption intensities was generally satisfactory. The calculated scale factors for the studied molecules were larger than commonly calculated for other neutral molecules. The basis set effect on the calculated results was generally small. Differences and similarities between the calculated frequencies and scale factors by the different methods were rationalized in terms of the optimized geometries.

Introduction

Recently, the calculated vibrational frequencies and IR absorption intensities using the density functional theory (DFT) have drawn much attention that the use of the DFT method for the vibrational analysis is now routine. This wide interest in the vibrational frequencies calculated by the DFT method is due to its excellent accuracy to computational expense ratio.[1] On the other hand, the existence of different density functionals led to many reports which compare between the vibrational frequencies[1−11] and other molecular properties[12] obtained by these functionals. Most of these publications conclude that the B3LYP functional[1] is the preferred method for the vibrational analysis.

In a previous publication,[2] a thorough comparison among the optimized geometries, vibrational frequencies, and force field scale factors obtained by the B3LYP, LDA, BVWN, and BLYP functionals, as well as the HF and MP2 methods, was made. The similarities and differences between the calculated frequencies and scale factors obtained by these methods were rationalized in terms of the optimized geometries. It was concluded that the B3LYP and LDA functionals behave similarly and that the BLYP and BVWN functionals behave similarly and different from the B3LYP and LDA functionals. One advantage of the B3LYP functional is that the calculated vibrational frequencies are generally overestimated and the overestimation decreases with decrease of frequency, a behavior which is similar to the MP2 and HF calculated frequencies.[2,14−16] This property is not found in the BLYP and BVWN functionals. Consequently, scaling the B3LYP force field improves the agreement between the calculated and experimental frequencies where it remained unchanged for the BLYP and BVWN functionals.[2,9] The calculated frequencies for the C−H stretching modes by the LDA functional are not as overestimated as those obtained by the B3LYP functional and some bands, mainly out-of-plane, are underestimated. Consequently, scaling the LDA force field did not improve the average error as with the B3LYP method, but the average error was better than that obtained with the BLYP and BVWN methods. It was also concluded that the basis set effect, as usually known,[2,6,7] is small.

Yet with the growing interest in the DFT method, no comprehensive comparison between the different density functionals, according to the best of our knowledge, was reported for the vibrational analysis of anions which is the purpose of the current publication. There are though some reports of the

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calculated frequencies by the DFT method for ionic species.[17-22] The most important of these is the calculated frequencies of *N*,*N*,*N*′,*N*′ -tetramethyl-*p* -phenylenediamine radical cation.[22] In that publication the author reported scale factors larger than those obtained for neutral molecules. Also Schaefer and coworkers in a few recent publications[18,23] indicated that the DFT method is applicable to anions, contrary to what was previously proposed. This was demonstrated by calculating the electron affinities and vibrational frequencies of SiF_n^- ($n = 1-5$) by different DFT methods.

In the present publication, we report the vibrational spectra of **2** and **3**. In addition we compare the optimized geometries, vibrational frequencies, force field scale factors, and IR absorption intensities of **1**, **2**, and **3** at the B3LYP, LDA, BVWN, BLYP, HF, MP2, AM1, PM3, and MNDO levels of theory. To investigate the basis set effect, the calculations of **1** were done using four moderate size basis sets, with and without diffuse functions. The diffuse functions are known to be necessary for calculating the chemical properties of anions. The basis sets used are the BS1, BS2, BS3 and BS4 basis sets. For **2** and **3** the calculations were performed using the BS1 and BS2 basis sets only.

The experimental fundamental vibrations used for comparison with the calculated frequencies of **1** are those reported by Törnkvist et al.[24] The authors also reported the calculated vibrational frequencies and IR absorption intensities of **1** with the MNDO, HF/4-21G(N*) and MP2/6-31G* methods. For **2** and **3**, the experimental vibrational frequencies reported in the current work were used for comparison with the calculated results. Although there is an experimental IR spectrum of sodium tetrazolate monohydrate previously reported,[25] the reported frequencies were not comparable to the calculated frequencies reported in the present publication, while there is no experimental spectrum of **2**, we know of, previously reported.

Experimental Details

Both the 1,2,4-triazole and tetrazole samples were obtained from Sigma Chemical Co. Tetrazole was used without further purification. 1,2,4-triazole was recrystallized by dissolving in hot water (60 °C) and then slowly cooling to room temperature. Infrared and Raman spectra of the 1,2,4-triazole and tetrazole anions were measured in aqueous 0.5 M NaOH solution at pH 12. Infrared spectra were also remeasured in NaOD solution in D_2O at pD 12. Powder samples were directly added to 0.5 M NaOH (NaOD) solution until the resulting pH (pD) reached 12. Corning 145 pH meter was used to determine pH. The infrared spectra of these solutions were recorded on an FTS-40 Biorad Digilab FTIR spectrometer at 4 cm^{-1} resolution. A homemade cell consisting of BaF_2 windows separated by a 15-μm Teflon spacer was used. Infrared and Raman spectra were corrected by subtracting identically obtained spectra of just the solvent. Raman spectra were measured with 90° axial excitation/transverse viewing geometry using a spectrometer assembled in house.[26] This spectrometer consists of an Ar ion laser (Coherent Innova 300), a 0.64-m spectrograph (ISA J-Y 640), and an intensified diode array detector (PAR 1420 with an OMA III controller). The excitation wavelength was the 488.0-nm argon line. An interference filter was used to remove the plasma lines from the excitation beam. After collimation, scattered light was passed through a holographic notch filter (Kaiser) and focused onto the entrance slit of the spectrograph. A slit width of 100 μm and a 600 groove/mm grating were used to yield a resolution of 6−8 cm^{-1}. An 1800 groove/mm grating was used to remeasure the Raman spectrum of just the out-of-plane bending region (600−900 cm^{-1}). For polarized measurements, a Polaroid analyzer followed by a depolarizer was inserted into the scattered light beam. Depolarization ratios were calculated from peak areas obtained by fitting the peaks with Gaussian/Lorentzian functions.

Computational Details

The optimized geometries, vibrational frequencies and IR absorption intensities were calculated for **1**, **2**, and **3** under the C_{2v} symmetry constraint. The calculations were performed at the B3LYP,[1] LDA,[27] BLYP,[28] BVWN, HF,[29] and MP2[30] levels of theory using the BS1,[31] BS2,[31] BS3,[32] and BS4[32] basis sets for **1** and using the BS1 and BS2 basis sets for **2** and **3**. The MP2 calculations were performed keeping the 1s orbitals of the heavier centers frozen (MP2/fc). The number of basis functions of **1** with the BS1, BS2, BS3, and BS4 basis sets are 85, 107, 80, and 133, respectively. For **2** and **3**, the number of basis functions are 80/101 and 104/130, respectively, with the BS1/BS2 basis sets. In addition, the calculations were performed at the AM1,[33] PM3[34] and MNDO[35] semiempirical levels of theory.

All calculations were performed using the Gaussian94[36] program. The force fields were calculated by the analytical method. Conversion of the Cartesian coordinate force fields to internal coordinate force fields, scaling of the internal coordinate force fields and calculation of the frequencies is as described elsewhere.[2,14,37] Under the C_{2v} symmetry constraint, the 15 fundamental vibrations of **1** and **2** are classified as $6A_1$, $5B_2$, $2A_2$, and $2B_1$. For **3** under the C_{2v} symmetry, the 12 fundamental vibrations are classified as $5A_1$, $4B_2$, A_2, and $2B_1$.

Results and Discussion

Optimized Geometries. The calculated optimized geometries of **1**, **2**, and **3** are given in Tables 1, 2, and 3, respectively. The atom numbering is shown in Figure 1. First, we mention a summary about the predicted geometries by different methods. It is know that the HF-predicted bond lengths are underestimated,[5] the MP2 predicted bond lengths are usually overestimated,[5,38] and the DFT-predicted bond lengths are often overestimated.[2,5,6,8] The bond angles predicted by the different DFT methods show little dependence on the functional used.[2] The BLYP- and LDA-functionals-predicted bond lengths are 0.01−0.02 Å too long.[2,5,6] The B3LYP-predicted geometry has the best agreement with the experimental geometry.[2,8,14-16]

Our previous results for five-membered heterocyclic molecules[2,14-16] show not only that the MP2-predicted geometry is only slightly worse than the B3LYP-predicted geometry but also that the B3LYP-predicted geometry has poor prediction of some bond lengths and angles, as the C−S bond length and NSN bond angle, which is not observed by the MP2-predicted geometry. The LDA-predicted geometry is worse than the MP2-predicted geometry. The BVWN- and BLYP-predicted geometries are close to each other ,and both are worse than the LDA-predicted geometry.

Several observations can be made about the results in Table 1 for the optimized geometry of **1**. The bond lengths and angles predicted by the BLYP and BVWN methods by the four basis sets used in this study are very close to each other. With the exception of the C−H bond length, the maximum difference between the bond lengths predicted by the BLYP and BVWN methods is not more than 0.003 Å and those of the bond angles is not more than than 0.3°. The predicted C−H bond length by the BVWN method is shorter by about 0.006 Å than that predicted by the BLYP method. The bond lengths and angles

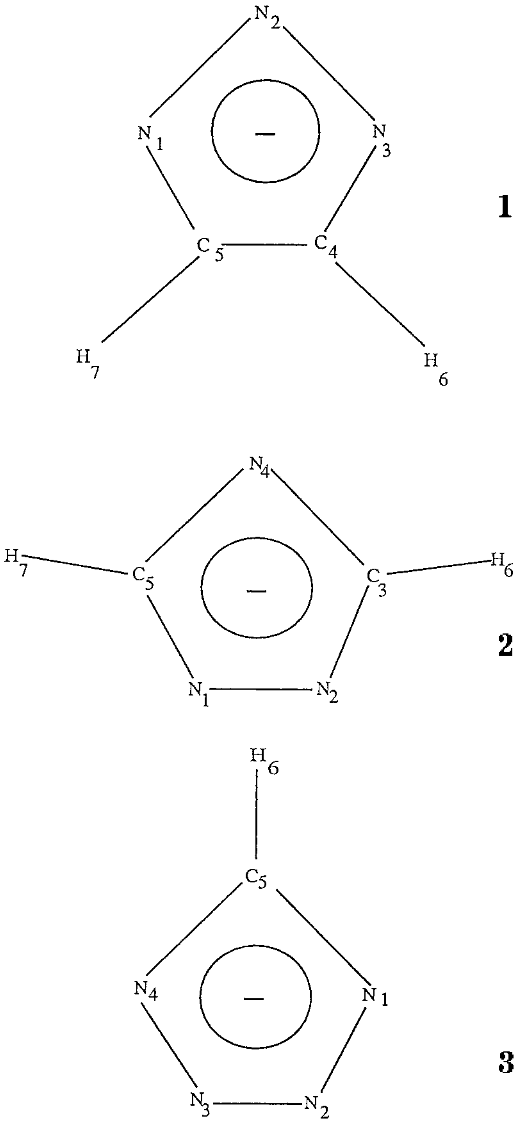

Figure 1. Atom numbering of 1,2,3-triazole (**1**), 1,2,4-triazole (**2**), and tetrazole(**3**).

predicted by the B3LYP and LDA methods are also very close to each other, but the difference between the bond lengths is larger than that between the BLYP and BVWN predicted bond lengths. Except for the C−H bond length, the B3LYP-predicted bond lengths are longer by about 0.006 Å than the LDA-predicted bond lengths. The C−H bond length predicted by the B3LYP method is shorter by about 0.01 Å than that predicted by the LDA method. The bond angles differ by not more than 0.2° in most of the cases. The B3LYP- and LDA-predicted bond lengths, as was reported for furan and thiophene,[2] are shorter than the BLYP- and BVWN-predicted bond lengths. A difference of about 0.01−0.03 Å is found between the LDA- and BLYP-predicted bond lengths. The bond angles are very similar.

The MP2-predicted geometry is closer to the BLYP- and BVWN-predicted geometries than the B3LYP- and LDA-predicted geometries, contrary to what was found for furan and thiophene.[2] The MP2-predicted bond lengths are about 0.01 Å shorter than the BVWN-predicted bond lengths, and the bond angles differ by not more than 0.2°. Generally, the MP2-predicted geometry is in between the LDA- and BLYP-predicted geometries. The bond lengths predicted by the BS3 and BS4 basis sets are longer by about 0.005 Å than those predicted by the BS1 and BS2 basis sets, and the bond angles are very similar. Except for the C−H bond length, the MP2/fc/BS1-predicted geometry is very close to the MP2/full/6-31G*-predicted geometry reported by Törnkvist et al.[24] to within 0.002 Å for the bond lengths and 0.1 degree for the bond angles. The predicted C−H bond length by Törnkvist et al.[24] is longer than that predicted in this work using the BS1 basis set by 0.005 Å. The HF-predicted geometries have the shortest bond lengths. The bond lengths predicted by the BS3 and BS4 basis sets, as with the MP2-predicted geometry, are about 0.005 Å longer than those predicted by the BS1 and BS2 basis sets, and the bond angles are very similar.

The effect of the basis set on the predicted geometries by the different DFT methods is, as expected, small. The difference in most of the cases is not more than 0.003 Å for the bond lengths and 0.3° for the bond angles from the BS1-predicted geometries. The noticeable difference is for the C−H bond length by the BS3 basis set which is predicted to be 0.007 Å longer than that predicted by the BS1 basis set by the four DFT methods.

Similar observations for **1** are found for **2** and **3** with the exception that for **2** and **3** the N_1-N_2 B3LYP-predicted bond length is longer by about 0.01 Å than that predicted by the LDA method; the MP2 predicted geometry is closer to the B3LYP and LDA geometries than the BLYP and BVWN geometries. Also, the effect of the basis set effect on the predicted geometries is very small except with the DFT functional; the CNC bond angle of **2** using the BS2 basis set is bigger by about 1° than that predicted by the BS1 basis set, and the NCN bond angle of **2** and **3** with the BS2 basis set is smaller by about 1° than that with the BS1 basis set.

The predicted N−N bond lengths by the AM1, PM3, and MNDO methods are in most of the cases shorter even than those predicted at the HF level. The C−C bond length of **1** and the N−C bond lengths of all anions are the longest among all methods used. The C−H bond length and the bond angles are comparable to those obtained by the other methods. The only available experimental geometry is a X-ray geometry measured for sodium tetrazolate monohydrate.[39] Due to the limitations of the X-ray method, it not expected that this experimental geometry to be of accuracy comparable to that obtained by the microwave or electron diffraction methods. However, the agreement between the calculated and experimental geometry of **3** is qualitatively satisfactory.

Vibrational Frequencies. The measured IR and Raman spectra of **2** and **3** are given in Figures 2 and 3, respectively. The calculated and experimental frequencies of **1**, **2**, and **3** are given in Tables 4, 5, and 6, respectively. Appended in Tables 4−6 are the average errors with respect to the scaling assignment (SA). In this assignment, the experimental frequencies were assigned to the calculated frequencies in decreasing frequency order according to the Raman polarization data, whenever available. The IR frequencies, whenever available, rather than the Raman frequencies were used in the SA. All of the out-of-plane modes were excluded from the SA since some are observed only in the KBr pellet spectrum, as for **1**, or observed as a very weak features in the Raman spectra for which no reliable polarization data is available. Bands at 3114 and 3103 cm^{-1} of **2** were also observed as very weak bands and were excluded from the SA. Also a very weak band of **1** observed at 1230 cm^{-1} was excluded from the SA since this band had a high deviation from the corresponding calculated frequency, before and after scaling, by all methods. This band could be an impurity from the reacting species. All the other fundamental vibrations of **1**, **2**, and **3** were used in the SA. In the following

TABLE 1: Equilibrium Geometry for 1[a,b]

	B3LYP				LDA				BLYP			
coordinate	BS1	BS2	BS3	BS4	BS1	BS2	BS3	BS4	BS1	BS2	BS3	BS4
N_1-N_2	1.346	1.344	1.343	1.345	1.338	1.335	1.335	1.336	1.369	1.367	1.366	1.367
N_1-C_5	1.355	1.356	1.357	1.357	1.349	1.351	1.351	1.351	1.369	1.371	1.370	1.371
C_4-C_5	1.391	1.394	1.395	1.395	1.387	1.389	1.391	1.391	1.402	1.404	1.406	1.406
C_4-H_6	1.086	1.084	1.093	1.089	1.095	1.093	1.102	1.098	1.094	1.092	1.102	1.096
$N_1N_2N_3$	111.1	110.9	111.3	111.0	111.2	111.0	111.5	111.1	111.0	110.8	111.2	110.9
$N_2N_3C_4$	106.6	106.9	106.7	106.9	106.7	107.0	106.7	107.0	106.3	106.7	106.4	106.6
$N_3C_4C_5$	107.9	107.7	107.7	107.6	107.7	107.5	107.8	107.5	108.2	107.9	108.0	108.0
$N_3C_4H_6$	121.9	121.7	121.8	121.8	121.8	121.6	121.8	121.7	121.7	121.5	121.6	121.6
$C_5C_4H_6$	130.2	130.6	130.5	130.6	130.5	130.9	130.4	130.8	129.9	130.6	130.4	130.4

	BVWN				HF				MP2						
coordinate	BS1	BS2	BS3	BS4	BS1	BS2	BS3	BS4	BS1	BS2	BS3	BS4	AM1	PM3	MNDO
N_1-N_2	1.369	1.367	1.366	1.367	1.309	1.308	1.307	1.309	1.361	1.362	1.358	1.367	1.309	1.315	1.303
N_1-C_5	1.368	1.369	1.369	1.370	1.334	1.336	1.336	1.339	1.360	1.363	1.365	1.369	1.386	1.385	1.381
C_4-C_5	1.400	1.402	1.404	1.403	1.377	1.380	1.381	1.382	1.389	1.392	1.401	1.403	1.429	1.396	1.412
C_4-H_6	1.089	1.086	1.096	1.091	1.075	1.073	1.082	1.079	1.092	1.081	1.095	1.092	1.082	1.084	1.079
$N_1N_2N_3$	110.9	110.7	111.2	110.9	111.5	111.4	111.7	111.6	110.9	110.6	111.4	110.9	113.9	110.4	112.9
$N_2N_3C_4$	106.3	106.6	106.3	106.6	107.1	107.3	107.1	107.2	106.3	106.6	106.3	106.5	107.6	108.8	107.6
$N_3C_4C_5$	108.3	108.1	108.1	108.0	107.1	107.0	107.1	107.0	108.3	108.1	108.0	108.1	105.5	106.0	106.0
$N_3C_4H_6$	121.7	121.6	121.7	121.7	122.2	122.2	122.2	122.2	121.6	121.4	121.7	121.5	123.9	122.9	123.1
$C_5C_4H_6$	130.0	130.3	130.2	130.3	130.6	130.8	130.7	130.8	130.1	130.5	130.3	130.4	130.6	131.1	130.9

[a] Bond lengths in angstroms and angles in degrees. [b] BS1, BS2, BS3, and BS4 stand for 6-31G**, 6-31++G**, cc-pVDZ, and aug-cc-pVDZ basis sets, respectively.

TABLE 2: Equilibrium Geometry for 2[a,b]

	B3LYP		LDA		BLYP		BVWN		HF		MP2				
coordinate	BS1	BS2	BS1	BS2	BS1	BS2	BS1	BS2	BS1	BS2	BS1	BS2	AM1	PM3	MNDO
N_1-N_2	1.380	1.377	1.364	1.360	1.404	1.400	1.405	1.402	1.353	1.351	1.382	1.383	1.297	1.330	1.299
N_2-C_3	1.338	1.339	1.337	1.338	1.353	1.354	1.351	1.352	1.310	1.312	1.348	1.351	1.396	1.369	1.378
C_3-N_4	1.356	1.356	1.349	1.349	1.370	1.370	1.369	1.369	1.337	1.338	1.358	1.360	1.381	1.376	1.370
C_3-H_6	1.089	1.086	1.098	1.096	1.097	1.094	1.091	1.088	1.078	1.075	1.084	1.082	1.087	1.087	1.082
$N_1N_2C_3$	110.4	110.2	110.6	110.6	110.2	110.0	110.0	109.8	111.0	110.8	110.4	110.2	113.6	111.2	113.0
$N_2C_3N_4$	115.6	114.9	115.5	114.7	116.0	115.2	116.1	115.3	115.0	114.6	115.7	115.1	111.6	108.7	111.3
$C_3N_4C_5$	99.2	100.0	99.2	100.0	98.9	99.8	98.9	99.8	99.5	100.0	99.1	99.8	101.6	105.7	102.2
$N_2C_3H_6$	121.9	122.1	121.9	122.1	121.7	122.0	121.8	122.0	122.1	122.3	121.7	121.8	124.1	126.1	124.4
$N_4C_3H_6$	122.5	123.0	122.7	123.3	122.2	122.9	122.2	122.7	122.9	123.2	122.6	123.1	124.3	125.2	124.4

[a ,b]See corresponding footnotes in Table 1.

TABLE 3: Equilibrium Geometry for 3[a,b]

	B3LYP		LDA		BLYP		BVWN		HF		MP2					
coordinate	BS1	BS2	BS1	BS2	BS1	BS2	BS1	BS2	BS1	BS2	BS1	BS2	AM1	PM3	MNDO	exptl[c]
N_1-N_2	1.353	1.352	1.343	1.341	1.376	1.376	1.376	1.374	1.322	1.321	1.360	1.361	1.306	1.321	1.303	1.348
N_2-N_3	1.325	1.324	1.322	1.321	1.346	1.345	1.345	1.344	1.283	1.283	1.348	1.350	1.320	1.305	1.307	1.310
N_1-C_5	1.340	1.341	1.337	1.337	1.354	1.355	1.353	1.354	1.317	1.318	1.346	1.348	1.391	1.370	1.377	1.329
C_5-H_6	1.086	1.083	1.094	1.093	1.094	1.091	1.088	1.085	1.074	1.072	1.081	1.079	1.085	1.086	1.079	0.911
$N_1N_2N_3$	106.2	106.4	106.4	106.8	105.2	106.0	105.2	105.6	107.8	107.8	105.2	105.6	113.8	113.0	113.6	109.5
$N_1C_5N_4$	113.4	112.9	113.2	112.6	114.1	113.4	114.1	113.5	112.4	112.1	113.8	113.3	108.0	106.0	107.8	112.5
$N_2N_1C_5$	103.5	103.9	103.6	104.0	103.3	103.6	103.3	103.7	103.7	104.0	103.6	103.9	105.1	107.5	105.4	104.3
$N_1C_5H_6$	123.3	123.6	123.4	123.7	123.0	123.3	122.9	123.2	123.8	124.0	123.6	123.3	126.0	127.0	126.1	123.8

[a,b]See corresponding footnotes in Table 1. [c] Reference 39.

discussion, since the out-of-plane modes were excluded from the SA and the great anharmonicity of the C−H modes, referring to the average error refers to the in-plane modes rather than the total average error unless otherwise indicated.

The calculated frequencies of **1**, **2**, and **3** indicate that, among the levels of theory used, the calculated vibrational frequencies by the B3LYP method have the lowest average error. This is compared to the highest average error obtained by the B3LYP method for furan and thiophene,[2] with the exception of the HF and MP2 methods. The calculated frequencies of the C−H stretching modes by the B3LYP method have the highest average error among the DFT functionals used. Although the LDA-predicted bond lengths are slightly shorter than the B3LYP-predicted bond lengths, most of the LDA-calculated frequencies are at lower frequencies than those calculated by B3LYP method and some are underestimated compared to the experimental frequencies. Consequently, the average error obtained by the LDA method is larger than that obtained by the B3LYP method using the same basis set. The calculated C−H stretching frequencies by the LDA method are predicted at lower frequencies and in better agreement with the experimental frequencies than those predicted by the B3LYP method. This is in agreement with the longer C−H bond length predicted by the LDA method than that predicted by the B3LYP method.

Noting that the BLYP- and BVWN-predicted geometries are close to each other and that the predicted bond lengths by both

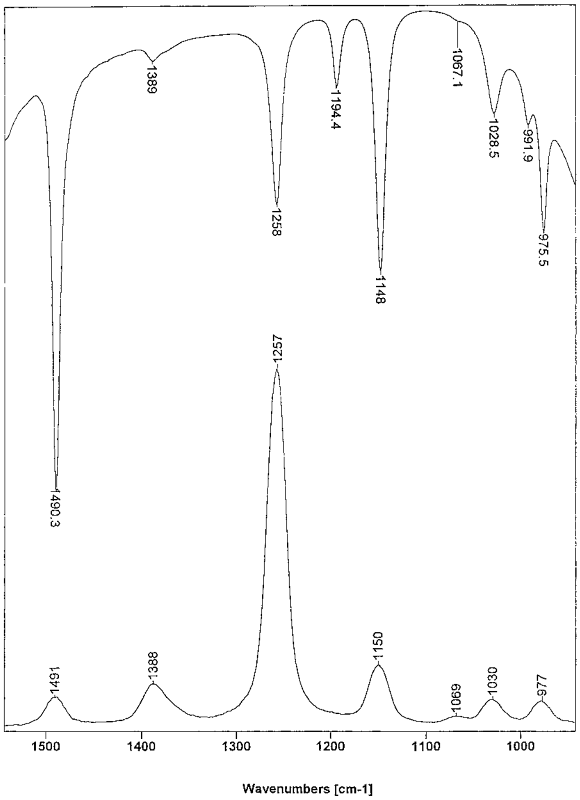

Figure 2. FTIR (top) and FT Raman (bottom) spectra of 1,2,4-triazole (**2**) anion.

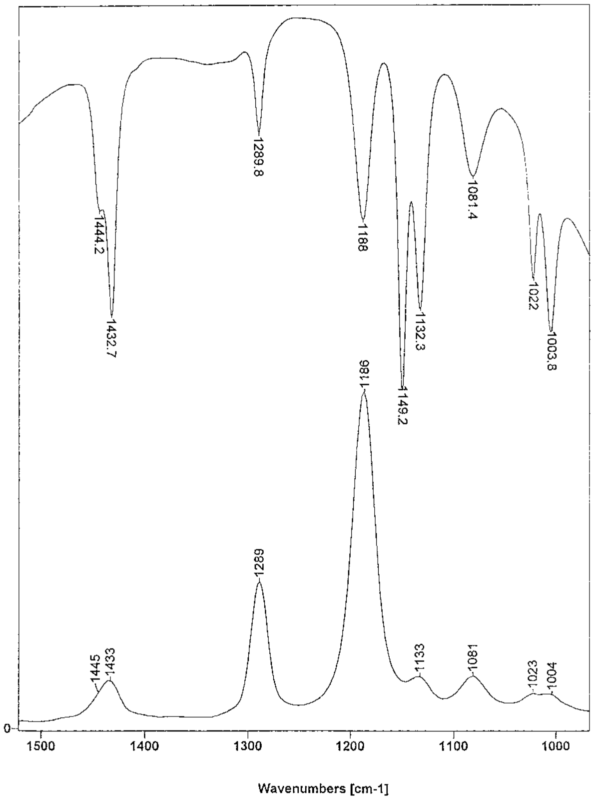

Figure 3. FTIR (top) and FT Raman (bottom) spectra of tetrazole (**3**) anion.

methods are longer than those predicted by the B3LYP and LDA methods, the calculated frequencies by the BLYP and BVWN methods are close to each other and most of the calculated frequencies by both methods are underestimated. The average error obtained by both methods is about twice that obtained by the LDA method. This is compared to the lowest average error obtained by the BVWN method for furan and thiophene using the BS1 basis set.[2] Some calculations, as the BLYP/BS2, predict the C−H stretching frequencies in excellent agreement with the experimental frequencies as the predicted C−H bond length with BLYP/BS2 is close to that predicted by the LDA method.

Although the total average error by the MP2 method is bigger than that obtained by the DFT methods, the average error for the in-plane modes is smaller than that obtained by the BLYP and BVWN methods, as was also reported for furan and thiophene.[2] Some calculated frequencies by the MP2 method are underestimated as the MP2-predicted geometry is closer to the BLYP, and BVWN-predicted geometries than that predicted by the B3LYP and LDA methods. The calculated frequencies at the MP2/BS1 level in this work are very close to those predicted at the MP2/6-31G* level reported by Törnkvist et al.[24] The difference between the calculated frequencies for the C−H stretching modes by the above two methods is not more than 30 cm^{-1} and for the other modes is not more than 4 cm^{-1} except for ν_{12} where the difference is 11 cm^{-1}. Notice that the predicted geometries by both calculations are very close to each other with the exception of the predicted C−H bond length at the former level is shorter than that at the latter level by about 0.005 Å. The HF-calculated frequencies have the highest overestimation in accordance with the HF-predicted bond lengths are the shortest among the ab initio methods used in this work.

The effect of the basis set and inclusion of the diffuse functions, as was the case with the predicted geometries, is usually small with the calculated frequencies by the BS1 basis set have generally the lowest average error.

The calculated frequencies by the semiempirical methods are generally overestimated with the exception of the lower frequency in-plane modes which are underestimated. In general the calculated frequencies by the semiempirical methods are grossly overestimated by 100−250 cm^{-1}, with the calculated frequencies by the PM3 method have the lowest average error and those calculated by the MNDO method have the highest average error.

It is worth noting that the calculated frequencies by the B3LYP and MP2 methods and the corresponding experimental frequencies of ν_2 /ν_3 /ν_7 for **3** are at 1296/1192/1169, 1279/1145/1234, and 1189/1188/1150 cm^{-1}, respectively, with the calculated frequency order assignment without observing the Raman polarization data would lead to a wrong assignment with the MP2 method, but not with the B3LYP method. This is also observed with the BLYP and BVWN methods but not with the LDA and HF methods.

Scale Factors. The calculated scale factors using 1SF scaling and the corresponding average errors are appended in Tables 4, 5, and 6 for **1**, **2**, and **3**, respectively. In the scaling step, the AS assignment of the studied molecules in Tables 4−6 was used.

A clear feature of the calculated scale factors for the three studied anions is that they are bigger than those reported for other neutral molecules[2,8−10,14−16] but are close to those obtained by Brouwer using the UBLYP/6-31G* and UB3LYP/6-31G* methods. The calculated force field scale factors of furan and thiophene[2] at the B3LYP, LDA, BLYP, BVWN, HF, and MP2 levels using the BS1 basis set are 0.927, 0.963, 0.983, 0.965, 0.819, and 0.894, respectively. The calculated force field scale factors using 1SF reported by Rauhut et al.[8] are 0.990 and 0.928 at the BLYP and B3LYP levels, respectively, using the 6-31G* basis set. The calculated frequency scale factors using 1SF

TABLE 4: Calculated Vibrational Frequencies (cm^{-1}) for 1[a]

		B3LYP				LDA				exptl[b]		
symmetry	no.	BS1	BS2	BS3	BS4	BS1	BS2	BS3	BS4	IR	Raman	SA[c]
A_1	1	3198	3220	3179	3210	3139	3159	3126	3155		3135	3135
	2	1473	1455	1456	1448	1458	1442	1443	1435	1439	1439	1439
	3	1233	1225	1229	1222	1247	1244	1247	1241		1207	1207
	4	1163	1160	1169	1161	1175	1174	1182	1175	1146	1143	1146
	5	1106	1095	1089	1085	1083	1071	1068	1061	1097	1096	1097
	6	961	952	950	947	934	926	918	919	963	964	963
B_2	7	3170	3196	3150	3185	3112	3135	3098	3129		3116	3116
	8	1436	1417	1416	1407	1408	1392	1392	1385	1412	1412	1412
	9	1156	1150	1138	1142	1166	1162	1160	1156	1230[d]		
	10	1067	1058	1062	1054	1063	1059	1047	1049	1068		1068
	11	967	962	967	960	939	934	939	934		972	972
A_2	12	769	775	775	788	738	740	745	764		725	
	13	671	668	678	676	664	658	672	670		668	
B_1	14	770	757	763	755	748	733	746	734	800[e]		
	15	734	730	736	732	726	723	722	724	773[e]		
error[f]	C−H	59	83	39	72	4	22	14	17			
	in-plane[g]	15	11	12	12	22	25	29	29			
	total	24	25	17	24	18	24	26	27			
SF[h]		0.965	0.962	0.978	0.964	0.995	0.991	1.006	0.996			
error[f]		10	20	12	23	18	23	23	26			

		BLYP				BVWN				HF			
symmetry	no.	BS1	BS2	BS3	BS4	BS1	BS2	BS3	BS4	BS1	BS2	BS3	BS4
A_1	1	3099	3129	3079	3121	3131	3126	3113	3153	3373	3391	3362	3376
	2	1413	1395	1395	1387	1421	1405	1403	1398	1609	1593	1595	1586
	3	1164	1158	1162	1156	1162	1158	1160	1155	1357	1355	1362	1347
	4	1082	1080	1087	1080	1079	1079	1084	1079	1325	1318	1327	1315
	5	1068	1056	1048	1047	1076	1066	1057	1058	1194	1183	1181	1172
	6	909	900	900	896	914	907	907	904	1072	1065	1061	1056
B_2	7	3070	3104	3049	3096	3102	3136	3083	3128	3343	3365	3331	3348
	8	1370	1350	1349	1342	1380	1364	1360	1355	1593	1577	1578	1562
	9	1094	1091	1072	1082	1100	1099	1080	1090	1300	1285	1291	1272
	10	957	949	959	949	948	943	950	944	1226	1220	1211	1209
	11	932	926	931	925	937	933	936	932	1059	1055	1058	1049
A_2	12	725	726	732	742	734	737	744	750	904	914	898	902
	13	636	637	647	649	640	640	649	651	747	740	747	737
B_1	14	738	722	732	721	745	732	740	731	865	856	854	848
	15	699	694	699	697	700	696	701	699	823	816	823	812
error[f]	C−H	41	9	62	17	9	15	28	15	233	253	221	237
	in-plane[g]	51	61	59	65	48	56	56	60	141	133	134	124
	total	49	51	60	55	40	48	50	51	159	157	151	147
SF[h]		1.044	1.035	1.059	1.041	1.027	1.027	1.026	1.026	0.834	0.833	0.842	0.842
error[f]		33	42	27	44	33	33	31	31	37	29	35	28

		MP2							
symmetry	no.	BS1	BS2	BS3	BS4	AM1	PM3	MNDO	AD[i]
A_1	1	3287	3298	3242	3255	3295	3160	3496	C−H str[j]
	2	1526	1500	1500	1477	1560	1556	1657	C−C str + C−H def[k]
	3	1270	1259	1261	1238	1476	1422	1518	C−N str
	4	1137	1125	1126	1097	1407	1295	1468	N−N str + ring def
	5	1112	1094	1095	1075	1117	1047	1179	C−C str + C−H def + ring def
	6	942	926	929	905	943	893	980	ring def + C−H def
B_2	7	3259	3272	3213	3228	3286	3145	3483	C−H str
	8	1444	1422	1414	1388	1590	1510	1656	C−N str + C−H def
	9	1214	1202	1197	1174	1445	1251	1517	C−N str + C−H def
	10	1075	1056	1064	1033	1140	1057	1219	N−N str
	11	958	948	950	934	952	894	921	ring def
A_2	12	737	697	757	759	844	831	919	C−H wag[l]
	13	628	547	658	655	608	567	581	ring torsion
B_1	14	763	729	761	752	821	764	875	C−H wag
	15	722	700	726	710	720	628	674	ring torsion
error[f]	C−H	148	160	102	116	165	27	364	
	in-plane[g]	31	28	25	37	120	99	175	
	total	54	54	40	53	129	84	212	
SF[h]		0.924	0.928	0.951	0.957	0.858	0.939	0.773	
error[f]		34	42	34	47	79	86	78	

[a] See footnote *b* in Table 1. [b] Reference 24. [c] Assignment used in scaling. [d] Assignment as fundamental is questionable; see text. [e] KBr Pellet. [f] Average error in cm^{-1}. [g] Excluding C−H stretching modes. [h] Scale factor. [i] Approximate description based on B3LYP/6-31G** force field. Only values greater than 10% are considered. [j] str = stretching. [k] def = deformation. [l] wag = wagging.

scaling reported by Scott et al.[9] are 0.8992, 0.9370, 0.9945, and 0.9614 at the HF/6-31G**, MP2/6-31G*, BLYP/6-31G* and B3LYP/6-31G* levels, respectively. These correspond to 0.8086, 0.8780, 0.9890, and 0.9243, respectively, for force field

TABLE 5: Calculated Vibrational Frequencies (cm^{-1}) for 2[a]

		B3LYP		LDA		BLYP		BVWN		exptl		
symmetry	no.	BS1	BS2	BS1	BS2	BS1	BS2	BS1	BS2	IR	Raman[b]	SA[c]
A_1	1	3157	3191	3096	3126	3061	3102	3095	3135	3114		
	2	1524	1499	1497	1474	1453	1426	1465	1442	1490	1491(p,0.22)	1490
	3	1255	1254	1255	1256	1188	1188	1189	1190		1257(p,0.05)	1257
	4	1175	1166	1174	1169	1126	1116	1133	1124	1148	1150(p,0.15)	1148
	5	1042	1041	1071	1066	958	961	957	958	1029	1030(p,0.12)	1029
	6	985	975	961	952	943	930	938	931	976	977(p,0.36)	976
B_2	7	3149	3186	3089	3121	3053	3096	3087	3130	3103		
	8	1407	1389	1393	1377	1339	1320	1350	1334	1389	1388(dp,0.65)	1389
	9	1265	1270	1285	1291	1197	1203	1195	1202	1258		1258
	10	1214	1207	1177	1170	1163	1156	1172	1167	1194		1194
	11	990	980	971	961	951	940	955	946	992		992
A_2	12	826	823	790	784	780	774	789	787			
	13	710	704	709	701	679	672	679	674			
B_1	14	826	826	787	788	780	779	791	791			
	15	706	696	699	688	679	669	679	672		964	
error[d]	C−H											
	in-plane[e]	15	9	18	22	46	55	42	49			
	total	15	9	18	22	46	55	42	49			
SF[f]		0.973	0.988	0.986	0.999	1.075	1.094	1.068	1.082			
error[d]		9	8	18	22	21	11	19	14			

		HF		MP2					
symmetry	no.	BS1	BS2	BS1	BS2	AM1	PM3	MNDO	AD[g]
A_1	1	3333	3361	3251	3275	3252	3112	3486	C−H str[h]
	2	1699	1675	1534	1500	1672	1548	1731	C−H def[i] + C−N str
	3	1403	1396	1250	1244	1506	1435	1563	C−N str
	4	1276	1267	1206	1191	1405	1232	1495	C−H def + C−N str
	5	1171	1170	1071	1055	1109	1001	1197	N−N str
	6	1082	1073	971	959	934	855	928	ring def
B_2	7	3324	3355	3244	3269	3244	3105	3481	C−H str
	8	1570	1553	1449	1418	1456	1458	1538	C−N str + C−H def
	9	1394	1392	1298	1292	1411	1356	1503	C−N str
	10	1319	1313	1221	1211	1163	1060	1265	C−H def + C−N str
	11	1084	1076	983	968	961	889	967	ring def
A_2	12	973	973	789	738	839	783	916	C−H wag
	13	782	775	702	667	682	603	641	ring torsion
B_1	14	972	971	799	771	851	785	908	C−H wag
	15	767	758	702	681	626	567	590	ring torsion
error[d]	C−H								
	in-plane[e]	140	131	32	24	121	97	178	
	total	140	131	32	24	121	97	178	
SF[f]		0.796	0.808	0.949	0.975	0.818	0.933	0.738	
error[d]		15	12	21	20	85	85	86	

[a] See footnote *b* in Table 1. [b] Polarization and polarization ratio between parenthesis. p: polarized. dp: depolarized. [c,d,e,f,g] See footnotes *c*, *f*, *g*, *h*, and *i*, respectively, in Table 4. [h] str = stretch. [i] def = deformation. [j] wag = wagging.

scaling. Those reported by Wong[10] using 1SF frequency scaling are 0.9427, 0.9833, 0.9940, 0.9820, and 0.9613 at the MP2, LDA, BLYP, BVWN, and B3LYP levels, respectively, using the 6-31G* basis set. These correspond to force field scale factors of 0.8887, 0.9669, 0.9880, 0.9643, and 0.9241, respectively. These scale factors are quite close to those obtained by us for neutral five-membered heterocyclic molecules[2,14−16] but smaller than those calculated for studied anions. Those reported by Brouwer for *N*,*N*,*N*′,*N*′ -tetramethyl-*p*-phenylenediamine radical cation using frequency scaling are 0.982 and 1.020 by the UBLYP and UB3LYP methods, respectively. These correspond to force field scale factors of 0.964 and 1.040, respectively. This is in agreement with our observation that the scale factors of the studied molecules are bigger than those of neutral molecules.

The BLYP and BVWN scale factors are bigger than 1.0 since all the calculated frequencies by both methods are underestimated and both have the longest bond lengths among the DFT methods used. The LDA scale factors are close to 1.0 since some of the calculated frequencies are underestimated and some are overestimated. The B3LYP scale factors are less than 1.0 since most of the calculated frequencies are overestimated as the B3LYP method has the shortest predicted bond lengths. The calculated scale factors by the B3LYP and LDA methods for the studied anions are generally less divergent than those obtained by the other methods. The effect of the basis set and inclusion of diffuse functions, as was observed for the optimized geometries and calculated frequencies, is small. The largest difference is found for the MP2 method. For the semiempirical methods, the PM3 scale factors are the biggest and the MNDO scale factors are the smallest since the PM3 had the smallest average error and the MNDO had the biggest average error. However, the PM3 scale factors are the least divergent and the average error obtained by the three semiempirical methods is very close to each other.

As was observed for furan and thiophene,[2] the B3LYP average error is the lowest followed by the LDA average error, although for **3** this order is reversed. The semiempirical methods have the highest average error, about 90 cm^{-1}. The BS1 and BS3 have average errors close to each other, but the addition of the diffuse functions, BS2 and BS4, is accompanied by bigger average errors except at the HF level.

TABLE 6: Calculated Vibrational Frequencies (cm^{-1}) for 3[a]

		B3LYP		LDA		BLYP		BVWN		exptl		
symmetry	no.	BS1	BS2	BS1	BS2	BS1	BS2	BS1	BS2	IR	Raman[b]	SA[c]
A_1	1	3199	3228	3139	3165	3101	3137	3135	3171	3114	3136	3114
	2	1296	1297	1294	1298	1219	1222	1220	1224	1289	1290(p,0.03)	1289
	3	1192	1189	1192	1191	1099	1096	1096	1095	1188	1186(p,0.05)	1188
	4	1075	1063	1111	1105	992	977	993	982	1081	1081(p,0.13)	1081
	5	1022	1018	999	995	939	940	931	932	1022	1023(p)	1022
B_2	6	1473	1457	1452	1438	1398	1380	1408	1393	1433	1433(dp,0.72)	1433
	7	1169	1166	1169	1171	1120	1114	1129	1124	1149		1149
	8	1143	1136	1131	1120	1070	1065	1071	1066	1132	1133(dp,0.73)	1132
	9	1009	998	1005	994	934	923	929	921	1004	1004(dp,0.65)	1004
A_2	10	754	746	752	743	717	709	717	711		760	
B_1	11	830	832	792	794	784	786	796	798			
	12	722	715	717	710	690	684	691	687		697	
error[d]	C−H	85	114	25	51	13	23	21	57			
	in-plane[e]	12	11	12	13	67	73	66	71			
	total	20	22	14	18	61	68	61	69			
SF[f]		0.962	0.959	0.983	0.980	1.057	1.050	1.043	1.034			
error[d]		17	23	11	16	41	51	49	58			

		HF		MP2					
symmetry	no.	BS1	BS2	BS1	BS2	AM1	PM3	MNDO	AD[g]
A_1	1	3380	3400	3290	3308	3265	3123	3507	C−H str[b]
	2	1484	1478	1279	1274	1533	1477	1651	C−N str
	3	1396	1389	1145	1123	1479	1445	1568	N−N str
	4	1252	1239	1109	1094	1409	1210	1515	N−N str
	5	1133	1127	1005	992	951	891	986	ring def
B_2	6	1648	1632	1499	1473	1647	1526	1724	C−H def + C−N str
	7	1296	1295	1234	1224	1391	1248	1476	C−H def + C−N str
	8	1273	1265	1145	1128	1136	1042	1222	ring def + N--N str
	9	1141	1129	1001	981	938	888	1015	ring def + N--N str + C−H def
A_2	10	842	836	743	714	753	640	707	ring tosion + C−H wag
B_1	11	974	970	810	786	852	796	918	C−H wag + ring torsion
	12	796	787	711	691	685	609	647	ring torsion + C−H wag
error[d]	C−H	286	176	194	151	9	393		
	in-plane[e]	165	156	32	32	182	137	241	
	total	176	139	48	50	178	123	258	
SF[f]		0.797	0.800	0.929	0.934	0.798	0.907	0.699	
error[d]		35	27	43	52	128	115	125	

[a] See footnote *b* in Table 1. [b] See footnote *b* in Table 5. [c ,d,e,f,g]See footnotes *c*, *f*, *g*, *h*, and *i*, respectively, in Table 4. [h] str = stretch. [i] def = deformation. [j] wag = wagging.

TABLE 7: Calculated IR Absorption Intensities (km/mol) for 1 Using the 6-31G Basis Set**

symmetry	no.	B3LYP	LDA	BLYP	BVWN	HF	MP2	AM1	PM3	MNDO	exptl
A_1	1	73.6	58.9	90.3	99.0	69.0	58.2	12.0	13.1	0.8	
	2	0.3	0.4	0.5	0.5	0.1	0.3	7.1	4.4	6.7	m[b]
	3	0.5	0.5	0.3	0.3	5.5	0.0	0.1	23.3	1.4	
	4	7.8	6.7	6.5	2.3	9.2	0.3	2.5	13.7	15.0	s
	5	4.4	4.8	3.7	8.2	3.3	8.2	3.0	2.5	0.3	m
	6	1.8	2.1	1.4	1.6	2.0	1.4	0.5	0.8	3.9	s
B_2	7	54.6	40.9	67.6	73.7	52.5	42.4	9.0	11.6	0.7	
	8	9.0	9.3	8.3	8.1	11.5	3.6	11.8	48.0	16.9	m
	9	0.5	2.1	4.2	5.6	5.6	0.4	0.9	36.8	1.0	w
	10	28.5	24.7	17.7	11.1	25.7	30.4	7.0	10.4	1.9	vs
	11	16.3	18.0	21.8	27.9	18.0	12.4	4.2	4.4	4.2	
A_2	12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
	13	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
B_1	14	22.5	15.2	17.8	19.1	36.3	26.2	77.9	58.6	28.4	
	15	0.8	9.7	1.2	0.7	0.4	1.8	2.4	2.9	1.1	

[a] Reference 24. [b] vs: very strong. s: strong. m: medium. w: weak. vw: very weak.

IR Absorption Intensities. The calculated IR absorption intensities of **1**, **2**, and **3** are given in Tables 7, 8, and 9, respectively, using the BS1 basis set only as the calculated IR absorption intensities showed little dependence on the basis set used. Except with the semiempirical methods, good qualitative agreement between the calculated and experimental intensities is found but the agreement is not as excellent as previously reported.[1,2,3,8,15,16,40] For example, ν_2 and ν_6 of **1**, ν_3 of **2**, and ν_2 of **3** are not predicted to be as intense as observed experimentally. The agreement with the semiempirical methods is generally less satisfactory.

Bands corresponding to the C−H stretching modes are predicted by all methods used, except by the semiempirical methods, to be very intense while most of these bands are too weak to be observed experimentally. This is contrary to what was observed for neutral five-membered heterocyclic molecules.[2,14−16] This was also observed by Langhoff for polycyclic aromatic hydrocarbon neutrals, cations, and anions.[21]

TABLE 8: Calculated IR Absorption Intensities (km/mol) for 2 Using the 6-31G Basis Set**

symmetry	no.	B3LYP	LDA	BLYP	BVWN	HF	MP2	AM1	PM3	MNDO	exptl[a]
A_1	1	9.9	7.6	12.3	13.6	9.2	8.4	3.9	4.1	0.2	
	2	41.5	40.7	35.5	35.5	63.1	31.4	34.5	118.6	53.3	vs[b]
	3	0.3	0.0	0.2	0.5	0.6	2.5	1.1	0.0	0.7	
	4	18.8	4.0	20.8	24.4	21.1	12.7	3.8	11.9	1.2	vs
	5	17.0	27.4	2.2	0.6	33.4	15.8	14.3	18.9	8.1	m
	6	10.8	8.4	18.8	19.9	11.4	8.1	3.7	7.2	2.4	m
B_2	7	170.8	137.9	196.0	210.5	180.1	139.7	34.5	29.7	0.0	
	8	4.8	7.5	4.7	4.2	0.8	14.8	0.8	3.5	1.4	vw
	9	18.7	12.7	15.3	15.5	35.5	11.0	1.5	9.0	0.1	s
	10	0.9	0.0	0.8	1.8	7.4	0.2	0.1	0.5	0.1	m
	11	9.9	11.7	9.9	9.3	10.3	9.7	6.1	6.9	5.5	w
A_2	12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
	13	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
B_1	14	7.7	8.5	7.9	8.2	5.5	15.2	75.4	43.6	22.8	
	15	18.8	18.3	14.2	14.9	34.7	16.8	28.7	23.3	19.3	

[a] This work. [b] See footnotes *b* in Table 7.

TABLE 9: Calculated IR Absorption Intensities (km/mol) for 3 Using the 6-31G Basis Set**

symmetry	no.	B3LYP	LDA	BLYP	BVWN	HF	MP2	AM1	PM3	MNDO	exptl[a]
A_1	1	56.5	42.7	69.4	75.7	57.3	45.3	28.8	26.8	2.6	
	2	0.3	0.2	0.2	0.2	0.0	1.5	4.7	10.9	1.8	m[b]
	3	8.1	5.5	6.3	6.8	16.8	5.9	12.0	17.1	15.4	s
	4	4.2	5.8	1.3	2.1	5.8	10.3	0.6	8.5	14.9	m
	5	12.5	11.5	15.6	14.7	10.2	6.5	2.7	2.6	2.9	w
B_2	6	17.4	18.3	14.5	14.1	26.7	13.2	19.8	85.1	30.7	vs
	7	6.3	2.7	11.6	13.6	11.4	0.6	3.5	19.0	1.9	vs
	8	14.8	17.1	5.2	4.4	21.0	18.2	7.8	9.2	4.1	vs
	9	15.9	14.4	17.9	18.5	13.3	10.2	2.3	5.6	0.8	w
A_2	10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
B_1	11	6.4	7.2	6.3	6.3	5.4	10.2	48.4	27.2	17.1	
	12	6.8	6.6	5.1	5.4	13.1	5.3	10.8	7.5	7.1	

[a] This work. [b] See footnotes *b* in Table 7.

It is interesting to notice the similarity between the experimental IR and Raman spectra of **2** and **3**. For example, the pattern of bands in the Raman spectra of **2**/ **3** at 1491/1432, 1388/1289, 1257/1187, 1150/1133, 1030/1022, and 977/1005 cm^{-1} is quite similar and of comparable intensity. This pattern is well reproduced by the calculated IR spectra of **2** and **3** except ν_{10} of **2** and ν_7 of **3** (both correspond to C−H deformation + C−N stretching modes) are predicted to be weaker than observed experimentally. The spectra of **1**, especially the IR spectra, is somewhat different from those of the other two molecules.

Conclusion

In the present publication, the vibrational spectra of **2** and **3** were presented. A comparison between the optimized geometries, vibrational frequencies, scale factors, and IR absorption intensities for the three anions, **1**, **2**, and **3**, was made. The calculations were performed at the same levels of theory as those reported previously for furan and thiophene,[2] B3LYP, BLYP LDA, BVWN, HF, and MP2 using basis sets without diffuse functions, BS1 and BS3, and with diffuse functions, BS2 and BS4. The calculated results were compared with the experimental data reported in this work for **2** and **3** and available in the literature for **1**. An important conclusion is that the scale factors obtained for the studied anions are bigger than those obtained for neutral molecules and are similar to those obtained for a radical cation using the UBLYP and UB3LYP methods.[22] Since scale factors for common use are calculated as an average scale factors for a large number of molecules[8−10] rather than for single molecules, this conclusion indicate that ionic species require a unique scale factor separate from those calculated for neutral molecules.

The presented experimental spectra of the studied anions in the reported in this work were measured for the solution phase rather than the gas phase since measurement of the gas-phase spectrum of most anions is not practical. It is not clear how the interaction of the anions with the solvent molecules or the cation may effect the results. For this reason, the calculations were extended to include the 1,2,3-triazole−Na^+ complex. The calculations of the latter were done at the same levels as for **1** using the BS1 and BS2 basis sets. Although these results are not presented in the current publication for space reasons, the calculated results were very similar to those obtained for **1**, except with the BS2 basis set the Na−N_2 bond length was shorter by about 0.04 Å and the Na−N_2−N_1 bond angle was bigger by about 5° with the B3LYP method. The calculated frequencies for the modes corresponding to the Na^+ by the B3LYP BS1/BS2 basis sets are 349/355, 125/53, and 122/51 cm^{-1}. This indicates that the diffuse functions have big effect on the results related to the cation part. There is no experimental data available in this far-IR region to judge these results.

The results were related as much as possible to the optimized geometires. Rationalization of the behavior of different density functionals is not possible since these functionals were optimized with respect to thermodynamic properties rather than with respect to vibrational frequencies. However, it is clear that the three-parameter B3LYP functional with the HF component out−performs the other functionals. The performance of the semiempirical methods described the modes best among all methods used.

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