Rotational spectra, conformational structures, and dipole moments of thiodiglycol by jet-cooled FTMW and ab initio calculations

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Abstract

The rotational spectra of three low-energy conformers of thiodiglycol (TDG) ($HOCH_2CH_2SCH_2CH_2OH$) have been measured in a molecular beam using a pulsed-nozzle Fourier-transform microwave spectrometer. To determine the likely conformational structures with ab initio approach, conformational structures of 2-(ethylthio)ethanol (HOEES) ($CH_3CH_2SCH_2CH_2OH$) were used as starting points together with the consideration of possible intramolecular hydrogen bonding in TDG. Three lower-energy conformers have been found for TDG at the MP2 = Full/6311G** level and ab initio results agree nicely with experimentally determined rotational constants. In addition, Stark measurements were performed for two of the three conformers for dipole moment determinations, adding to our confidence of the conformational structure matches between experimental observations and ab initio calculations. Of the three lower-energy conformers, one displays a compact folded-like structure with strong hydrogen bonding between the two hydroxyl groups and the central sulfide atom. Two other conformers have relatively open chain-like structures with hydrogen bonding between each of the hydroxyl groups to the central sulfur atom, of which one has pure b-type dipole moment according to the ab initio results.

1. Introduction

This work describes an experimental jet-cooled Fourier-transform microwave (FTMW) study of the rotational spectrum and dipole moments of thiodiglycol, briefly noted as TDG ($HOCH_2CH_2SCH_2CH_2OH$), and theoretical ab initio conformational calculations. This species is a hydrolysis degradation product of mustard gas. Since TDG is among the family of compounds related to the mustard gas chemical agents, it is therefore of interest from both a theoretical and practical viewpoint. The present study is part of an ongoing effort aimed at setting up a microwave database for chemical agents and families of related compounds (stimulants, degradation products, hydrolysis, and oxidation products).

These molecules are relatively large, and can exist in the gas phase as distinct conformational isomers associated with internal torsional rotations about the bonds joining the heavy atoms forming the molecular backbone. Typically these conformational changes are hindered by substantial potential barriers, thus permitting the molecules to exist as a variety of different conformers with differing energies. Tunneling between the conformations is very slow, on the timescale of the rotational motions; hence the different conformers are quasi-stable in the Fourier-transform microwave

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(FTMW) experiments and appear as distinct isomeric species with separate and well-defined spectra and molecular structures. Conformational stabilization by intramolecular hydrogen-bond interaction is an interesting aspect of the present study. Strong hydrogen bonding tends to produce compact molecular structures in many organic and biologically important molecules. The conformation of the molecules in which an intramolecular hydrogen bond is formed between a hydroxyl hydrogen atom and a sulfur atom has been studied for several compounds that contain the $-SCH_2CH_2OH$ group. Previous microwave spectroscopic studies have shown that the molecules of 2-mercaptoethanol ($HSCH_2CH_2OH$) [1] and 2-(methylthio)ethanol (MTE) ($CH_3SCH_2CH_2OH$) [2,3] adopt a conformation in the gas phase that is stabilized by intramolecular $-OH\cdots S$ hydrogen bond. This characteristic has also been confirmed by our recent studies of 2-(ethylthio)ethanol (HOEES) ($CH_3CH_2SCH_2CH_2OH$). [4] In the cases of MTE and HOEES, the dominant hydrogen bonding is between the hydroxyl hydrogen atom and the sulfur atom ($-OH\cdots S$). An additional $-CH\cdots O$ intramolecular interaction between the methyl hydrogen and the hydroxyl oxygen atom will also be possible for the 'compact' conformers, and their cooperative effect may give rise to high stability of this particular conformation. Such 'compact' conformer structures were observed in the matrix isolation experiment for MTE [3] and were predicted by ab initio calculations for HOEES as low-energy conformers and yet we failed to detect these in the FTMW jet condition for HOEES. One explanation for this could be the uncertainty in calculated ab initio electronic energy for large compounds like HOEES. In the present study, we have observed three low-energy conformers for TDG, the lowest one displays a compact structure with two types of hydrogen bonding of $-OH\cdots S$ and $-OH\cdots O$ in which the latter

gives water dimer-like bonding and stabilizes the overall energy enormously.

Full structure determination of a molecule of this size is difficult experimentally. To overcome this, we seek to match rotational constants and dipole moment components to those found using ab initio calculations. Once the conformational isomers are matched, ab initio calculations give estimates of the molecular structures without additional effort. This dual approach has been used successfully in the previous studies of the parent molecules, diethyl sulfide [5] and HOEES [4].

In the present work, we report on observations and assignments in the jet-cooled FTMW spectrum of TDG. We discuss the experimental identification of three distinct conformers: conformer I (GG'), conformer II (sym-GG), and conformer III (asym-GG) and then describe ab initio calculations that have produced good structural matches for the three observed conformers. Experimental Stark-effect measurements will be described in order to determine dipole moments for conformer I (GG') and conformer II (sym-GG).

2. Experimental

A commercially available sample of TDG (CAS#111-48-8) was used at its stated purity of 99+%. Since the vapor pressure of TDG is rather low ($<1 \times 10^2$ Pa), a small sample of approximately 200 μL was transferred to a reservoir in the pulsed molecular beam valve [6]. The reservoir was then heated to 160–180 °C in order to increase the vapor pressure of the sample in the carrier gas. The compact FTMW spectrometer described by Suenram et al. [7] was used to record survey scans from 12 to 22 GHz and the large FTMW spectrometer [8,9] was used for Stark-effect experiments. The composite of the broadband scans is shown in Fig. 1. Spectral
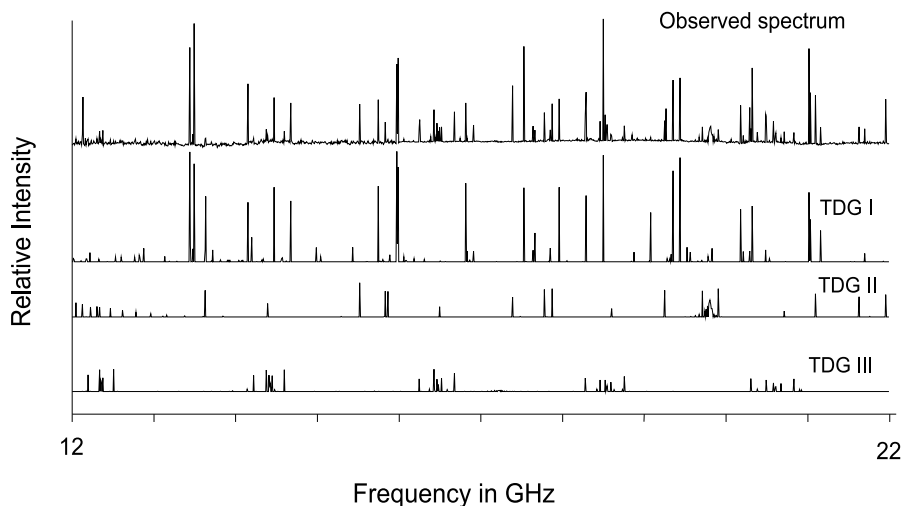

Fig. 1. Survey scan of TDG. The upper trace shows the experimental spectrum. The lower traces show the simulated spectra for the three observed conformers.

assignments were obtained using the jb95 spectral fitting program [5,10]. The most intense transitions in the spectrum are b-type, *R*-branch transitions that belong to two different conformers; conformer I (GG$'$) and conformer II (sym-GG), where conformer I has a near zero kappa value, $\kappa = (2B - A - C)/(A - C)$, while the conformer II is near prolate rotor of $\kappa \approx -1$ with *R*-branches occurring at intervals spaced by approximately the A and $B + C$ values of the rotational constants for conformers I and II, respectively. A computer simulation of these is also shown in Fig. 1. Other transitions in the spectrum arise from a-type transitions for conformer I (GG$'$) and a- and c-type transitions for conformer III (asym-GG). The observed rotational transitions are given in Tables 1–3. The resulting rotational parameters are given in Table 4.

Without isotopic data, it was difficult to relate the assigned spectra to a particular conformational isomer. In order to ameliorate the situation, ab initio calculations were carried out to find the low-energy conformers of TDG for conformational structural estimation.

3. Ab initio structure determination of TDG

The quantum chemistry calculational tool selected for use in this work is the GAUSSIAN 98 ab initio package [11,12] installed on the NIST SGI computers.

Table 1
Measured transition frequencies for thiodiglycol conformer I (GG$'$)

Selection rule	J'	K'_a	K'_c	J''	K''_a	K''_c	Frequency[a] (MHz)	Obs. − calc. (kHz)
B	5	0	5	4	1	4	13437.6459	0.4
A	5	1	5	4	1	4	13448.7924	0.8
A	5	0	5	4	0	4	13478.2807	1.3
B	5	1	5	4	0	4	13489.4272	1.8
B	4	2	3	3	1	2	13635.6615	−0.3
B	3	3	1	2	2	0	14153.6417	0.0
B	3	3	0	2	2	1	14469.6904	1.6
B	5	1	4	4	2	3	14670.9423	−0.2
B	5	2	4	4	1	3	15745.4399	−0.9
B	6	0	6	5	1	5	15973.7367	0.9
A	6	1	6	5	1	5	15976.5961	0.3
A	6	0	6	5	0	5	15984.8832	1.3
B	6	1	6	5	0	5	15987.7426	0.7
A	5	4	2	4	4	1	16059.7738	1.0
B	4	3	2	3	2	1	16817.6329	−0.7
A	5	3	2	4	3	1	16832.5997	−0.1
A	5	2	3	4	2	2	16910.1817	−1.2
B	6	1	5	5	2	4	17528.0291	−0.2
A	6	2	5	5	2	4	17638.0701	0.8
B	6	2	4	5	3	3	17661.4958	0.7
A	6	1	5	5	1	4	17844.8219	−1.5
B	6	2	5	5	1	4	17954.8629	−0.5
B	4	3	1	3	2	2	18287.8413	−0.8
B	7	0	7	6	1	6	18496.7572	−2.1
A	7	1	7	6	1	6	18497.4604	−0.6
A	7	0	7	6	0	6	18499.6166	−2.8
B	7	1	7	6	0	6	18500.3197	−1.3
A	6	3	4	5	3	3	18869.4661	−1.7
B	5	3	3	4	2	2	19073.3351	0.8
B	4	4	1	3	3	0	19349.9131	0.7
B	4	4	0	3	3	1	19437.8408	−0.9
A	6	2	4	5	2	3	19824.6473	0.9
B	7	1	6	6	2	5	20178.8874	1.2
A	7	2	6	6	2	5	20212.8796	1.8
A	7	1	6	6	1	5	20288.9265	0.3
B	7	2	6	6	1	5	20322.9167	−1.1
A	6	3	3	5	3	2	20484.4244	0.2
B	8	0	8	7	1	7	21016.1684	−0.8
A	8	1	8	7	1	7	21016.3344	−1.4
B	6	3	4	5	2	3	21032.6195	0.4
B	7	2	5	6	3	4	21154.1429	−0.1
A	7	3	5	6	3	4	21698.5333	−0.6
B	9	0	9	8	1	8	23534.6670	1.5
B	9	1	9	8	0	8	23534.8720	1.3

[a] The estimated type B ($k = 1$) uncertainties on the frequency measurements are 4 kHz.

Table 2
Measured transition frequencies for thiodiglycol conformer II (sym-GG)

Selection rule	J'	K'_a	K'_c	J''	K''_a	K''_c	Frequency[a] (MHz)	Obs. – calc. (kHz)
B	4	2	3	4	1	4	12043.5176	1.8
B	5	2	4	5	1	5	12124.7480	−1.0
B	8	0	8	7	1	7	12303.4296	−0.4
B	7	2	6	7	1	7	12336.5350	1.5
B	5	1	5	4	0	4	13627.9701	2.4
B	9	0	9	8	1	8	14393.2530	−3.3
B	6	1	6	5	0	5	15515.0885	−0.5
B	2	2	1	1	1	0	15828.4516	−3.3
B	2	2	0	1	1	1	15860.8422	1.6
B	10	0	10	9	1	9	16492.0022	3.2
B	7	1	7	6	0	6	17388.0096	0.3
B	3	2	2	2	1	1	17777.8532	1.4
B	3	2	1	2	1	2	17875.4000	−0.8
B	11	0	11	10	1	10	18598.2025	1.5
B	8	1	8	7	0	7	19247.5597	0.8
B	13	3	10	13	2	11	19627.2294	−4.3
B	12	3	9	12	2	10	19673.3915	−1.7
B	11	3	8	11	2	9	19709.9833	0.9
B	4	2	3	3	1	2	19711.1454	−3.6
B	10	3	7	10	2	8	19738.2665	3.3
B	9	3	6	9	2	7	19759.4853	2.1
B	8	3	5	8	2	6	19774.8466	3.0
B	7	3	4	7	2	5	19785.4755	1.7
B	6	3	3	6	2	4	19792.4110	0.4
B	5	3	2	5	2	3	19796.5829	−0.1
B	4	3	1	4	2	2	19798.7977	−3.0
B	3	3	0	3	2	1	19799.7411	−5.6
B	3	3	1	3	2	2	19800.7235	−3.4
B	4	3	2	4	2	3	19801.7352	−2.9
B	5	3	3	5	2	4	19803.4247	−1.4
B	6	3	4	6	2	5	19806.0731	3.5
B	7	3	5	7	2	6	19810.0009	2.4
B	8	3	6	8	2	7	19815.5966	4.4
B	9	3	7	9	2	8	19823.2782	1.7
B	10	3	8	10	2	9	19833.5243	3.1
B	11	3	9	11	2	10	19846.8407	4.5
B	12	3	10	12	2	11	19863.7665	−2.0
B	13	3	11	13	2	12	19884.8915	−6.2
B	4	2	2	3	1	3	19907.2235	−1.4
B	12	0	12	11	1	11	20710.3111	−2.3
B	9	1	9	8	0	8	21094.7152	1.1
B	5	2	4	4	1	3	21628.3478	−1.9
B	5	2	3	4	1	4	21957.0977	3.1

[a] The estimated type B ($k = 1$) uncertainties on the frequency measurements are 4 kHz.

The internal Z-matrix was used to define the molecular configuration for all GAUSSIAN calculations.

Considering the important role of the intramolecular hydrogen bonding and the structural similarity between HOEES and TDG, it is reasonable to guess the possible conformers of TDG by borrowing geometrical parameters directly from HOEES. Seven possible existing conformers had been constructed with the hydroxyl hydrogen hydrogen-bonded to central sulfur atom or to the oxygen on the other hydroxyl group. Full structural optimizations for these seven starting conformers are then carried out at HF/6-31G* and MP2 = Full/6-311G** theory levels, respectively. Ab initio dipole moments were then transformed to principle axis sys-

tem. The calculated rotational constants, dipole moment values in the principal axis system, and relative energy (zero-point corrected) form the three criteria in our attempts to match the ab initio conformers to the experimental observations and we, in our matching process, keep in mind careful consideration of various expected uncertainties in current ab initio calculations.

The rotational constants of the three low-energy conformers, together with their dipole moments agree well with the three experimental observations with the max% difference in rotational values of 5% at MP2 = Full/6-311G** theory level. The ab initio calculation results are listed in Table 5, and their visualization structures are displayed in Fig. 2. Table 5 also gives

Table 3
Measured transition frequencies for thiodiglycol conformer III (asym-GG)

Selection rule	J'	K'_a	K'_c	J''	K''_a	K''_c	Frequency[a] (MHz)	Obs. − calc. (kHz)
A	6	1	6	5	1	5	12191.2187	−1.3
A	6	0	6	5	0	5	12334.0780	0.8
A	6	2	5	5	2	4	12353.0135	1.2
A	6	4	3	5	4	2	12358.5682	1.4
A	6	3	4	5	3	3	12359.3358	1.2
A	6	3	3	5	3	2	12359.5858	1.8
A	6	1	5	5	1	4	12510.1385	0.9
A	7	1	7	6	1	6	14220.7628	0.9
A	7	0	7	6	0	6	14380.4346	0.0
A	7	2	6	6	2	5	14410.1475	0.0
A	7	3	5	6	3	4	14420.1143	2.2
A	7	3	4	6	3	3	14420.6729	0.1
A	7	2	5	6	2	4	14444.3662	1.4
A	7	1	6	6	1	5	14592.5263	2.0
A	8	1	8	7	1	7	16249.2894	−1.1
C	6	1	5	5	0	5	16370.8850	−2.1
A	8	0	8	7	0	7	16422.6526	−1.7
C	3	2	1	2	1	1	16434.3088	1.2
A	8	2	7	7	2	6	16466.5002	0.3
A	8	5	4	7	5	3	16478.6389	−0.8
A	8	4	5	7	4	4	16479.2580	−1.4
A	8	4	4	7	4	3	16479.2678	−0.4
A	8	3	6	7	3	5	16481.2385	−0.5
A	8	3	5	7	3	4	16482.3596	0.4
A	8	2	6	7	2	5	16517.5314	−1.6
A	8	1	7	7	1	6	16673.6310	−0.9
A	9	1	9	8	1	8	18276.7026	−0.9
A	9	0	9	8	0	8	18460.3217	−2.4
A	9	2	8	8	2	7	18521.9584	−1.0
A	9	5	5	8	5	4	18538.8783	−0.2
A	9	4	6	8	4	5	18539.9603	−2.7
A	9	4	5	8	4	4	18539.9857	1.6
A	9	3	7	8	3	6	18542.7240	0.8
A	9	3	6	8	3	5	18544.7709	−2.8
A	9	2	7	8	2	6	18594.2728	−0.6
C	4	2	3	3	1	3	18729.9466	−0.5
A	9	1	8	8	1	7	18753.2317	−1.2
A	10	1	10	9	1	9	20302.9147	0.4
C	5	2	3	4	1	3	20385.0885	1.4
A	10	0	10	9	0	9	20493.1510	0.8
A	10	2	9	9	2	8	20576.4185	1.4
A	10	5	6	9	5	5	20599.2623	1.0
A	10	3	8	9	3	7	20604.5572	0.2
A	10	3	7	9	3	6	20608.0650	0.1
A	10	2	8	9	2	7	20674.7564	1.0
A	10	1	9	9	1	8	20831.0805	−1.1
C	5	2	4	4	1	4	20895.5746	−2.1
C	8	1	7	7	0	7	20922.5336	2.1
A	11	0	11	10	0	10	22520.9890	2.1

[a] The estimated type B ($k = 1$) uncertainties on the frequency measurements are 4 kHz.

main dihedral angles for the molecular backbone structure. As seen from Fig. 2, the lowest-energy conformer (GG′) with the two hydroxyl ethyl subunits on the same side of the C–S–C plane possesses a structure much different from the other two. In this conformer, one of the hydroxyl hydrogen forms a hydrogen bond to one of the lone pairs of electrons on the sulfur atom (–OH···S), while the hydrogen on the second hydroxyl forms another type of hydrogen bond (–OH···O) with

the oxygen atom on the first hydroxyl group. Because thiodiglycol has a longer backbone chain in comparing with HOEES [4] and MTE [3], the –OH···O interaction becomes much stronger, which is indicated by the smaller –OH···O hydrogen-bonding distance of only about 1.90 Å at MP2 = Full/6-311G** level ab initio calculation. This strong –OH···O hydrogen-bonding interaction is thought to explain why this "closed" structure lies at the lowest energy at our current

Table 4
Rotational parameters and dipole moments for the three observed conformers of thiodiglycol[a]

Parameter	I (GG')	II (sym-GG)	III (asym-GG)
A (MHz)	2543.0120(3)	4951.5310(5)	4474.103(3)
B (MHz)	1845.4959(2)	1006.7946(2)	1056.2669(2)
C (MHz)	1259.29598(8)	974.6064(2)	1003.0494(2)
Δ_J (kHz)	0.6321(2)	0.6443(1)	0.4070(5)
Δ_{JK} (kHz)	−1.114(7)	−11.702(3)	−4.837(3)
Δ_K (kHz)	1.808(12)	65.39(5)	26.8(5)
δ_J (kHz)	0.205(1)	0.0124(6)	0.0561(4)
δ_K (kHz)	0.361(7)	−0.397(73)	1.965(98)
Δ (u Å^2)	−71.27	−85.49	−87.93
μ_a (10^{-30} C m)	1.814(20)	—	—
[Debye]	[0.544(6)]		
μ_b (10^{-30} C m)	5.11(10)	5.106(30)	—
[Debye]	[1.531(30)]	[1.531(9)]	
μ_c (10^{-30} C m)	0.253(3)	—	—
[Debye]	[0.076(1)]		

[a] All uncertainties are type A with coverage factor $k = 1$ or one standard deviation values [14].

Table 5
Ab initio (MP2 = Full/6-311G**) rotational constants (A, B, C), dipole moments, relative energies, and backbone dihedral angles for thiodiglycol

MP2 = Full/ 6-311G**	I (GG')	II (sym-GG)	III (asym-GG)
A (MHz) [%][a]	2532 [−0.4]	5214 [5.3]	4440 [−0.8]
B (MHz) [%]	1909 [3.4]	993 [−1.4]	1078 [2.0]
C (MHz) [%]	1294 [2.8]	958 [−1.7]	1016 [1.3]
μ_a (Debye) [%]	−0.49 [10]	0.00	1.17
μ_b (Debye) [%]	1.30 [15]	1.67 [9]	−0.38
μ_c (Debye) [%]	−0.18	0.00	−0.77
D_{HOCC} (°)	−85	56	−66
D_{OCCS} (°)	71	−61	58
D_{CCSC} (°)	−70	−79	−98
D_{CSCC} (°)	115	−79	−80
D_{SCCO} (°)	−55	−61	−61
D_{CCOH} (°)	65	56	56
$E_{rel(elec. + ZPE)}$ (cm^{-1})[b]	0	854	905

[a] Percent difference between theory and experiment: % = 100 × (ab initio − exp)/exp.
[b] ZPE stands for zero-point energy. 1 cm^{-1} = 0.01196268 kJ/mol.

calculation (MP2 = Full/6-311G**). Both of the other two conformers, sym-GG and asym-GG, have a larger A value, which comes from the fact that the two hydroxyl ethyl subunits hydrogen-bond to the central sulfide along opposite directions to the C–S–C plane. Due to symmetry, sym-GG has near zero μ_a, μ_c dipole moment components. The only conformational difference between sym-GG and asym-GG is that one of the hydroxyl methyl groups rotates to its next staggered position by 120°. These two open structure conformers are almost isoenergetic at both HF and MP2 theory level calculations. From their structures in Fig. 2 and bond distances given in Section 5, the hydrogen-bonding directions in conformer II (sym-GG) are closer to the two un-covalent-bonded hybrid orbit directions of the sulfur atom, than in conformer III (asym-GG). The skewed bonding direction of one of the hydrogen bonds in conformer III (asym-GG) leads to a slight increase in its overall energy, which seems to be consistent to our experimental observations.

To reduce the possibility that any other low-energy conformers might have been overlooked, we also carried out independent limited-dimension potential energy scans for TDG, as we did for HOEES [4]. As for HOEES, we generated two 2-D potential contours in D_{OCCS}–D_{CCSC} and D_{CCSC}–D_{CSCC} plots, as well as several 1-D scans. However, we found no further interesting low-energy local minima. Among the seven hydrogen-bonded forms, four conformers have much higher energies, relatively small dipole moments, and poor agreement between the ab initio rotational constants and the observed values. This leads us to believe that the assigned conformer matches are likely the lowest-energy possible candidates in this molecule.

4. Stark-effect measurements

Stark-effect measurements were carried out on conformers I and II, while the spectrum of conformer III was too weak for these measurements. For this purpose a large FTMW spectrometer [8,9] was used where the
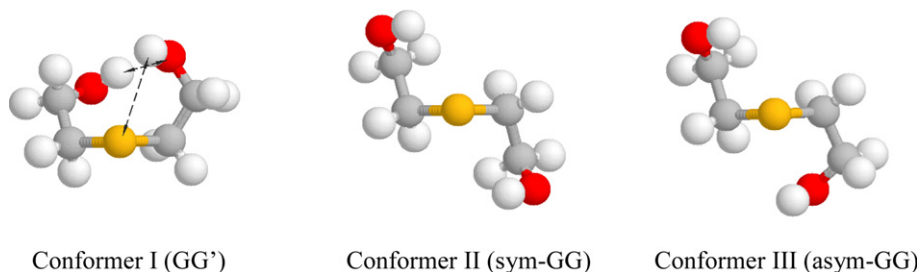

Conformer I (GG')   Conformer II (sym-GG)   Conformer III (asym-GG)

Fig. 2. The lower-energy conformational isomers of thiodiglycol in the energy ordering given at ab initio MP2 = Full/6-311G** level. The dashed arrows indicate the types of intramolecular hydrogen bonding presented in conformer I (GG'). The dipole moment components, μ_a and μ_c, are near zero in conformer II (sym-GG) due to symmetry.

nozzle was located perpendicular to the direction of the molecular beam and the direction of the electric field produced by the $25\,cm \times 25\,cm$ Stark plates. The configuration and calibration of the field with the $J = 1$–0 of OCS has been described previously [13]. For conformer I, the measurements included the $M = 0$ and 1 components of the 2_{20}–1_{11} transition, the $M = 0$, 1, and 2 components of the 3_{31}–2_{20} transition, and the $M = 1$, 2, and 3 components of the 4_{04}–3_{13} transition with frequency shifts up to 1.2 MHz. All three dipole moment components could be determined and these are listed in Table 4.

For conformer II the measurements included the $M = 0$ and 1 components of the 2_{21}–1_{10} and 2_{20}–1_{11} transitions, the $M = 0$, 1, and 2 components of the 3_{13}–2_{02} transition, and the $M = 0$, 1, 2, and 3 components of the 4_{14}–3_{03} and 4_{23}–3_{12} transitions with frequency shifts up to 1.6 MHz. For this conformer only b-type transitions have been observed. In the preliminary fits to the Stark-effect data, attempts were made to fit all three dipole moment components. In this case μ_a^2 was found to be negative and $\mu_c = 0.1(1) \times 10^{-30}\,C\,m$ [0.03(3) D], so both were indeterminate. The fitting was repeated with only μ_b fit yielding a value of $5.106(30) \times 10^{-30}\,C\,m$ [1.531(9) D], which is also listed in Table 4. This is consistent with the ab initio calculations discussed above which show an ac-symmetry plane and the fact that only b-type transitions were observable. Attempts to observe a- and c-type transitions for this conformer were also negative.

In Table 5, ab initio dipole moment values are compared with experimentally determined ones discussed above for those with large values. In general the % differences range from 9 to 15% in comparison with ab initio results shown in Table 5. Though transitions for conformer III were too weak to allow experimental Stark-effect observations, ab initio calculated dipole moments for this conformer do agree with the observed intensities of the rotational transitions which are strong μ_a and weak μ_c types.

5. Discussion and conclusions

Three lower-energy conformers have been observed experimentally and have been matched with ab initio calculations. The observation of the conformer I (GG′) is particularly interesting as this conformer displays compact folded-like structure. Similar partners were calculated in ab initio studies for HOEES [4], however, they were not observed experimentally. This remains one of the perplexing issues left with our study of the HOEES molecule and we think that one reason could be a low barrier to interconversion ($<400\,cm^{-1}$) down to other low-energy conformers in the molecular beam expansion and another reason is the uncertainty in current ab initio calculated energy. The observation of the conformer I in TDG supports our earlier explanation that current ab initio theory gives reasonably good structural information. However, one should view relative conformational energy ordering based on calculated ab initio energy with caution.

The increased stability of conformer I of TDG is likely a result of the two hydrogen bonds, one being a much stronger –OH···O bond, while in HOEES only the –OH···S bonding has been observed under the molecular beam condition. To shed light on this issue, it might be worthwhile comparing the calculated hydrogen bonds in the TDG conformers with some known dimers and those in HOEES. For conformer I of TDG the hydrogen bonds are $R(H_1···S) = 2.609\,Å$ and $R(H_{17}···O) = 1.899\,Å$, where subscript 1 and 17 refer to the two hydrogen-bonded hydrogen atoms on each end of the TDG molecule. Conformer II hydrogen-bond values are $R(H_1···S) = 2.614\,Å$ and $R(H_{17}···S) = 2.615\,Å$ and for conformer III the values are $R(H_1···S) = 2.618\,Å$ and $R(H_{17}···S) = 2.667\,Å$. For comparison, in water dimer $R(H···O) = 1.99\,Å$ [15] and in HOH–SH$_2$ dimer $R(H···S) = 2.597\,Å$ [16]. For conformer I the H···O hydrogen bond is about 0.1 Å shorter than that in water dimer, indicating bonding nearly the same strength as in water dimer, about 5 kcal/mol [17]. The H···S bonds in all three conformers of TDG are slightly longer than in HOH–SH$_2$ dimer, ranging from 0.02 to 0.06 Å longer also indicating substantial strength of interaction. The comparison of the H···S bonds in TDG and HOEES is also quite favorable. For HOEES conformer I (TG) and conformer II (GG) the hydrogen-bond distance is $R(H···S) = 2.642\,Å$. There is little doubt that hydrogen bonding is a major contributor to the stabilization of conformer I in TDG.

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[12] Certain commercial products are identified in this paper in order to specify adequately the experimental or theoretical procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for purpose.

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