

Ab initio study of small organic azides

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Abstract

Ab initio MP2(full)/TZ2P//MP2(full)/TZ2P calculations of the following organic alkyl azides were carried out: hydrazoic acid (1), methyl azide (2), ethyl azide (3), 3-azidopropine (4), azidoacetonitrile (5), azido-2-butine (6), allylazide (7), 2-azido-1,3-butadiene (8). Fully optimized geometries of all rotational conformers of these molecules were calculated. Ab initio MP2 analytical force fields were computed and the theoretical vibrational wavenumbers were obtained. Good agreement is found between the theoretical and experimental IR/Raman and microwave spectra, and also for structures obtained by electron diffraction. © 1997 Elsevier Science B.V.

Keywords: Ab initio; Organic azides; Vibrational spectra

1. Introduction

The present study is devoted to the ab initio investigation of small organic azides. The azido group $-N_3$ can be formally derived from hydrazoic acid HN_3 , which was first prepared in 1890 [1]. The correct chain structure was proposed in 1911 [2]. The linear structure of the azido group in NaN_3 and KN_3 was confirmed by an X-ray study in 1925 [3] and by Raman spectroscopy in 1934 [4]. Later, the structures of methyl azide [5] and cyanuric azide [6] were determined by gaseous electron diffraction and X-ray diffraction, respectively, and a chain (possibly linear) structure for the azido group, with two widely differing NN bonds, was found.

Individual azides can be classified as organic azides, ionic azides or coordinative azides. Organic azides can be divided into two classes, i.e. alkyl or

aryl. Small alkyl organic azides, to which our work is devoted, are highly explosive materials. Several papers dealing with both theoretical and experimental studies of the conformation and IR/Raman spectra of small alkyl organic azides have been published [7]. Many azides have been studied theoretically over the last 10 years, ranging from hydrazoic acid (1) [8–10] to simple alkyl azides, e.g. methyl azide (2) [8–10], ethyl azide (3) [9–11], allylazide (7) [12–14], vinyl azide [9], formyl azide [9], azidoacetonitrile (5) [15], azido-2-butine (6) [16], 2-azido-1,3-butadiene (8) [17], 2,3-diazido-1,3-butadiene [18], 3-azidopropine (4) [19], 4-azidobutine [20,21]. In many of these studies the force fields were derived partly from HF ab initio data and partly from empirical ones.

In this study, we use a more sophisticated theoretical approach and larger basis set than in the previous calculations [8–21]. All the calculations in this study were carried out with the same basis set and therefore the results are inwardly consistent. The

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MP2 level of theory was chosen because it includes the major part of the correlation energy and the calculations are reasonably fast. A further advantage of the MP2 level is the implementation of analytical second derivatives in the GAUSSIAN program package [22].

The main goal of our work was to evaluate the theoretical conformational potential of simple alkyl azides and to provide a theoretical interpretation of the IR/Raman spectra of selected organic azides at the MP2(full)/TZ2P//MP2(full)/TZ2P level of theory. The MP2 force field allows the direct comparison of computed and measured IR/Raman wavenumbers without the need to use any scaling factors [23,24]. Earlier papers on alkyl azides [8–21] contain HF or “mixed” (HF + empirical) force fields.

In this paper, we have recomputed at the MP2 level of theory the following azides (see Fig. 1): hydrazoic acid (1), methyl azide (2), ethyl azide (3), 3-azidopropine (4), azidoacetonitrile (5), azido-2-butene (6), allylazide (7), 2-azido-1,3-butadiene (8). The previously published papers dealing with organic azides usually used smaller basis sets and only the HF level of theory.

2. Methods

Ab initio molecular orbital calculations were performed using the GAUSSIAN [22] and TURBOMOLE [25] programs. Some geometry optimizations were carried out with the SPARTAN [26] program. All calculations were carried out using the Huzinaga TZ + 2P basis sets [27] and the geometry optimizations were carried out at the MP2(full)/TZ2P level of theory, where all internal coordinates were optimized and no symmetry assumptions were made. All calculated geometries correspond to true energy minima. The enthalpies of the alkyl azides at zero absolute temperature (ΔH^0) were calculated as the sum of the MP2(full)/TZ2P//MP2(full)/TZ2P energies and the ZPE energies.

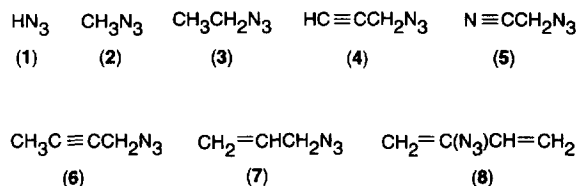


Fig. 1. Formulae of molecules under study.

3. Results and discussion

3.1. Structure, charge distribution and vibrational spectra of the azido group

Both theoretical (ab initio) and experimental (X-ray diffraction and electron diffraction) methods [8–21] provide the following common structural features for alkyl organic azides: the azido group has a chain structure with two different NN bond lengths (Table 1), which is slightly bent—the NNN angle is around 174° , see Table 1.

The MP2 calculated charges on C₁, N₁, N₂, N₃ (atom numbering is shown in Fig. 2) for all the computed molecules are listed in Table 2. The charges on the individual atoms were calculated by natural bond orbital analysis [22]. The listed values of the charge distribution are in good agreement with a previous investigation [21], see Fig. 2.

The energies of all the calculated conformers of all the molecules are listed in Table 3. Selected optimized and experimental geometry parameters of the computed molecules are shown in Table 1. For all molecules where comparison with experiment is available, the computed internal coordinates are in good agreement with the experimental data. The only exception is the NNN angle in methyl azide (2), for which we calculated a value of 173.4° while the experimental value was incorrectly assumed to be 180.0° [9]. The calculated vibrational frequencies agree very well with the experimental frequencies and the assignment is the same as in former calculations of the computed molecules; some details and exceptions are discussed below. All the computed molecules were studied by IR/Raman spectroscopy, and the following also by microwave spectroscopy (hydrazoic acid (1) [9], methyl azide (2) [9]) and electron diffraction (methyl azide (2) [9], 3-azidopropine (4) [19], azidoacetonitrile (5) [15], azido-2-butene (6) [16], allylazide (7) [12], 2-azido-1,3-butadiene (8) [17]). Tables 4–11 give the computed and measured vibrational spectra.

The azido group has four characteristic vibrational modes—two stretching and two bending ones. The calculated parameters of both azide nitrogens—bond distances, force constants and PED (potential energy distribution, showing (in %) which molecular movements are mainly involved in a fundamental

Table 1
Selected optimized geometry parameters of the computed alkyl azides (bond lengths in Å, angles in deg)

$N_1N_2N_3X_4X_5X_6$ molecule	N_1N_2	N_2N_3	N_1X_4	$X_3X_6^a$	$N_1N_2N_3$	$N_2N_3X_4$	$N_2N_3X_4X_5$	$N_1X_4X_5X_6^b$
Hydrazoic acid (1)	1.143	1.244	1.016		171.6	109.5		
Hydrazoic acid (1) exp.	1.134(2)	1.243(5)	1.015(15)		171.3(50)	108.8(40)		
Methyl azide (2)	1.148	1.235	1.476		173.4	114.0	180.0	
Methyl azide (2) exp.	1.130(5)	1.216(4)	1.468(5)		180.0 ^c	116.8(3)		
Ethyl azide ^d (3) gauche	1.149	1.235	1.484		173.7	113.9	65.1	
Ethyl azide (3) anti	1.149	1.236	1.484		173.7	114.1	180.0	
3-Azidopropine (4) gauche	1.147	1.239	1.486	1.211	173.5	113.2	51.3	
3-Azidopropine (4) anti	1.148	1.238	1.486	1.209	173.4	112.8	180.0	
3-Azidopropine (4) exp.	1.137(5)	1.241(9)	1.495	1.226(10)	171.2(43)	112.4(16)	46(7)	
Azidoacetone (5) gauche	1.145	1.243	1.474	1.166	172.9	113.3	59.8	
Azidoacetone (5) anti	1.146	1.240	1.476	1.165	173.0	112.6	180.0	
Azidoacetone (5) exp.	1.135(4)	1.245(5)	1.475(6)	1.154(5)	173(3)	115.4(11)	52(5)	
Azido-2-butene (6) gauche	1.147	1.238	1.491	1.213	173.7	113.1	47.7	
Azido-2-butene (6) anti	1.148	1.238	1.489	1.211	173.5	112.8	180.0	
Azido-2-butene (6) exp.	1.112(5)	1.240(6)	1.474(15)	1.208(6)	174(5)	116.5(14)	37(10)	
Allylazide (7) GG	1.148	1.237	1.494	1.333	174.5	112.4	61.1	250.3
Allylazide (7) GG'	1.149	1.236	1.490	1.331	173.6	113.8	-66.1	243.8
Allylazide (7) GA	1.149	1.236	1.488	1.330	173.7	113.7	185.2	236.9
Allylazide (7) SG	1.148	1.237	1.475	1.330	173.1	114.1	70.9	3.5
Allylazide (7) SA	1.148	1.235	1.477	1.330	173.5	113.9	180.0	0.0
Allylazide (7) exp.	1.138(4)	1.236(5)	1.475(2)	1.331(7)	174(5)	115.1(2)	60.0(10)	240.0
2-Az.-1,3-but. ^e (8) trans, syn	1.147	1.235	1.424	1.342	174.1	115.5	0.0	180.0
2-Az.-1,3-but. (8) trans, anti	1.148	1.238	1.426	1.339	171.5	117.5	219.1	197.1
2-Az.-1,3-but. (8) cis, syn	1.147	1.237	1.427	1.340	174.3	115.4	0.2	35.6
2-Az.-1,3-but. (8) cis, anti	1.147	1.239	1.424	1.338	172.1	116.9	192.3	45.8
2-Az.-1,3-but. (8) exp.	1.143(4)	1.253(6)	1.434(7)	1.350(4)	176.5(3.5)	116.8(1.1)	0.0	180.0

^a C=C, C=C or C=N respectively.

^b C=C-C-N dihedral angle for allylazide, C=C-C=C dihedral angle for 1-azido-1,3-butadiene.

^c Assumed.

^d No experimental data available.

^e Abbreviation for 2-azido-1,3-butadiene.

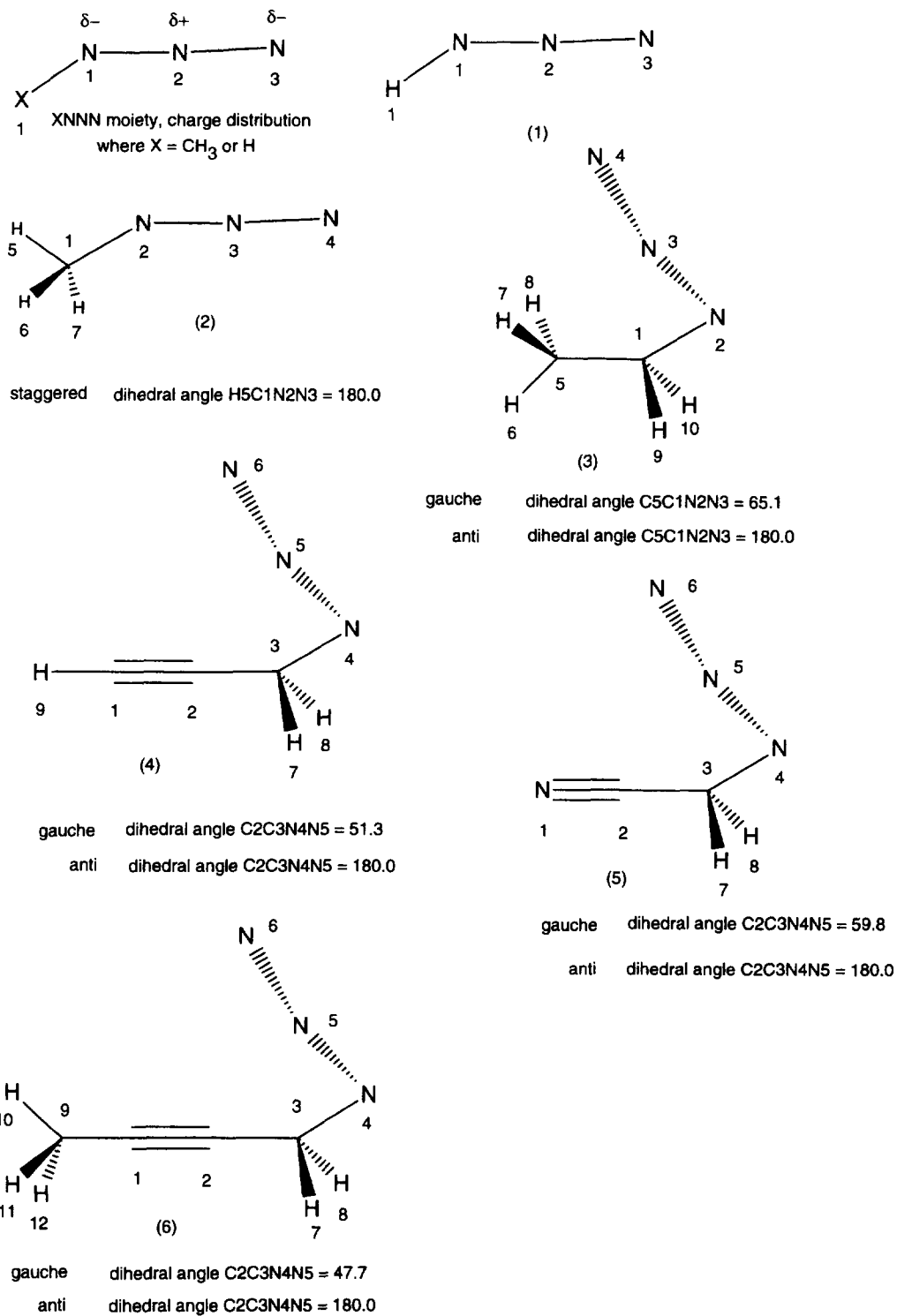


Fig. 2. The organic azides under study, their atom numbering and their selected dihedral angles.

vibration) [28]—revealed that the two stretching vibrations are best interpreted as triple N≡N and double N=N vibrations rather than as symmetric and asymmetric NNN modes. Owing to the high polarity of both bonds, the above-mentioned modes are among the strongest bands in the IR spectra, with relatively narrow ranges of 2110–2130 cm⁻¹ for the N≡N stretch vibration and 1210–1290 cm⁻¹ for the N=N stretch vibration. The corresponding calculated values are 2250–2280 cm⁻¹ and 1240–1300 cm⁻¹, respectively. The calculated N≡N stretch vibrations are over-estimated by 7% with respect to the measured ones, but the calculated N=N vibrations only by 1–2%. As

can be seen from the PED, both modes interact and the N≡N mode mixes in about 25% of the N=N mode. For the -CH₂N₃ moiety, the N=N mode is usually also mixed with the CH₂ twisting and neighbouring C-N stretching modes, which give two strong bands in the IR spectra in the above-mentioned wavenumber range. The assignment of these absorptions is not, therefore, straightforward.

The azido group is slightly bent and so two azido group deformation vibrations can be divided on bending in-plane (bip) and bending out-of-plane (bop, N=N torsion) modes. The latter barely mixes with other modes and is conformationally nearly

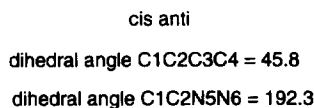
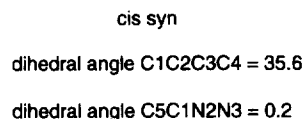
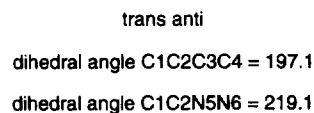
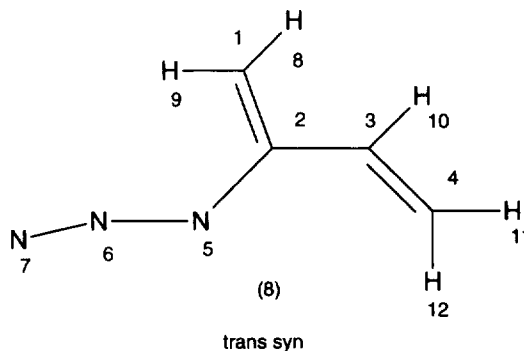
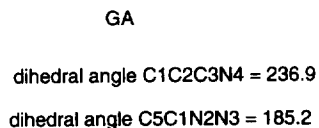
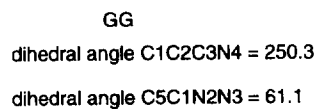
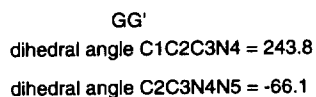
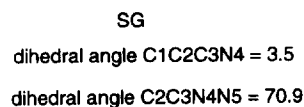
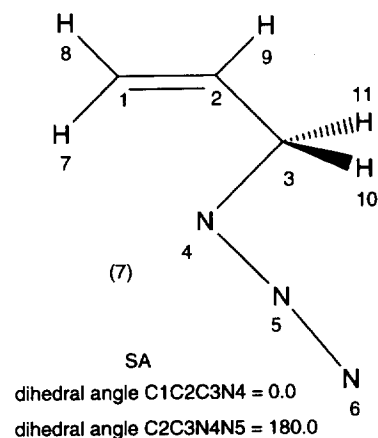


Fig. 2. Continued.

Table 2

Atomic charges on individual atoms of the computed molecules^a using natural bond orbital analysis at the MP2 level

Molecule	Atom			
	C ₁ ^b	N ₁	N ₂	N ₃
Hydrazoic acid (1)	0.37	-0.54	0.22	-0.05
Methyl azide (2)	-0.39	-0.32	0.21	-0.08
Ethyl azide (3) gauche	-0.20	-0.32	0.21	-0.08
3-Azidopropine (4) gauche	-0.29	-0.31	0.22	-0.05
Azidoacetonitrile (5) gauche	-0.31	-0.31	0.21	-0.02
Azido-2-butine (6) gauche	-0.27	-0.31	0.22	-0.06
Allylazide (7) GG	-0.25	-0.32	0.21	-0.07
2-Azido-1,3-butadiene ^c (8)	-0.33	-0.32	0.23	-0.04

^a For the most stable conformer.^b H₁ atom for hydrazoic acid (1).^c Trans, syn conformer.

constant. This band appears in the very narrow range of 550–565 cm⁻¹ and is usually weak. The calculated values are slightly underestimated and lie in the range 540–560 cm⁻¹. The bip mode shows considerable conformational sensitivity and, according to the PED, interacts with the C–N=N bending mode. It appears in the IR spectra as a medium or weak band

in the range 620–710 cm⁻¹. The calculated values reflect very well the changes in wavenumber for different conformers (e.g. 716 and 666 cm⁻¹ for the gauche and anti conformers of 3-azidopropine, respectively) and are practically in the same wavenumber interval. We will now discuss in more detail the individual azides.

Table 3

Calculated MP2(full)/TZ2P//MP2(full)/TZ2P, ZPE(MP2) and $\Delta H^0 = \text{MP2(full)/TZ2P//MP2(full)/TZ2P} + \text{ZPE(MP2)}$ energies of the computed molecules^a

Molecule	Energy		
	MP2	ZPE	ΔH^0
Hydrazoic acid (1)	-164.5258354	55.91	-164.5045392
Methyl azide (2)	-203.7434255	133.73	-203.6924893
Ethyl azide (3) gauche	-242.9738584	209.78	-242.8939564
Ethyl azide (3) anti	-242.9734183	209.22	-242.8937323
3-Azidopropine (4) gauche	-279.7384001	157.13	-279.6785521
3-Azidopropine (4) anti	-279.7353750	156.35	-279.6758230
Azidoacetonitrile (5) gauche	-295.8311150	129.65	-295.7817340
Azidoacetonitrile (5) anti	-295.8287024	128.96	-295.7795844
Azido-2-butine (6) gauche	-318.9743555	233.52	-318.8854135
Azido-2-butine (6) anti	-318.9710833	232.73	-318.8824393
Allylazide (7) GG	-280.9764180	221.98	-280.8918680
Allylazide (7) GG'	-280.9743262	221.94	-280.8897952
Allylazide (7) GA	-280.9736634	221.22	-280.8894044
Allylazide (7) SG	-280.9750884	222.04	-280.8905184
Allylazide (7) SA	-280.9740939	221.29	-280.8898109
2-Azido-1,3-butadiene (8) trans, syn	-318.9956439	232.85	-318.9069579
2-Azido-1,3-butadiene (8) trans, anti	-318.9912767	^b	^b
2-Azido-1,3-butadiene (8) cis, syn	-318.9916945	^b	^b
2-Azido-1,3-butadiene (8) cis, anti	-318.9899577	^b	^b

^a MP2 and ΔH^0 energies are in u, and ZPE in kJ mol⁻¹.^b ZPE and ΔH^0 were not computed.

Table 4
Observed and calculated fundamental vibrational frequencies of hydrazoic acid (1)

No.	Fundamental	Obs. ^a	Ab initio	PED ^b
$\nu_1 A'$	N–H stretch	3336	3542	99 N–H s
ν_2	N \equiv N stretch	2129	2292	73 N \equiv N s, 24 N=N s
ν_3	N=N stretch	1264	1253	33 N=N s, 25 N \equiv N s, 21 N=N–H δ
ν_4	N=N–H bend	1151	1133	84 N=N–H δ , 55 N=N s
ν_5	N \equiv N=N bend	537	549	98 N \equiv N=N δ
$\nu_6 A''$	N=N torsion	606	577	99 N=N τ

^a From Ref. [9].

^b Potential energy distribution for ab initio frequencies.

3.2. Hydrazoic acid (1) and methyl azide (2)

Hydrazoic acid (1) [8,9] (Fig. 2) and methyl azide (2) [8,9] (Fig. 2) are the simplest azide molecules. The calculated frequencies of hydrazoic acid (1) are in very good agreement with the observed ones (Table 4). The largest overestimations, 6–8%, are found for the high frequency fundamentals, but the differences are smaller for all other frequencies; N=N stretch, N=N–H bend and N=N torsional vibrations are slightly underestimated. In contrast to earlier calculations [8,9], the experimental band at 1264 cm^{-1} has now been calculated as a N=N stretch. This assignment is in agreement with all other organic azides where this mode is in the range 1200–1300 cm^{-1} . The experimental band of 1151 cm^{-1} , formerly

assigned as a N=N stretch, is now calculated to be a N=N–H bending mode. It is an extensively mixed N=N mode, and its high IR intensity can be attributed to this mixing and the very high polarity of the N–H bond.

3.3. Ethyl azide (3)

Ethyl azide (3) (Fig. 2) [9,11] can exist as two distinct conformers—gauche and anti—both arising from rotation with respect to the C₁–N₂ bond, see Fig. 2. The calculated energy difference between the two conformers is only 0.59 kJ mol^{-1} ([MP2(full)/TZ2P//MP2(full)/TZ2P] + ZPE), the gauche conformer being the more stable. This is in excellent agreement with the experimental value of (0.56 \pm 0.1 kJ mol^{-1}) [11].

Table 5
Observed and calculated fundamental vibrational frequencies of methyl azide (2)

No.	Fundamental	Obs. ^a	Ab initio	PED ^b
$\nu_1 A'$	CH ₃ asym. stretch	3023	3217	92 CH ₃ as
ν_2	CH ₃ sym. stretch	2935	3076	93 CH ₃ ss
ν_3	N \equiv N stretch	2106	2281	73 N \equiv N s, 26 N=N s
ν_4	CH ₃ asym. bend	1456	1527	93 CH ₃ a δ
ν_5	CH ₃ sym. bend	1417	1462	103 CH ₃ s δ
ν_6	N=N stretch	1272	1302	57 N=N s, 23 C–N s, 17 N \equiv N s
ν_7	CH ₃ rocking	1132	1158	79 CH ₃ ro
ν_8	C–N stretch	910	920	81 C–N s, 24 N=N s
ν_9	N \equiv N=N bend	666	687	54 N \equiv N=N δ , 21 C–N=N δ
ν_{10}	C–N=N bend	245	231	90 C–N=N δ , 44 N \equiv N=N δ
$\nu_{11} A''$	CH ₃ asym. stretch	2962	3153	100 CH ₃ as
ν_{12}	CH ₃ asym. bend	1465	1524	94 CH ₃ a δ
ν_{13}	CH ₃ rocking	1087	1127	94 CH ₃ ro
ν_{14}	N=N torsion	560	554	96 N=N τ
ν_{15}	CH ₃ torsion	100	136	100 CH ₃ τ

^a From Ref. [9].

^b Potential energy distribution for ab initio frequencies.

Table 6
Observed and calculated vibrational frequencies of ethyl azide (3)

No.	Fundamental	Obs. ^{a,b}	Ab initio ^b	Obs. ^{a,c}	Ab initio ^c	PED ^d
ν_1	CH ₂ asym. stretch	3000	3190	2952	3120	44 CH ₂ as, 42 CH ₃ as
ν_2	CH ₃ asym. stretch	2988	3178	2996	3190	70 CH ₃ as, 19 CH ₂ as
ν_3	CH ₃ asym. stretch	2976	3163	2988	3183	83 CH ₃ as, 14 CH ₂ as
ν_4	CH ₂ sym. stretch	2952	3086	2910	3070	49 CH ₂ ss, 39 CH ₃ ss
ν_5	CH ₃ sym. stretch	2943	3086	2929	3096	60 CH ₃ ss, 30 CH ₂ ss
ν_6	N = N stretch	2114	2273	2114	2275	74 N = N s, 26 N=N s
ν_7	CH ₂ asym. bend	1471	1527	1460	1518	49 CH ₂ δ , 46 CH ₃ a δ
ν_8	CH ₃ asym. bend	1464	1517	1471	1530	66 CH ₃ δ , 27 CH ₂ δ
ν_9	CH ₃ asym. bend	1450	1514	1450	1512	68 CH ₃ δ , 24 CH ₂ δ
ν_{10}	CH ₃ sym. bend	1382	1419	1388	1424	90 CH ₃ s δ
ν_{11}	CH ₂ wagging	1337	1381	1345	1374	83 CH ₂ wa
ν_{12}	CH ₂ twisting	1286	1324	1240	1304	63 CH ₂ tw
ν_{13}	N=N stretch	1249	1276	1279	1290	44 N=N s, 20 C-N s, 13 N = N s
ν_{14}	CH ₃ rocking	1139	1163	1124	1131	30 CH ₃ ro, 38 CH ₂ ro
ν_{15}	CH ₃ rocking	1081	1107	1107	1148	44 CH ₃ ro, 30 C-C s
ν_{16}	C-C stretch	990	1007	1022	1039	49 C-C s, 23 C-N s
ν_{17}	C-N stretch	845	859	857	865	51 C-N s, 12 C-C s
ν_{18}	CH ₂ rocking	799	810	805	815	53 CH ₂ ro, 46 CH ₃ ro
ν_{19}	N=N = N bend	657	684	630	660	45 N=N = N δ , 18 C-N=N δ
ν_{20}	N=N torsion	565	557	562	554	95 N=N τ
ν_{21}	C-C-N bend	406	404	390	383	80 C-C-N δ
ν_{22}	CH ₃ torsion	260	281		256	79 CH ₃ τ
ν_{23}	C-N=N bend	190	185	190	175	71 C-N=N δ , 30 N=N = N δ
ν_{24}	C-N torsion	55	81	55	61	98 C-N τ

^a From Ref. [11].

^b Gauche conformer.

^c Anti conformer.

^d Potential energy distribution for ab initio frequencies of gauche conformer.

3.4. 3-Azidopropine (4), azidoacetonitrile (5) and azido-2-butine (6)

3-Azidopropine (4) (Fig. 2) [19], azidoacetonitrile (5) (Fig. 2) [15] and azido-2-butine (6) (Fig. 2) [16] can exist in two distinct conformations—gauche and anti—with respect to rotation around the C₂–C₃ bond, and both are indeed calculated to be minima on the PES. It is clear from IR/Raman spectroscopy [15,16,19] and especially from electron diffraction studies [15,16,19] that at room temperature all three molecules exist only as the gauche conformer. The computed energy ([MP2(full)/TZ2P//MP2(full)/TZ2P] + ZPE, in kJ mol⁻¹) differences between both conformers are 7.16 for 3-azidopropine (4), 5.64 for azidoacetonitrile (5) and 7.81 for azido-2-butine (6), the gauche conformer being the more stable in all cases. These results agree with the experimental observation of only the gauche conformers. The exception

is azidoacetonitrile (5), for which the calculated energy difference is too small. The energy difference of 5.64 kJ mol⁻¹ means that a sample of azidoacetonitrile (5) at room temperature would consist of about 10% of the anti conformer; however, both IR/Raman spectroscopy and electron diffraction detected only one conformer. The reason for this discrepancy is probably insufficient accuracy of calculations.

Comparison of the calculated frequencies for the gauche and anti conformers of 3-azidopropine (4) and azido-2-butine (6) with the experimental [19,16] ones (Tables 7, and 9) is consistent with the conclusion that the observed conformer is the gauche one. The calculated frequencies for the gauche conformer of azidoacetonitrile (5) revealed better agreement with the experimental frequencies [15] of the liquid (5), while the calculated frequencies for the anti conformer showed better agreement with the crystal (5) (Table 8). Hence, our calculations support the

Table 7
Observed and calculated fundamental vibrational frequencies of 3-azidopropine (4)

No.	Fundamental	Obs. ^a	Ab initio ^b	Ab initio ^c	PED ^d
ν_1	C–H stretch	3331	3486	3489	96 \equiv C–H s
ν_2	CH ₂ asym. stretch	2985	3175	3113	77 CH ₂ as, 21 CH ₂ ss
ν_3	CH ₂ sym. stretch	2923	3087	3066	79 CH ₂ ss, 23 CH ₂ as
ν_4	N \equiv N stretch	2130	2276	2284	74 N \equiv N s, 25 N=N s
ν_5	C \equiv C stretch	2110	2132	2147	83 C \equiv C s
ν_6	CH ₂ deformation	1453	1508	1507	101 CH ₂ δ
ν_7	CH ₂ wagging	1340	1371	1369	86 CH ₂ wa
ν_8	N=N stretch	1247	1284	1282	26 N=N s, 50 CH ₂ tw
ν_9	CH ₂ twisting	1218	1252	1255	44 CH ₂ tw, 27 N=N s, 14 C–N s
ν_{10}	CH ₂ rocking	981	1013	994	77 CH ₂ ro
ν_{11}	C–C stretch	948	964	996	62 C–C s, 12 C–N s
ν_{12}	C–N stretch	868	883	936	68 C–N s, 14 N=N s
ν_{13}	N=N \equiv N bend	692	716	666	39 N=N \equiv N δ , 24 C–N=N δ
ν_{14}	H–C \equiv C lin. bend	669	655	655	110 H–C \equiv C δ
ν_{15}	H–C \equiv C lin. bend	637	638	632	111 H–C \equiv C δ
ν_{16}	N=N torsion	558	552	549	84 N=N τ
ν_{17}	C–C–N bend	501	512	492	33 C–C–N δ , 18 C–C \equiv C δ
ν_{18}	C–C \equiv C lin. bend	304	300	298	106 C–C \equiv C δ
ν_{19}	C–N=N bend	245	240	232	53 C–N=N δ , 38 C–C \equiv C δ
ν_{20}	C–C \equiv C lin. bend	160	163	129	41 C–C \equiv C δ , 31 C–N=N δ
ν_{21}	C–N torsion		59	46	87 C–N τ

^a From Ref. [19].

^b Gauche conformer.

^c Anti conformer.

^d Potential energy distribution for ab initio frequencies of gauche conformer.

Table 8
Observed and calculated fundamental vibrational frequencies of azidoacetonitrile (5)

No.	Fundamental	Obs. ^{a,b}	Ab initio ^b	Obs. ^{a,c}	Ab initio ^c	PED ^d
ν_1	CH ₂ asym. stretch	2996	3188	2962	3126	78 CH ₂ as, 19 CH ₂ ss
ν_2	CH ₂ sym. stretch	2939	3096	2929	3076	80 CH ₂ ss, 21 CH ₂ as
ν_3	N \equiv N stretch	2115	2274	2118	2288	74 N \equiv N s, 25 N=N s
ν_4	C \equiv N stretch	2258	2199	2257	2216	88 C \equiv N s
ν_5	CH ₂ deformation	1430	1501	1424	1505	101 CH ₂ δ
ν_6	CH ₂ wagging	1335	1372	1330	1374	91 CH ₂ wa
ν_7	CH ₂ twisting	1265	1299	1221	1260	51 CH ₂ tw, 26 N=N s, 15 CH ₂ wa
ν_8	N=N stretch	1217	1258	1288	1291	26 N=N s, 17 C–N s, 43 CH ₂ tw
ν_9	CH ₂ rocking	990	1017	968	996	77 CH ₂ ro
ν_{10}	C–C stretch	925	949		983	49 C–C s, 28 C–N s, 10 N=N s
ν_{11}	C–N stretch	875	891	937	948	46 C–N s, 23 C–C s, 13 C–C–N δ
ν_{12}	N=N \equiv N bend	685	713	621	660	41 N=N \equiv N δ , 23 C–N=N δ
ν_{13}	N=N torsion	555	554	552	543	65 N=N τ , 13 C–C–N δ
ν_{14}	C–C–N bend	525	527	518	519	16 C–C–N δ , 28 N=N τ , 18 C–C \equiv N δ
ν_{15}	C–C \equiv N lin. bend	347	341	354	344	93 C–C \equiv N δ
ν_{16}	C–C \equiv N lin. bend	260	253	272	248	37 C–C \equiv N δ , 44 C–N=N δ , 27 N=N \equiv N δ
ν_{17}	C–N=N bend	221	182	171	138	37 C–N=N δ , 34 C–C–N δ , 29 C–C \equiv N δ
ν_{18}	C–N torsion	80	59		45	85 C–N τ

^a From Ref. [15].

^b Gauche conformer.

^c Anti conformer.

^d Potential energy distribution for ab initio frequencies of gauche conformer.

Table 9

Observed and calculated fundamental vibrational frequencies of azido-2-butine (**6**)

No.	Fundamental	Obs. ^a	Ab initio ^b	Ab initio ^c	PED ^d
ν_1	CH ₃ asym. stretch	2983	3170	3169	96 CH ₃ as
ν_2	CH ₂ asym. stretch	2959	3169	3107	62 CH ₂ as, 17 CH ₂ ss
ν_3	CH ₃ asym. stretch	2959	3169	3169	83 CH ₃ as
ν_4	CH ₃ sym. stretch	2938	3090	3090	100 CH ₃ as
ν_5	CH ₂ sym. stretch	2938	3083	3062	78 CH ₂ ss, 23 CH ₂ as
ν_6	N = N stretch	2130	2277	2284	72 N = N s, 24 N=N s
ν_7	C = C stretch	2235	2263	2277	79 C = C s
ν_8	CH ₂ deformation	1460	1510	1507	94 CH ₂ δ
ν_9	CH ₃ deformation	1460	1508	1509	84 CH ₃ δ
ν_{10}	CH ₃ deformation	1460	1507	1508	90 CH ₃ δ
ν_{11}	CH ₃ deformation	1378	1428	1428	104 CH ₃ δ
ν_{12}	CH ₂ wagging	1341	1372	1371	84 CH ₂ wa
ν_{13}	N=N stretch	1251	1279	1279	27 N=N s, 47 CH ₂ tw
ν_{14}	CH ₂ twisting	1215	1252	1254	47 CH ₂ tw, 24 N=N s, 12 C-N s
ν_{15}	C-C asym. stretch	1146	1176	1191	85 C-C as
ν_{16}	CH ₃ rocking	1030	1070	1070	80 CH ₃ ro
ν_{17}	CH ₃ rocking	1030	1067	1068	81 CH ₃ ro
ν_{18}	CH ₂ rocking	980	1007	993	86 CH ₂ ro
ν_{19}	C-N stretch	880	892	932	84 C-N s, 17 N=N s
ν_{20}	C-C sym. stretch	772	772	796	36 C-C ss, 28 C-C-N δ
ν_{21}	N=N = N bend	672	690	650	36 N=N = N δ , 14 C-N=N δ , 29 C-C s
ν_{22}	N=N torsion	556	552	550	87 N=N τ
ν_{23}	C-C-N bend	490	501	468	29 C-C-N δ , 23 C-C = C δ
ν_{24}	C-C = C lin. bend	375	351	352	94 C-C = C δ
ν_{25}	C-C = C lin. bend	315	311	300	56 C-C = C δ
ν_{26}	C-N=N bend	230	214	197	53 C-N=N δ , 21 N=N = N δ
ν_{27}	C-C = C lin. bend	200	186	187	62 C-C = C δ
ν_{28}	C-C = C lin. bend	140	116	82	53 C-C = C δ
ν_{29}	C-N torsion		43	41	77 C-N τ
ν_{30}	CH ₃ torsion		12	21	112 CH ₃ τ

^a From Ref. [16].^b Gauche conformer.^c Anti conformer.^d Potential energy distribution for ab initio frequencies of gauche conformer.

authors' interpretation of the experimental spectra [15] according to which the large frequency shifts in ν_7 , ν_{10} , ν_{11} , ν_{12} are due to crystallization [15], and the fact that in the vapor and liquid phases the gauche conformer is present whereas in the crystal the anti conformer prevails.

3.5. Allylazide (**7**)

Allylazide (**7**) (Fig. 2) [12–14] can exist in five distinct conformations labelled GG, GG', GA, SG and SA (G = gauche, A = anti; the first and second letters mark the conformations with respect to the C₂–C₃ and C₃–N₄ bonds, respectively). Electron

diffraction studies [12–14] suggest the presence of the GG and SG conformers or of the GG, GG' and SG conformers. The latter experimental results agree with the computed data. According to temperature dependent Raman studies in the liquid phase [12–14], the following order of energies of the conformers and enthalpy differences (in kJ mol⁻¹) were derived: GG (0.0), SG (1.3), GG' (3.5), GA (4.4), SA (4.4). IR spectra in an Ar matrix [12–14] gave a similar ordering: GG (0.0), SG (1.5), GG' (2.9), GA (4.4). The computed results ([MP2(full)/TZ2P//MP2(full)/TZ2P] + ZPE) reveal the following ordering and differences in terms of energies: GG (0.0), SG (3.54), SA (5.40), GG' (5.44), GA (6.47). The order of calculated

Table 10
Observed and calculated fundamental vibrational frequencies of (a) the GG and SG conformations and (b) the GG', SA and GA conformations of allylazide (7)

(a)						
No.	Fundamental	Obs. ^{a,b}	Ab initio ^{a,b}	Obs. ^{a,c}	Ab initio ^{a,c}	PED ^d
ν_1	=CH ₂ asym. stretch	3101	3289	3101	3300	96 =CH ₂ as
ν_2	C–H stretch	3020	3214	2998	3190	92 C–H s
ν_3	=CH ₂ sym. stretch	2998	3187	3020	3206	95 =CH ₂ ss
ν_4	>CH ₂ asym. stretch	2971	3177	2971	3148	77 > CH ₂ as, 17 > CH ₂ ss
ν_5	>CH ₂ sym. stretch	2886	3084	2886	3066	82 > CH ₂ ss, 19 > CH ₂ as
ν_6	N ≡ N stretch	2113	2265	2113	2273	74 N ≡ N s, 25 N=N s
ν_7	C=C stretch	1648	1684	1654	1693	72 C=C s, 21 =CH ₂ δ
ν_8	>CH ₂ deformation	1458	1512	1440	1500	96 > CH ₂ δ
ν_9	=CH ₂ deformation	1421	1466	1415	1458	70 =CH ₂ δ, 12 CH ro
ν_{10}	>CH ₂ wagging	1333	1365	1346	1373	76 > CH ₂ wa
ν_{11}	C–H rocking	1302	1320	1281	1318	53 C–H ro, 13 C=C s
ν_{12}	>CH ₂ twisting	1251	1280	1222	1253	49 > CH ₂ tw, 24 > CH ₂ wa, 17 N=N s
ν_{13}	N=N stretch	1212	1245	1277	1311	36 N=N s, 11 N ≡ N s, 22 > CH ₂ tw
ν_{14}	>CH ₂ rocking	1128	1158	970	1020	22 > CH ₂ ro, 22 =CH ₂ ro, 15 C–C s
ν_{15}	CH ₂ =CH trans wag	999	1025	1003	1030	64 C=C τ, 33 CH wa
ν_{16}	C–C stretch	970	985	924	953	39 C–C s, 26 > CH ₂ ro
ν_{17}	=CH ₂ wagging	934	951	920	941	101 =CH ₂ wa
ν_{18}	=CH ₂ rocking	920	938	1062	1086	47 =CH ₂ ro, 28 > CH ₂ ro, 13 C–C s
ν_{19}	C–N stretch	887	896	856	874	74 C–N s, 13 N=N s
ν_{20}	N=N ≡ N bend	712	729	688	715	28 N=N ≡ N δ, 16 C–N=N δ
ν_{21}	CH ₂ =CH cis wag	608	630	559	564	21 CH wa, 15 C=C τ, 21 N=N ≡ N δ
ν_{22}	N=N torsion	565	555	543	540	95 N=N τ
ν_{23}	C–C=C bend	420	421	295	292	77 C–C=C δ
ν_{24}	C–C–N bend	354	349	567	570	67 C–C–N δ
ν_{25}	C–N=N bend	232	218	226	232	66 C–N=N δ, 33 N=N ≡ N δ
ν_{26}	C–N torsion	100	100	75	76	77 C–N τ, 16 C–C τ
ν_{27}	C–C torsion	75	64	175	135	77 C–C τ, 79 C–N τ

stabilities and the energy differences are in reasonably good agreement with the measured values [12–14], except for the order of the SA and GG' conformers, but both conformers have very similar enthalpies.

3.6. 2-Azido-1,3-butadiene (8)

2-Azido-1,3-butadiene (8) (Fig. 2) [17] can exist in four different conformations—trans, syn; trans, anti; cis, syn; cis, anti (see Fig. 2). The most stable calculated conformer is trans, syn, in agreement with the experimental observations (IR/Raman spectroscopy [17] and electron diffraction [17]) which reveal only this conformer. The higher stability of the trans, syn conformer is probably caused by conjugative stabilization of the C=C, N=N and N ≡ N bonds in

the planar structure of this conformer. The other conformers cannot be stabilized by conjugation, because they are not planar. We can see from Table 3 that rotation around the C₂–C₃ bond is less energy demanding than rotation around the C–N bond (i.e. the cis, syn conformer is more stable than the trans, anti conformer).

4. Conclusions

Ab initio calculations of organic alkyl azides reveal that they can exist as several rotational isomers. IR/Raman spectroscopy [11,15–17,19] and electron diffraction [15–19] studies suggest that ethyl azide (3) consists of two conformers—gauche and anti. According to these studies, the following azides

Table 10 Continued

(b)							
No.	Fundamental	Obs. ^{a,e}	Ab initio ^c	Obs. ^{a,f}	Ab initio ^f	Obs. ^{a,g}	Ab initio ^g
ν_1	=CH ₂ asym. stretch	3101	3289	3101	3303	3101	3290
ν_2	C–H stretch	3020	3200	3020	3210	3020	3215
ν_3	=CH ₂ sym. stretch	2998	3187	2998	3195	2998	3189
ν_4	>CH ₂ asym. stretch	2971	3177	2971	3090	2971	3115
ν_5	>CH ₂ sym. stretch	2886	3075	2886	3048	2886	3057
ν_6	N≡N stretch	2113	2274	2113	2282	2113	2275
ν_7	C=C stretch	1642	1691	1648	1698	1648	1698
ν_8	>CH ₂ deformation	1458	1508	1458	1501	1458	1508
ν_9	=CH ₂ deformation	1421	1470	1421	1460	1421	1470
ν_{10}	>CH ₂ wagging	1324	1362	1371	1377	1333	1355
ν_{11}	C–H rocking	1300	1327	1322	1326	1316	1319
ν_{12}	>CH ₂ twisting	1270	1292	1212	1248	1235	1257
ν_{13}	N=N stretch	1231	1252	1266	1300	1241	1283
ν_{14}	>CH ₂ rocking	1128	1168	970	1009	1128	1163
ν_{15}	CH ₂ =CH trans wag	999	1028	999	1026	999	1029
ν_{16}	C–C stretch	970	965	955	970	970	986
ν_{17}	=CH ₂ wagging	936	957	928	939	920	953
ν_{18}	=CH ₂ rocking	922	956	1085	1110	899	920
ν_{19}	C–N stretch	873	886	899	916	948	966
ν_{20}	N=N≡N bend	719	731	624	660	657	688
ν_{21}	CH ₂ =CH cis wag	597	629	556	561	606	626
ν_{22}	N=N torsion	554	551		548	556	553
ν_{23}	C–C=C bend	420	420		571	420	417
ν_{24}	C–C–N bend	335	341	275	275	339	334
ν_{25}	C–N=N bend	232	201		153	232	165
ν_{26}	C–N torsion	75	54		45		46
ν_{27}	C–C torsion	100	108	232	171		104

^a From Ref. [14].

^b GG conformer.

^c SG conformer.

^d Potential energy distribution for ab initio frequencies of GG conformer.

^e GG' conformer.

^f SA conformer.

^g GA conformer.

exist only as one conformer: 3-azidopropine (**4**) (gauche), azidoacetonitrile (**5**) (gauche), azido-2-butene (**6**) (gauche), 2-azido-1,3-butadiene (**8**) (trans, syn). Ab initio MP2(full)/TZ2P//MP2(full)/TZ2P calculated relative stabilities are in full agreement with the experimental data, except for azidoacetonitrile (**5**). Allylazide (**7**) can exist as five distinct conformers. The experimental [12–14]/theoretical data reveal the following energy order of conformers: GG, SG, GG', SA and GA. It is clear from the present study and from earlier investigations [12–21] that the most stable conformer of alkyl azides with a multiple bond (C=C, C≡C, C≡N, etc.) in the alkyl group is

that in which π conjugation with the azido group is maximized.

Unscaled computed vibrational spectra at the MP2(full)/TZ2P level agree well with the measured IR/Raman frequencies. Most of our assignments are the same as obtained in former studies, but the experimental bands of hydrazoic acid (**1**) of 1264 cm⁻¹ and 1151 cm⁻¹ were assigned differently than in previous papers [8,9]. According to our calculations, the two stretching vibrations of the azido group should be interpreted as belonging to triple N≡N and double N=N vibrations, rather than to two NNN symmetric and asymmetric modes. Two azido group deformation

Table 11
Observed and calculated fundamental vibrational frequencies of the trans, syn conformation of 2-azido-1,3-butadiene (8)

No.	Fundamental	Obs. ^a	Ab initio	PED ^b
$\nu_1 A'$	CH ₂ asym. stretch	3115	3304	90 *CH ₂ as
ν_2	CH ₂ asym. stretch	3113	3303	90 CH ₂ as
ν_3	C–H stretch	3037	3219	88 C–H s
ν_4	CH ₂ sym. stretch	3025	3200	91 *CH ₂ ss
ν_5	CH ₂ sym. stretch	3002	3199	83 CH ₂ ss
ν_6	N \equiv N stretch	2121	2254	73 N \equiv N s, 27 N=N s
ν_7	C=C stretch	1639	1688	51 C=C s, 21 *C=C s
ν_8	C=C stretch	1590	1623	51 *C=C s, 20 C=C s
ν_9	CH ₂ deformation	1420	1475	46 CH ₂ δ , 30 *CH ₂ δ
ν_{10}	CH ₂ deformation	1381	1426	39 *CH ₂ δ , 23 CH ₂ δ
ν_{11}	C–N stretch	1312	1344	31 C–N s, 23 N=N s, 16 C–C s
ν_{12}	C–H rocking	1275	1318	52 C–H ro
ν_{13}	N=N stretch	1227	1254	39 N=N s, 15 N \equiv N s
ν_{14}	CH ₂ rocking	1034	1051	48 CH ₂ ro, 27 *CH ₂ ro
ν_{15}	CH ₂ rocking	920	949	34 *CH ₂ ro, 15 CH ₂ ro
ν_{16}	C–C stretch	839	848	20 C–C s, 25 C–N s, 23 C–N=N δ
ν_{17}	N=N \equiv N bend	620	641	37 N=N \equiv N δ , 13 C–N=N δ
ν_{18}	C–C=C bend	550	556	44 C–C=C δ , 31 C–N ro
ν_{19}	C–N rocking	445	447	27 C–N ro, 44 *C–C=C δ
ν_{20}	C–C=C bend	254	255	33 *C–C=C δ , 36 C–C=C δ
ν_{21}	C–N=N bend		151	69 C–N=N δ , 31 N=N \equiv N δ
$\nu_{22} A''$	CH ₂ =CH trans wag	981	1010	64 C=C τ , 31 CH wa
ν_{23}	CH ₂ wagging	928	927	101 CH ₂ wa
ν_{24}	CH ₂ wagging	841	832	102 *CH ₂ wa
ν_{25}	CH ₂ =CH cis wag	735	749	27 CH wa, 16 C=C τ
ν_{26}	CH ₂ =CN trans wag	685	698	59 *C=C τ , 22 CN wa
ν_{27}	N=N torsion	548	529	97 N=N τ
ν_{28}	CH ₂ =CN cis wag	345	445	61 CN wa, 9 *C=C τ
ν_{29}	C–C torsion	106	148	79 C–C τ
ν_{30}	C–N torsion	80	81	91 C–N τ

^a From Ref. [17].

^b Potential energy distribution for ab initio frequencies. Asterisk denotes contributions from vinyl with azido group.

vibrations can be assigned as bending in-plane (bip) and bending out-of-plane (bob, N=N torsion). The bip vibration, in contrast to the bob vibration, is conformationally sensitive and interacts with the C–N=N bending mode. The average overestimation of the calculated bands of small organic azides is 5%.

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