DFT Studies of Rotational Conformers of 4-Azido-N-Phenylmalemide

Sathya M. Perera and Lichang Wang[*]

School of Chemical and Biomolecular Sciences

Southern Illinois University Carbondale, Carbondale, IL 62901, USA

Abstract

DFT calculations were performed to study the rotational conformers of 4-Azido-N-Phenylmalemide using B3LYP with 7 basis sets, 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), and 6-311++G(df,pd). DFT studies show that the two isomers of 4-Azido-N-Phenylmalemide have the same energetics. Furthermore, the rotational barrier between the isomers is 0.17 eV in N, N-dimethylacetamide (NNDMA) and 0.15 eV in tetrahydrofuran (THF). These indicate that the isomers are present in the solvents and can be easily converted between them. The azido asymmetric stretch differs by about 1 cm^{-1} between the isomers in NNDMA and less than 1 cm^{-1} in THF. The most significant effect of rotational conformers is in the coupling strength of fermi resonances with the most impact in THF environment. Therefore, the current DFT results show that isomers of 4-Azido-N-Phenylmalemide can be mostly detected in THF by 2D IR technique. Furthermore, the results from seven basis set provide consistent conclusion on the isomers, dependence of the basis sets may be useful information to the development of functionals in DFT method and may be served as a useful tool to understand coupling of vibrational modes of complex molecules and their isomers.

[*]Corresponding author: lwang@chem.siu.edu

1. Introduction

Organic small molecule (OSM) based materials have been widely used in many technologies due to their abundance, facile synthesis, and ability of fine tuning the properties of interest through functionalization. As such many OSM studies have been carried out at the level of single molecules[1-35] as well as aggregates.[36-60] With the increase of complexity in OSM, structural isomers increase for the same chemical structure. Therefore, there were investigations of rotational conformers.[61-72] Examples of rotational conformers shown in Figure 1 is 4-Azido-N-Phenylmalemide, which was studied for the fermi resonance in its infrared spectrum[73] as a part of efforts to develop IR probes [74-78] based on the organic small molecules with carbon-deuterium bond, nitrile, thiocyanate, azide, cyanamide, alkyne, or carbon-fluoride functional groups[78-99] for detection of proteins.[100-103]
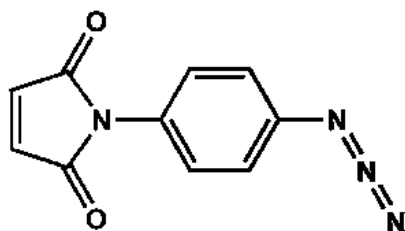

Figure 1. Chemical structure of 4-Azido-N-Phenylmalemide.

In the initial work on the DFT calculation of IR spectrum of 4-Azido-N-Phenylmalemide, we used only one isomer in the investigation. The rational of the choice comes from the assumption that the IR spectra of the two isomers will be very similar and will only be illustrated, if any, in dynamics IR measurements. Although the presence of rotational conformers may not affect much on the properties at single molecule level, it affects the aggregates during assembling. Therefore, it is important to study both isomers to understand the effect of conformers on the IR spectrum as well as the conversion between the isomers. Therefore, in this work, we carried out DFT

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calculations of the second rotational conformer of 4-azido- N-phenylmalemide (isomer 2 in Figure 2) as well as the conversion between the two rotational conformers.

2. Computational Details

Figure 2 depicts the two rotational conformers, also denoted as rotomers, of 4-Azido-N-Phenylmalemide. Geometry optimization and IR studies were done for isomer 2 as the same studies on isomer 1 were previously provided.[73] Furthermore, conversion between the two isomers was investigated in this work. All DFT calculations were carried out using Gaussian 16.[104]

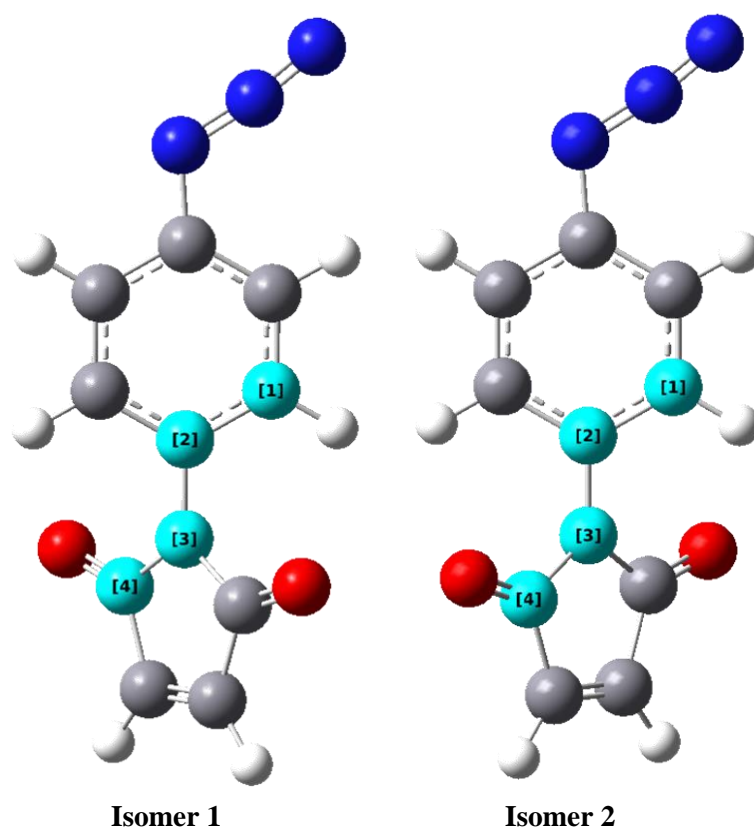**Isomer 1**   **Isomer 2**

Figure 2. The two rotational conformers of 4-Azido-N-Phenylmalemide. Blue, gray, white, and red balls represent N, C, H, and O atom, respectively. The labeled atoms are C atoms.

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B3LYP was used in all DFT calculations with seven basis sets, 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), and 6-311++G(df,pd). Two solvents, NNDMA (N, N-dimethylacetamide) and tetrahydrofuran (THF), were used to understand the solvent effects. The polarizable continuum model using the integral equation formalism variant (IEFPCM) was used for the solvent effect. Standard convergence criteria were used in the calculations, i.e., the self-consistent field, gradient, and energy convergence were set to be 10^{-8}, 10^{-4}, and 10^{-5} a.u., respectively. These convergence criteria have been also used in our previous work on other organic small molecules[105-109] as well as DFT calculations of isomer 1.[73] We note that the harmonic frequency results showed that no imaginary frequencies for the optimized isomer 2 ensuring that it is at the minimum of the potential energy surface. Furthermore, only one imaginary frequency exists in the transition state (TS) between the two isomers.

Anharmonic frequencies were obtained together with the cubic force constants of overtones and combination bands of isomer 2 to understand the Fermi resonance (FR) of the isomer. We used both cubic coupling constants K_{ijk} and third-order Fermi resonance parameter (TFR)[110,111] to determine the FRs. TFR for the triple of modes i, j, and k was calculated with

$$\text{TFR} = \frac{|K_{ijk}|}{\Delta \omega}, \quad (1)$$

$$\Delta \omega = |\omega_i + \omega_j - \omega_k|, \quad (2)$$

where k, i, j represents the corresponding fundamental mode. The combination band (or mode) of i and j is denoted as overtone when i=j. The combination modes (or bands) are considered resonant when TFR is of order ~1 or larger. To make sure all the possible couplings are included, we searched all the vibrational peaks of the

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isomer 2 within ± 130 cm^{-1} from the fundamental vibration of interest, just as we did for isomer 1.[73] The relative peak position ($\Delta\omega$') was calculated using

$$\Delta\omega' = \omega_{ij} - \omega_k, \quad (3)$$

where ω_{ij} and ω_k are the wavenumbers of combination band or overtone and fundamental vibration, respectively.

3. Results and Discussion

In what follows, we will first present the geometric and energetic results and make structural comparison between the two isomers. Then we will present the energetics of the conversion between the isomers. Finally, we will present the IR spectrum of isomer 2 and compare with that of isomer 1.

Table 1 summarized the energetics of the two isomers. We note that the rotational barrier is zero point energy corrected. As we expected, the two isomers have the same energy from all seven basis sets. Furthermore, the rotational barriers are about 0.17 eV in NNDMA and 0.15 eV in THF except for the two basis sets, 6-31G(d,p) and 6-311G(d,p). The energetics of both conformers indicates that they will equally present in solution and can be easily converted at room temperature between them. For generating uniformly dense aggregates, the presence of one conformer only is preferable. The low rotational barrier offers promising features when forming aggregates as maneuvering 4-Azido-N-Phenylmalemide in one isomer format is energetically feasible. When it is used as IR probe in certain biological situations, such as in matrix, one conformer may be preferred than another and this can lead to useful information in detection.

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Table 1. DFT calculated energies of isomers 1 and 2 and the rotational barrier

NNDMA

Basis set	Isomer 1 Energy (au)[*]	Isomer 2 Energy (au)	TS Energy (au)	Rotational Barrier (au)	Rotational Barrier (eV)
6-31G(d,p)	-754.087785	-754.087785	-754.084147	0.003638	0.10
6-31+G(d,p)	-754.118199	-754.118199	-754.112452	0.005747	0.16
6-31++G(d,p)	-754.118284	-754.118284	-754.112595	0.005689	0.16
6-311G(d,p)	-754.268672	-754.268672	-754.264753	0.003919	0.11
6-311+G(d,p)	-754.284428	-754.284428	-754.278363	0.006065	0.17
6-311++G(d,p)	-754.284547	-754.284547	-754.27847	0.006077	0.17
6-311++G(df,pd)	-754.315119	-754.315119	-754.308927	0.006192	0.17

THF

Basis set	Isomer 1 Energy (au)[*]	Isomer 2 Energy (au)	TS Energy (au)	Rotational Barrier (au)	Rotational Barrier (eV)
6-31G(d,p)	-754.08597	-754.08597	-754.082718	0.003252	0.09
6-31+G(d,p)	-754.115789	-754.115789	-754.110742	0.005047	0.14
6-31++G(d,p)	-754.115877	-754.115877	-754.110885	0.004992	0.14
6-311G(d,p)	-754.266697	-754.266697	-754.26323	0.003467	0.09
6-311+G(d,p)	-754.282019	-754.282019	-754.276657	0.005362	0.15
6-311++G(d,p)	-754.282137	-754.282137	-754.276764	0.005373	0.15
6-311++G(df,pd)	-754.312719	-754.312719	-754.307213	0.005506	0.15

Note: *date taken from Ref.73.

Although the two isomers have the same energy, slightly visible difference in dihedral angle labeled as 1-2-3-4, which is the most significant difference between the two isomers, is obtained from DFT calculations as shown in Table 2. It is evident that solvent plays important roles in the dihedral angle of the isomers. Another interesting observation from the DFT calculations is the very symmetric character of the isomers with respect to the azido-phenyl plane, which is not surprising as both conformers are exposed to the same electronic environment. We note that the dihedral angles from 6-31G(d,p) and 6-311G(d,p) basis sets are significantly different from the rest of DFT results.

Table 2. DFT calculated dihedral angle in Fig.2 (1-2-3-4, in degree) of isomers 1 and 2

Basis set	Isomer 1		Isomer 2	
	NNDMA	THF	NNDMA	THF
6-31G(d,p)	-132.6	-134.4	132.5	134.6
6-31+G(d,p)	-114.4	-118.9	114.6	118.9
6-31++G(d,p)	-114.7	-119.2	114.7	119.2
6-311G(d,p)	-128.6	-130.9	128.6	130.9
6-311+G(d,p)	-112.6	-118.2	112.6	118.1
6-311++G(d,p)	-112.4	-118.1	112.4	118.1
6-311++G(df,pd)	-113.8	-118.4		118.8

For the IR results of isomer 2 and the comparison with that of isomer 1, we used the DFT results from B3LYP/6-311+G(d,p) calculations. In Figure 3, we plotted the IR spectra of isomer 2 in NNDMA and THF together with the results of isomer 1. As shown in Figure 3, the IR spectra of two rotational conformers resemble each other, though there is a systematic small blue shift of all IR peaks in isomer 2. While the absorption intensity of the fundamental mode (54) is nearly identical in NNDMA, a visible increase in the absorption intensity by isomer 2 in THF. Furthermore, a significant blue shift (more than 1 cm^{-1}) in the overtone mode can be seen in THF. We note that there is a small peak around 2250 cm^{-1} region in THF is combination band of (28, 46), which does not appear to be significant from the DFT calculations using other basis set and therefore was not investigated further.
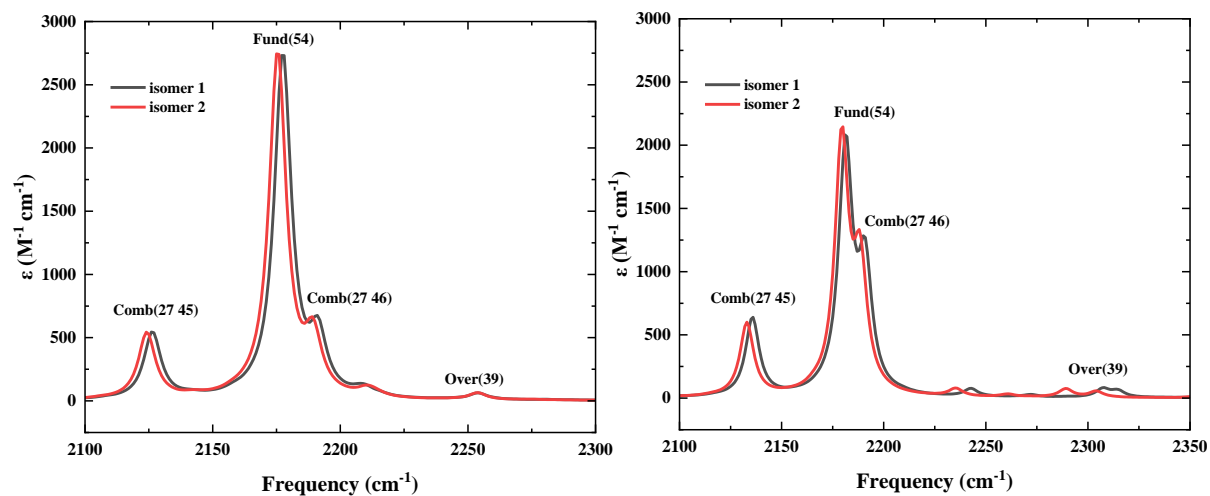
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Figure 3. IR spectra of two rotational conformers of 4-Azido-N-Phenylmalemide in NNDMA (left) and THF (right) obtained using B3LYP/6-311+G(d,p). Data for isomer 1 was taken from ref. 73.

Moreover, the differences in force constant and FR coupling strengths between the two conformers are shown in Table 3. There are a few noticeable differences in the data provided in Table 3. First, the FR strength of combination mode comprised of (27, 46) becomes visibly weaker in isomer 2, especially in THF. Second, THF is more effective solvent to differentiate the isomers, as parameter changes are largest between the isomers in THF. Third, the force constants of the isomers remain unchanged between two isomers in both solvent. We point out that future work in performing dynamics studies[111-115] will be interesting to capture the dynamic aspects of the conformer change and their impact in the spectra. Finally, synthesis of the molecules with preference of one isomer over the other will be difficult as the energetics of the isomers and low energy barrier for their conversion, though many catalysis research on synthesis of OSMs are active research.[116-145] Special confinement or matrix may help facilitate the formation of one isomer over the other.

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Table 3. The parameters obtained from B3LYP/6-311+G(d,p) of isomers 1 and 2

	K_{ijk} (cm⁻¹)		I (km mol⁻¹)		I/I_{54}		$\Delta\omega$ (cm⁻¹)		$\Delta\omega'$ (cm⁻¹)		TFR	
	NND MA	THF	NND MA	THF	NND MA	THF	NND MA	THF	NND MA	THF	NND MA	THF
Iso 1* Iso 2	-58.8 -58.8	-59.0 -59.0	152.6 151.4	177.2 165.3	0.193 0.191	0.315 0.289	-34.2 -33.5	-42.4 -39.9	-51.1 -51.3	-45.6 -46.5	1.721 1.756	1.393 1.480
Iso 1* Iso 2	13.2 13.2	14.7 14.6	128.3 126.8	282.6 281.4	0.160 0.160	0.502 0.492	13.5 13.7	-2.8 -3.4	13.8 13.8	9.6 8.9	0.978 0.962	5.235 4.319
Iso 1* Iso 2	-37.5 -37.5	-37.3 -37.3	14.1 14.1	13.9 13.8	0.018 0.018	0.025 0.024	78.9 80.9	76.9 81.7	76.4 78.5	133.3 124.5	0.476 0.464	0.485 0.456

Note: Top, middle, and bottom rows of data are for the combination band (27,45), (27, 46), and the overtone (39), respectively. *data taken from ref. 73.

In our previous DFT studies of 4-Azido-N-Phenylmalemide, DFT results indicated that employing different basis set may be a useful tool to understand the IR spectrum. Here we therefore performed calculations using six other basis sets in addition to 6-311+G(d,p) to the IR spectrum of isomer 2. The results are shown in Figures 4 and 5. There are a few observations that are worthwhile mentioning. First, the absorption profiles are similar predicted using different basis sets except the one from 6-31G(d,p). Second, the vibrational modes involved in generating absorption peaks within the frequency range of 2100-2300 cm⁻¹ are relatively consistent regardless of basis set used. Third, the addition of polarization and diffuse characters affect the geometry and properties of the molecule considerably. It is difficult, however, to decide whether these additions are capable of accurately describing the geometries and properties based only on the calculations. Therefore, a comparison with experimental data is necessary to identify the suitable basis set and understand the issues with the basis set usage.
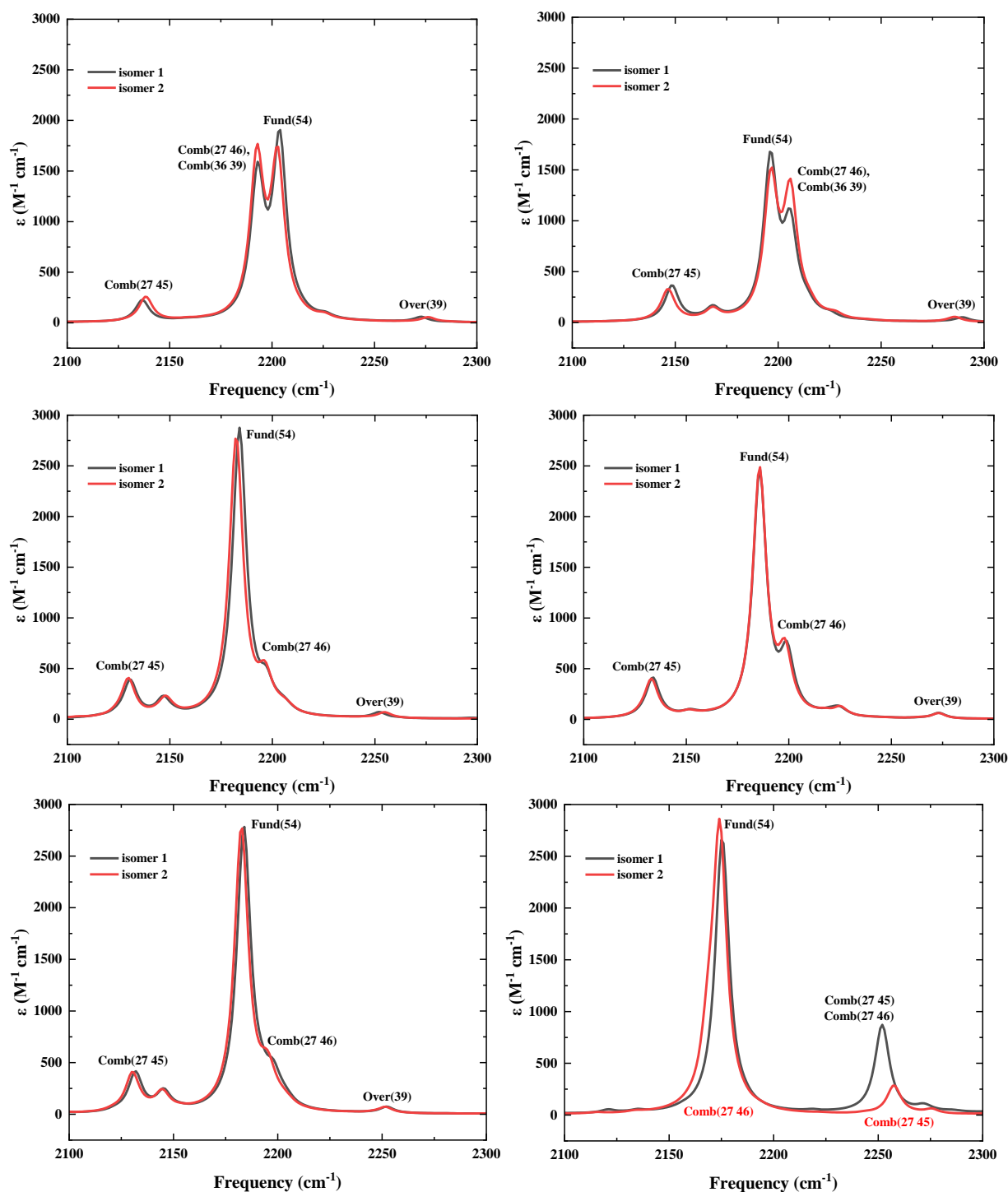
Figure 4. IR spectra of two rotational conformers of 4-Azido-N-Phenylmalemide in NNDMA (left) and THF (right) obtained using 6-31G(d,p) (top), 6-31+G(d,p) (middle), and 6-31++G(d,p) (bottom). Data for isomer 1 was taken from ref. 73.
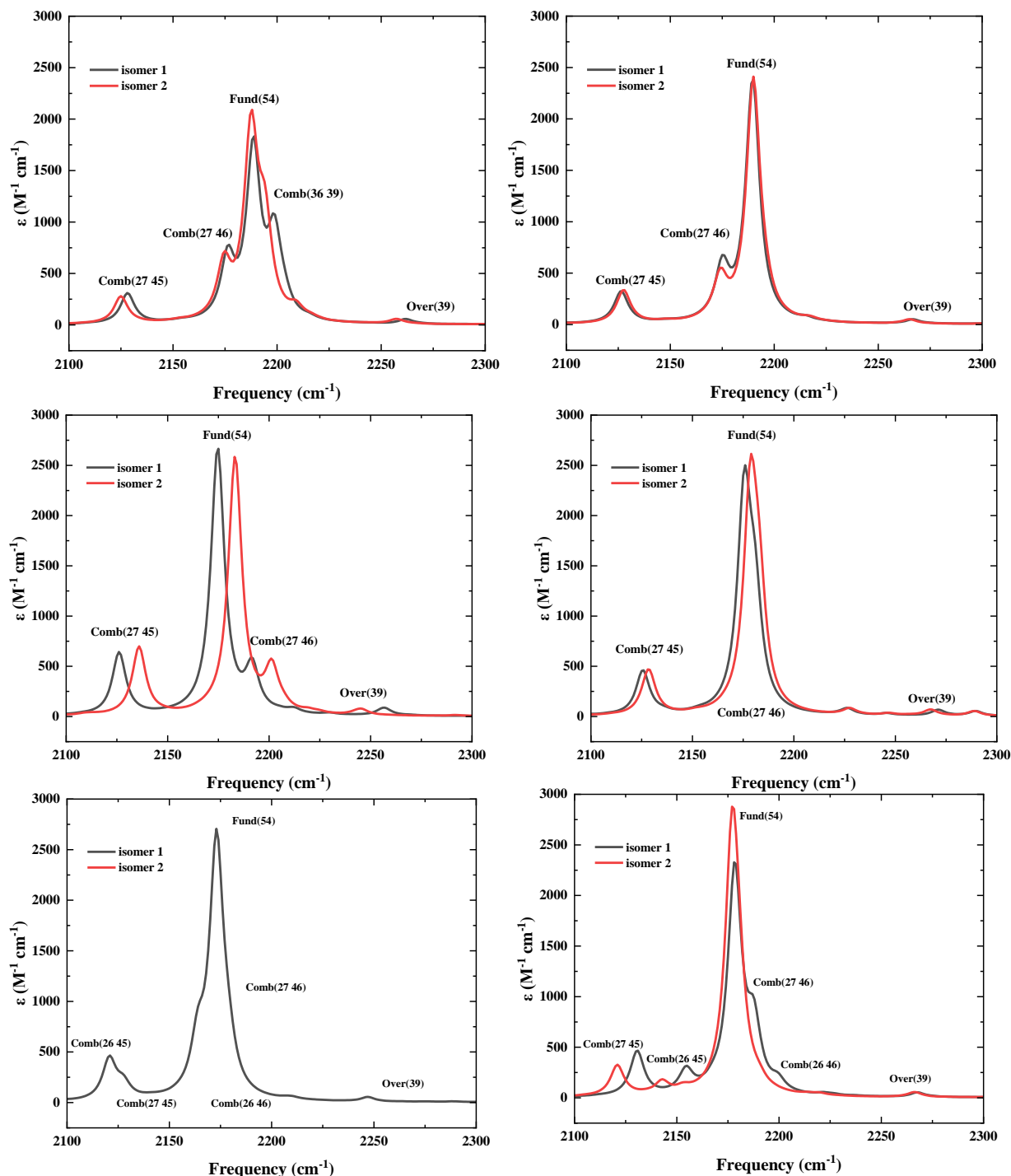
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Figure 5. IR spectra of two rotational conformers of 4-Azido-N-Phenylmalemide in NNDMA (left) and THF (right) obtained using 6-311G(d,p) (top), 6-311++G(d,p) (middle), and 6-311++G(df,pd) (bottom). Data for isomer 1 was taken from ref. 73.

Lastly, while differences are observed in IR spectra using different basis set as shown in Figures 3-5, it is surprising to see the difference between the fundamental frequency of two isomers predicted by 6-311++G(d,p). Furthermore, unlike other predictions, a red shift is predicted by 6-311++G(d,p) rather than small blue shift as predicted by the other basis set. We therefore looked into the parameters of the DFT results. Table 4 shows explicitly the absorption intensity and frequency of the isomers in NNDMA and THF. While the dihedral angles are the same amount but to opposite direction for both isomers, which is essentially the same as the other basis set, geometry changes are not the cause for the difference. We therefore looked more into the coupling induced by the use of different basis set and data similar to Table 3 for other basis sets are summarized in Tables 5-10.

Table 4. The dihedral angle (D), intensity (I), and frequency (ω) of fundamental mode 54 obtained from B3LYP/6-311++G(d,p) of isomers 1 and 2 for the two isomers.

	D (degree)	$\mathbf{I_{54}}$ (km mol^{-1})	$\mathbf{\omega_{54}}$ (cm^{-1})
NNDMA			
Iso 1*	-112.4	763.1	2174.7
Iso 2	112.4	741.7	2183.2
THF			
Iso 1*	-118.1	613.7	2175.6
Iso 2	118.1	614.1	2178.6

Note: *data for isomer 1 was taken from ref. 73.

Table 5. The parameters obtained from B3LYP/6-31G(d,p) of isomers 1 and 2.

	K_{ijk} (cm^{-1})		I (km mol^{-1})		I/I$_{54}$		$\Delta\omega$ (cm^{-1})		$\Delta\omega'$ (cm^{-1})		TFR	
	NND MA	THF	NND MA	THF	NND MA	THF	NND MA	THF	NND MA	THF	NND MA	THF
Iso 1* Iso 2	-57.4 -57.4	52.0 52.7	57.6 67.3	97.4 87.6	0.117 0.153	0.217 0.228	-56.8 -51.8	-39.3 -39.3	-67.0 -64.4	-47.9 -50.0	1.010 1.107	1.324 1.341
Iso 1* Iso 2	15.1 15.1	-14.2 -14.5	176.6 224.7	230.5 222.8	0.357 0.510	0.514 0.579	-11.0 -10.1	3.6 2.7	-11.1 -10.4	9.5 9.9	1.375 1.495	3.942 5.361
Iso 1* Iso 2	2.5 -2.5	2.4 2.4	217.1 218.3	24.8 127.2	0.439 0.496	0.055 0.330	-8.5 -6.6	12.5 8.2	-10.5 -9.9	11.4 8.8	0.290 0.372	0.189 0.289
Iso 1* Iso 2	-36.2 -36.2	-36.1 36.2	12.2 12.2	12.0 12.0	0.025 0.028	0.027 0.031	70.9 75.2	97.9 89.3	69.2 73.6	93.4 89.6	0.511 0.482	0.369 0.405

Note: From Top to bottom rows of data are for the combination band (27,45), (27, 46), (36,39), and the overtone (39), respectively. *data taken from ref. 73.

Table 6. The parameters obtained from B3LYP/6-31+G(d,p) of isomers 1 and 2.

	K_{ijk} (cm^{-1})		I (km mol^{-1})		I/I$_{54}$		$\Delta\omega$ (cm^{-1})		$\Delta\omega'$ (cm^{-1})		TFR	
	NND MA	THF	NND MA	THF	NND MA	THF	NND MA	THF	NND MA	THF	NND MA	THF
Iso 1* Iso 2	54.1 -54.3	56.8 -56.8	102.9 108.0	112.2 108.5	0.128 0.135	0.161 0.154	-39.5 -39.2	-42.8 -44.3	-53.4 -52.7	-52.1 -52.8	1.371 1.384	1.328 1.283
Iso 1* Iso 2	-11.4 11.4	-13.0 13.0	74.4 75.4	161.4 160.9	0.093 0.094	0.231 0.228	5.1 20.9	5.8 19.6	13.0 13.7	13.3 12.4	2.210 0.545	2.237 0.662
Iso 1* Iso 2	39.2 -39.2	-38.9 38.9	15.6 15.7	15.2 15.2	0.020 0.020	0.022 0.022	70.6 81.4	88.4 88.0	68.2 72.3	87.4 87.3	0.555 0.481	0.440 0.442

Note: Top, middle, and bottom rows of data are for the combination band (27,45), (27, 46), and the overtone (39), respectively. *data taken from ref. 73.

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Table 7. The parameters obtained from B3LYP/6-31++G(d,p) of isomers 1 and 2.

	K_{ijk} (cm⁻¹)		I (km mol⁻¹)		I/I_{54}		$\Delta\omega$ (cm⁻¹)		$\Delta\omega'$ (cm⁻¹)		TFR	
	NNDMA	THF	NNDMA	THF	NNDMA	THF	NNDMA	THF	NNDMA	THF	NNDMA	THF
Iso 1[*] Iso 2	-53.8 -53.8	-56.7 56.7	109.2 107.4	94.3 78.3	0.138 0.135	0.001 0.102	-39.0 -39.1	72.0 80.9	-52.0 -52.3	75.6 83.3	1.381 1.376	0.787 0.700
Iso 1[*] Iso 2	-11.2 11.2	12.9 -12.8	70.8 70.5	155.6 147.4	0.089 0.089	0.005 0.192	9.9 9.0	126.1 1.8	14.1 13.1	77.0 -5.4	1.132 1.245	0.102 7.121
Iso 1[*] Iso 2	39.2 39.1	-38.9 38.9	15.7 15.6	16.4 16.7	0.020 0.020	0.021 0.022	69.3 71.2	423.8 397.6	68.5 69.0	335.3 357.5	0.565 0.550	0.092 0.098

Note: Top, middle, and bottom rows of data are for the combination band (27,45), (27, 46), and the overtone (39), respectively. *data taken from ref. 73.

Table 8. The parameters obtained from B3LYP/6-311G(d,p) of isomers 1 and 2.

	K_{ijk} (cm⁻¹)		I (km mol⁻¹)		I/I_{54}		$\Delta\omega$ (cm⁻¹)		$\Delta\omega'$ (cm⁻¹)		TFR	
	NNDMA	THF	NNDMA	THF	NNDMA	THF	NNDMA	THF	NNDMA	THF	NNDMA	THF
Iso 1[*] Iso 2	-58.4 -58.4	58.4 -58.4	83.6 75.5	88.6 92.1	0.173 0.144	0.139 0.136	-49.5 -52.5	-52.3 -52.0	-60.4 -62.5	-63.3 -62.4	1.181 1.117	1.117 1.124
Iso 1[*] Iso 2	17.2 17.1	-18.1 18.1	168.2 149.6	145.4 115.6	0.349 0.285	0.228 0.171	-15.2 0.5	-15.7 -17.6	-12.3 -13.0	-14.6 -15.8	1.126 34.24	1.155 1.027
Iso 1[*] Iso 2	2.6 -2.6	-2.6 -2.6	226.9 248.8	1.2 1.0	0.470 0.474	0.002 0.002	10.4 6.4	-21.8 -23.4	10.1 6.7	-25.4 -26.0	0.253 0.413	0.118 0.110
Iso 1[*] Iso 2	-36.2 -36.2	35.7 -35.7	12.6 12.6	11.8 11.9	0.026 0.024	0.019 0.018	75.5 72.1	78.1 77.5	73.1 69.8	76.9 75.2	0.480 0.503	0.457 0.461

Note: From Top to bottom rows of data are for the combination band (27,45), (27, 46), (36,39), and the overtone (39), respectively. *data taken from ref. 73.

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Table 9. The parameters obtained from B3LYP/6-311++G(d,p) of isomers 1 and 2.

	K_{ijk} (cm^{-1}) NNDMA	K_{ijk} (cm^{-1}) THF	I (km mol^{-1}) NNDMA	I (km mol^{-1}) THF	I/I$_{54}$ NNDMA	I/I$_{54}$ THF	$\Delta\omega$ (cm^{-1}) NNDMA	$\Delta\omega$ (cm^{-1}) THF	$\Delta\omega'$ (cm^{-1}) NNDMA	$\Delta\omega'$ (cm^{-1}) THF	TFR NNDMA	TFR THF
Iso 1*	58.8	59.0	179.8	94.3	0.263	0.205	-37.5	-38.7	-48.6	-50.0	1.567	1.524
Iso 2	-58.8	-59.0	195.1	126.0	0.236	0.207	-50.8	-38.8	-47.3	-50.1	1.157	1.570
Iso 1*	-13.1	-14.6	124.7	155.6	0.169	0.458	16.8	-7.3	17.0	5.2	0.779	2.001
Iso 2	13.1	14.6	125.6	281.2	0.163	0.457	11.1	-9.3	18.1	4.2	1.182	1.571
Iso 1*	37.5	37.2	14.1	16.4	0.019	16.4	85.3	86.2	81.7	114.0	0.440	0.432
Iso 2	-37.5	-37.3	14.6	13.7	0.019	13.7	65.6	87.8	62.2	110.3	0.570	0.424

Note: Top, middle, and bottom rows of data are for the combination band (27,45), (27, 46), and the overtone (39), respectively. *data taken from ref. 73.

Table 10. The parameters obtained from B3LYP/6-311++G(d,p) of isomers 1 and 2.

	K_{ijk} (cm^{-1}) NNDMA	K_{ijk} (cm^{-1}) THF	I (km mol^{-1}) NNDMA	I (km mol^{-1}) THF	I/I$_{54}$ NNDMA	I/I$_{54}$ THF	$\Delta\omega$ (cm^{-1}) NNDMA	$\Delta\omega$ (cm^{-1}) THF	$\Delta\omega'$ (cm^{-1}) NNDMA	$\Delta\omega'$ (cm^{-1}) THF	TFR NNDMA	TFR THF
Iso 1*	12.3	55.3	41.2	127.4	0.0572	0.197	-49.6	-39.3	-45.6	-47.8	0.247	1.408
Iso 2		-57.1		87.8		0.124		-52.8		-57.7		1.081
Iso 1*	-3.1	-14.1	3.6	180.1	0.0050	0.279	-13.0	-0.1	0.0	9.3	0.240	553.4
Iso 2		14.5		187.9		0.264		-10.7		1.5		1.356
Iso 1*	57.9	-20.9	117.0	63.0	0.1625	0.098	-36.6	-26.8	-52.4	-23.8	1.582	0.780
Iso 2		-15.7		34.6		0.049		-29.9		-35.8		0.525
Iso 1*	38.0	37.9	12.7	12.7	0.0176	0.020	76.5	91.6	73.9	89.3	0.497	0.414
Iso 2		37.9		12.7		0.018		91.7		87.9		0.413

Note: From Top to bottom rows of data are for the combination band (27,45), (27, 46), (26,45), and the overtone (39), respectively. *data taken from ref. 73.

It is clear from comparison of data among Tables 5-10, the shape of electronic orbitals matter a great deal in the IR spectra. Particularly, the abnormal TFR value in THF from the 6-311++G(df, pd) calculation makes the results from this particular basis set more questionable. The results

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demonstrated that the polarization and diffusion of orbitals affect the coupling of modes and consequently affect the calculated IR spectra. More in-depth studies of the basis set effect, especially comparison with experiments, will be necessary for reliable prediction and better understanding of IR spectra of OSMs. Nonetheless, results from multiple basis sets can be used in tandem to understand and design IR probes.

4. Conclusions

To understand the properties of 4-Azido-N-Phenylmalemide, we performed DFT calculations of its two rotational conformers and the conversion between them using B3LYP with seven basis sets, 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), and 6-311++G(df,pd). DFT studies show that the two rotational conformers of 4-Azido-N-Phenylmalemide are energetically the same. The rotational barrier between the isomers is 0.17 eV in NNDMA and 0.15 eV in THF. These DFT results indicate that the isomers are present in the solvents and can be easily converted between them.

The azido asymmetric stretch (mode 54) was found to differ by about 1 cm^{-1} between the isomers in NNDMA and less than 1 cm^{-1} in THF. The most significant effect of rotational conformers is in the coupling strength of fermi resonances with the most impact in THF environment. The Fermi resonance consisting of modes 27 and 45 between the isomers is similar in NNDMA and THF, however, the Fermi resonance consisting of modes 27 and 46 differs significantly between the two isomers, especially in THF.

Therefore, the current DFT results show that isomers of 4-Azido-N-Phenylmalemide can be mostly detected in THF by 2D IR technique. Furthermore, the results from seven basis set provide consistent conclusion on the isomers, dependence of the basis sets may be useful information to

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the development of DFT functionals and may be served as a useful tool to understand coupling of

vibrational modes of complex molecules and the OSM isomers.

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