Using Torsional Forces to Explain the Gradient Temperature Raman Spectra of Endosulfan Isomers and its Irreversible Isomerization

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Keywords

endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-

benzodioxathiepine-3-oxide)

Gradient Temperature-dependent Raman spectroscopy (GTRS)

Raman ring-bending wavenumber

temperature-dependent conformational change

torsional force

Abstract

Since the 1950's, the broad-spectrum, organochlorine insecticide endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine-3-oxide) has been used on numerous crops. Due to its persistence, bioaccumulation, long-range transport, and adverse effects to human health and ecosystems, it was officially identified as a persistent organic pollutant (POP) in 2011. The last uses in the United States were phased out in 2016. Endosulfan consists of two diastereomers, α -endosulfan and β -endosulfan, and while the α -isomer exists as two asymmetrical, twist-chair enantiomers which interchange, the β -isomer is a symmetrical-chair conformation. In addition, the β -isomer was found to isomerize to the α -isomer. Gradient Temperature Raman Spectroscopy (GTRS) enables identification the molecular sites at which bending vibrational modes becomes twisting or wagging vibrational modes. Previous studies using GTRS and chemical calculations afforded evidence for specific bond movements and the irreversibility of the isomerization mechanism. However, not all of the vibrational modes observed in the spectra could be explained. Thus, new analyses of the GTRS data were conducted to examine the effects of torsional forces on the bond movement, which allowed for the identification of all the peaks. These newly-identified torsional forces provide further confirmation of the isomerization mechanism and its irreversibility. Finally, this isomerization explains why β -endosulfan is rarely detected in the atmosphere.

1. Introduction

Endosulfan (6,7,8, 9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine-3-oxide) (Fig. 1), a broad-spectrum organochlorine insecticide, was used on cereals, fruits, vegetables, and cotton from the 1950's until recently [1]. Endosulfan, however, is persistent, can be transported in the atmosphere over long distances, and poses adverse effects to aquatic ecosystems and to human health [e.g., 2-4]. Thus, the United States Environmental Protection Agency initiated a Memorandum of Agreement in 2010 and phased-out all uses of endosulfan in 2016 due to its environmental persistence and unacceptable exposure risks to farm workers and wildlife [5-7]. In 2011, the Parties to the Stockholm Convention on Persistent Organic Pollutants (POPs) of the United Nations Environmental Programme (UNEP) agreed to list endosulfan as a POP [8]. Although endosulfan is nearly completely banned globally, the environmental fate is still a concern.

Endosulfan is a mixture of three isomers, a set of enantiomers α_1 - and α_2 -endosulfan and β -endosulfan (Fig. 1), with the formulated material applied to crops consisting of a 70:30 isomeric ratio of α : β . In the early 1960's, the structure of these isomers was extensively studied and was thought to be resolved [9-12], but several environmental fate observations in the mid-1990's afforded curious results. Studies were conducted to determine the regional and long-range atmospheric transport of the endosulfan isomers. The results showed that β -endosulfan was rarely detected relative to α -endosulfan so much so that it was disregarded in the data analyses [13,14]. In other studies, while examining the Henry's Law Constants of endosulfan using a wetted-wall column, Rice et al [15,16] discovered that in the aqueous phase, β -endosulfan readily converts to α -endosulfan, that the α -endosulfan was virtually the only isomer observed in

air phase, and that the reverse process was not observed. The mechanism of this conversion could not be explained using the structure described in the 1960's, thus, the structure of α -endosulfan and β -endosulfan was revisited.

Reexamination of the ^1H -NMR data and new X-ray crystallography confirmed that β -endosulfan is symmetrical as was previously suggested, but surprisingly, α -endosulfan is composed of two asymmetrical enantiomers (Fig. 1) [17]. This new structure provided an obvious driving force for the conversion of β -endosulfan to α -endosulfan, namely, an increase in entropy. The increase in entropy also precluded the isomerization of α -endosulfan to β -endosulfan without a concomitant energy source added to the system. Finally, the isomerization also explained the observed overabundance of α -endosulfan and lack of β -endosulfan in the atmosphere [2,18]. A preliminary mechanism for β -endosulfan conversion to α -endosulfan and its irreversibility was proposed using data from differential scanning calorimetry (DSC) and NMR experiments and from computational chemistry calculations [18].

Direct evidence for specific bond movements and the irreversibility of the isomerization mechanism was obtained using chemical calculations and Gradient Temperature Raman Spectroscopy (GTRS), a technique recently developed in our laboratory [19,20]. GTRS allows for identification of the vibrational modes corresponding to the most elastic molecular sites and to differentiate them from the more inelastic or rigid sites. This gives rise to the sequence of molecular movements in the mechanism. In that study, the vibrational modes (110 cm^{-1} to 820 cm^{-1}) in the Raman spectra of the pure isomers were identified, however, the wavenumbers observed between 820 cm^{-1} to 1720 cm^{-1} could not be explained or assigned to specific bonds. The purpose of this manuscript is, therefore, to reexamine these data using the torsional forces to

identify the twisting and bending molecular motions of the bonds in the seven-membered ring, the rocking at the CH₂ and sites, and the wagging at the C–H sites.

2. Experimental section

2.1. Materials

Certified analytical grade β -endosulfan (nearly 100%) and α -endosulfan (99.8% α ; 0.2% β) were used as obtained (ChemServices, West Chester, PA).

2.2. Gradient Temperature Raman Spectroscopy (GTRS)

A Raman spectroscopy system to collect gradient temperature Raman spectra was assembled and is described elsewhere [20,21]. Briefly, the system consisted of a Raman spectrometer which accepts light through an input slit (5 mm long $\times$ 100 μ m wide) and detects a Raman shift range of 102.2 to 2538.1 cm^{-1} with a single-scan spectral resolution of 3.7 cm^{-1} . A 785-nm laser module served as the excitation source, and a fiber optic Raman probe acquired the Raman signals. A hotplate with a ceramic top surface was used to heat the samples which were held in a copper sample holder. Two thermocouple probes were attached to two sides of the sample area and were connected to a dual-input thermometer to measure the temperature of the samples. The Raman probe, the hotplate, and the sample materials were placed in a closed black box to avoid the influence of ambient light. The entire system was controlled using readily available system software.

Samples were collected from 50 °C to 100 °C at a heating rate of 1 °C per minute, and spectra collected whenever temperature at the sample increase another 0.2 °C step as measured from two thermocouples close to the sample cup. The spectra did not include the significant equilibration time between steps present in thermal studies in which temperature increases stepwise. Although spectra were collected every 0.2 °C, only the spectra every 10 °C starting at 50 °C were reported and used here. Phase transitions which occur over a narrower temperature range are easily accessible from the same data set.

2.3. Torsional angle calculations

Torsional angles for the endosulfan isomers were calculated using commercial computational chemistry software (HyperChem 8.0, Hypercube, Inc, <http://www.hyper.com/>). Calculations were all normalized to room temperature conformations. No calculations were conducted on the effect of adding thermal energy to each of the endosulfan isomer structures.

3. Results

3.1. Curvature, torque, torsion, and torsional angles

Connecting two discrete non-identical Cartesian points results in a line. Connecting three discrete non-linear points results in curvature contained in a plane. Connecting three discrete planar points to a fourth point that is off the plane results in torsion above or below the plane. Curvature, torsion, and torque are analogous to distance, velocity, and acceleration on the linear

scale. Inertia is the straight line a car will travel going into a curve, whereas torque is the force that enables a car to travel at a constant speed from the beginning to the end of a uniform curve [22-24].

Curvature and torsion are critical elements to the evaluation of the molecular forces. Torsion in one part of a molecule is expressed as relative to another site in the molecule (a plane) where torsion is assumed to be zero. It arises whenever a fourth atom is out of the plane with the previous three atoms. Torsion angles occur on every set of four backbone atoms and can overlap, *i.e.*, atoms 1–2–3–4, atoms 2–3–4–5, atoms 3–4–5–6, and so on. Furthermore, torsion angles in the reverse order atoms 4–3–2–1 are identical when the atoms in the sequence are symmetrical and when an even number of atoms exists in the atom set [25].

Three-dimensional structural interpretation of spectral data requires vibrational mode assignments that include at least four points, and at least four points are needed to ascertain any asymmetry. Bond movements that are in-plane are harmonic and symmetrical, whereas out-of-plane bond movements create torsion either above or below the plane. Including at least four points in vibrational modes allows for evaluation of the relative direction of torsion from site to site and for ascertaining the local sites of molecular stress due to torsion [23,24]. For example, the bond movements (*e.g.*, wagging) of the CH₂ in the simple hydrocarbon structure C1–C2H₂–C3 create torsion relative to C1–C2–C3 backbone plane which lies in the plane and does not move of the plane. Curiously, since this is actually a five-atom moiety, not four, the relative direction of the background plane cannot be assigned.

Curvature direction can be assigned as left-handedness or right-handedness. The relative direction of torque from out-of-plane torsion must be internally self-consistent. Twisting, wagging, and rocking vibrational modes in molecules remain symmetrical functions until

localized asymmetrical forces due to curvature and torque are included. Vibrational modes resulting from dihedral (torsion) angles that are not 0° or 180° always result in localized sites of torsion, curvature, and torque. Using oleic acid as an example, the wavenumber of C–C asymmetrical stretching (1057 cm^{-1}) is different than C–C symmetrical stretching (1093 cm^{-1}) [26,27]. C–C asymmetrical stretching requires at least a three atom model C1–C2–C3, where C1–C2 stretching is not equal to C2–C3 stretching. CH₂ twisting when C–C stretching is symmetrical need not be equal to CH₂ torsion when C–C stretching is asymmetrical. A simpler, more complete model of twisting includes four atoms, where atoms C1–C2–C3 are the frame of reference and atom four can be –H or –C4. A torsion angle above or below the plane containing C3 is created from the movement of the fourth atom out of the plane.

Similar sets of four-atom torsion angle matrices are observed in docosahexaenoic acid (DHA, 22:6n-3) and docosapentaenoic acid (n-6 DPA, 22:5n-6), both of which contain many overlapping examples of the H₂C1–(H–C2=C3–H)–C4H₂ moiety. The torsion angles of H–C1–C2–C3 are routinely different from the torsion angles created by C2–C3–C4–H. In addition, each hydrogen in the CH₂ (i.e., C–H_aH_b) sites need not have the identical torsion angle; torsion on one can be due to out-of-plane wagging and the other can just as easily be due to in-plane bending [28]. Curvature and pitch are also fundamental to the peptide backbone structure in the α -helical structure without considering any contribution of peptide side chains. The peptide backbone contains three units repeating in a four atom set in the pattern of A–B–C–A, B–C–A–B, and C–A–B–C. Beginning from curvature, the uniform torsion from A to A, from B to B, and from C to C, in and of itself, forms the shape of the α -helix [29,30]. The mathematical consequences on curvature, torsion, and torque under conditions of compression and expansion within a constant radius cylinder, such as the α -helix have been calculated [24].

3.2. Assigning torsion angles in endosulfan isomers

A seven-atom sequence 1–2–3–4–5–6–7 has torsion at atom 4 from 4–3–2–1 and from 4–5–6–7. In endosulfan, the seven-atom sequence is circular, and the numbering of sites can start at any atom in the ring. Furthermore, localized curvature, torsion, and torque would be present at every ring backbone atom, forward, and backward from the middle number. Three-atom-bond (planar) angles in the seven-membered ring for the endosulfan isomers were obtained from X-ray crystallographic data [17]. Values shown for the atom torsion angles were calculated [Table 1]. MM+ energy minimization algorithm was used to delocalized excess stress (torsion) among the backbone atoms and to fine-tune relative location of the hydrogens on $H_{ax}(H_{eq})$ –C4–(HC5–C6H)–C7 and C4–(HC5–C6H)–C7– $H_{ax}(H_{eq})$ moieties. The torsion angles involving the C5 and C6 axial hydrogens were also calculated. For both isomers, the chlorinated norbornene moiety are nearly identical and will be not be considered further, whereas the seven-membered rings are very different [Figs. 1, 2]. Seven (and only seven) four-atom, backbone torsion angles occur in the ring of all three isomers. The numbering of seven-membered ring atoms is counter clockwise and follows the literature for cyclo-1,3-dioxepane [31].

The torsion angles for the four atoms of each C7–C6–C5–C4 sequence are close to planar (7° , -3° , and 1° for α_1 -, α_2 -, and β -endosulfan, respectively) as would be expected, since these atoms are highly influenced by the rigid norbornene moiety. The torsional angles in the α_1 - and α_2 -enantiomers are clearly in opposite directions, e.g., the O1–S2–O3–C4 angle in the α_1 -isomer is -66° , whereas the corresponding angle in the α_2 -isomer is 71° . For the β -isomer, the magnitude of the torsion angles are virtually the same on the left side of the plane of symmetry as the

corresponding angles on the right side, but in the opposite direction, e.g., C7–O1–S2–O3 (-103°) versus O1–S2–O3–C4 ($+104^\circ$). Torsion angles in opposite directions correspond to torque in opposite directions, which is why the methylene groups (C7–H₂ and C4–H₂) of C7–C6–C5–C4 in the β -isomer twist up from the plane. The result is effectively zero net torque for the molecule as a whole.

The relative conformations for α -endosulfan and β -endosulfan from O3–C4–C5–C6 are comparable, whereas sites O1–C7–C6–C5 are not. O1 and O3 are below the plane of seven-membered ring in the β -isomer and C4 and C7 are above the plane. In the α -isomer, C4 and O1 are above the plane of the ring and O3 and C7 are below the ring. Thus, two sets of torsion angles exist that are different between the α -endosulfan and β -endosulfan backbone atoms.

The radius of curvature is the greater in the β -isomer. Distance from the C4 atom to the C7 atom in the β -isomer is 3.21 Å versus 3.06 Å in the α -isomers. This is evidence that in the β -isomer, the ring is expanded relative to the α -isomer, and that the ring in the α -isomers has contracted relative to the β -isomer. Additional torque is required for holding in place the larger β -isomer diameter, even though the net torque in the β -isomer will still be close to zero.

3.3. Spectral assignments

In the α -isomer at the C4H₂ site, one hydrogen is axial up from the ring and the other is equatorial, and at C7H₂, one hydrogen is axial below relative to plane of the ring and the other is equatorial. For the β -isomer, four hydrogens on C7–C6–C5–C4 site are all axial up relative to the plane of the ring and the other two hydrogens on C7 and C4 are equatorial. An alternative and useful description is that, in the α -isomers, the hydrogens in the sequence H_{ax}–C7–C6–H_{ax} are in

a *trans*-orientation, and the hydrogens in the sequence H_{ax}–C5–C4–H_{ax} are in a *cis*-orientation. GTRS spectral assignments are shown in Table 2.

3.3.1. Bending vibrational modes

The CH₂ bending vibrational mode at 1454 cm⁻¹ occurs in both the α - and β -isomers; it includes C4–H_{eq}, C4–H_{ax}, C7–H_{eq}, and C7–H_{ax} sites in the β -isomer, but is assignable to only three sites C4–H_{eq}, C4–H_{ax}, and C7–H_{eq} in the α -isomer (Fig. S1). The CH₂ bending mode at 1473 cm⁻¹ in the α -isomer was not observed in the β -isomer. Since the only two sites of CH₂ bending are at C7 and C4, this bending mode must include the C7–H_{ax down} site in the α -isomer. The intensity ratio of 1473 cm⁻¹:1454 cm⁻¹ ca. 1:3. The C7–H_{ax} bending mode at 1473 cm⁻¹ in the α -isomer may or may not include C7–H_{eq} site. CH₂ bending is relative to a molecular site that is not bending, such as the plane containing O1–C7–C6 or C7–C6–C5. Likewise, the vibrational mode at 1454 cm⁻¹ can be related to the C7–(C6H–C5H)–C4, a relatively inelastic structural moiety in both the α - and β -isomers.

3.3.2. Twisting vibrational modes

In the α -isomer, CH₂ twisting mode vibrational modes at 1380 cm⁻¹ and 1326 cm⁻¹ are observed (Fig. S2). In the β -isomer, two similar wavenumbers occur plus a third at 1302 cm⁻¹. Four different wavenumbers for CH₂ twisting vibrational modes relative to the C7–(C6H–C5H)–C4 moiety could occur: H_{ax}–C7–C6–C5, H_{eq}–C7–C6–C5, C6–C5–C4–H_{ax}, and C6–C5–C4–H_{eq}. The wavenumbers near 1380 cm⁻¹ in both the α - and β -isomers are assignable to twist at the

equatorial CH sites, $H_{eq}-C7-C6-C5$ and $C6-C5-C4-H_{eq}$. The wavenumber near 1380 cm^{-1} (roughly half the relative intensity at 1326 cm^{-1}) refers to one axial site $C6-C5-C4-H_{ax}$. In the β -isomer, the wavenumber at 1302 cm^{-1} can be assigned to $H_{ax}-C7-C6-C5$ twisting which is 78 cm^{-1} lower in wavenumber than $C6-C5-C4-H_{ax}$ twisting and 24 cm^{-1} lower in wavenumber than $H_{eq}-C7-C6-C5$. Thus, twisting is not identical at C7 and C4 sites in the β -isomer, and CH_2 twisting at axial sites is very different from twisting at equatorial sites. In the α -isomer, $H_{ax}-C7-C6-C5$ twisting appears to be absent.

3.3.3. Wagging vibrational modes

Wagging vibrational modes like bending and twisting wavenumbers occur relative to planes which are not wagging. The wavenumbers in the 1270 cm^{-1} to 1170 cm^{-1} range refer to wagging of $C6-H_{ax}$ relative to $C7-H_2$ hydrogens and $C5-H_{ax}$ relative to $C4-H_2$ hydrogens (Fig. S3). Two $H-C7-C6-H_{ax}$ and two $H_{ax}-C5-C4-H$ wagging vibrational modes can occur: $H_{eq}-C7-C6-H_{ax}$ and $H_{ax}-C7-C6-H_{ax}$, plus $H_{ax}-C5-C4-H_{eq}$ and $H_{ax}-C5-C4-H_{ax}$.

The $H_{ax}-C7-C6-H_{ax}$ wagging observed at 1096 cm^{-1} occurs only in the α -isomer, and the $H_{ax}-C7-C6-H_{ax}$ wagging at 1241 cm^{-1} occurs only in the β -isomer which is 145 cm^{-1} higher in wavenumber than in the α -isomer. At 1186 cm^{-1} , $H_{eq}-C7-C6-H_{ax}$ and $H_{ax}-C5-C4-H_{eq}$ wagging are observed in the β -isomer and at a wavenumber of 1191 cm^{-1} in the α -isomer. In contrast, $H_{ax}-C5-C4-H_{ax}$ wagging for the α - and β -isomer differs in wavenumber by 35 cm^{-1} (1151 cm^{-1} and 1116 cm^{-1} , respectively), even though the sites are structurally identical.

The wavenumber range of about 1075 to 875 cm^{-1} is assignable to wagging between the axial hydrogens $H-C6-C5-H$ (Fig. 3). Because both hydrogens are $axial_{up}$ relative to the seven-

membered ring, both wagging outward in parallel slightly increases the arc diameter, causing ring expansion (re), and both wagging inward in parallel slightly decreases the arc diameter, causing ring compression (rc). Wagging of the two hydrogens can also be anti-parallel to C6–C5 or anti-parallel in the opposite direction C5–C6. For the β -isomer, all four vibrational modes are present: anti-parallel modes differ by $\pm 12\text{ cm}^{-1}$ from 964 cm^{-1} ; the vibrational mode is shifted -59 cm^{-1} (re) and is shifted $+61\text{ cm}^{-1}$ (rc) from the same 964 cm^{-1} . Likewise, the two wagging vibrational modes in the α -isomer shifted -59 cm^{-1} (re) and $+61\text{ cm}^{-1}$ (rc) from 968 cm^{-1} , the single only anti-parallel vibrational mode in the α -isomer. In both isomers, the intensity of the wavenumber near 905 cm^{-1} (re) was about 25% larger in intensity than the peak near 1025 cm^{-1} (rc), i.e., wagging due to ring compression requires more energy than ring expansion.

3.3.4. Rocking vibrational modes

Vibrational modes of CH₂ bending, twisting, wagging, and rocking at C7–H₂ and C4–H₂ are occurring concurrently in both endosulfan isomers (Fig. 4). However, rocking at the C4–H₂ (745 cm^{-1}) site in the α -isomer is much more predominant than C7–H₂ rocking (848 cm^{-1} rc and 777 re cm^{-1}) site. The C4–H₂ rocking intensity signal for the β -isomer is only 4% of C4–H₂ rocking in the α -isomer, and the C7–H₂ rocking is also less intense than in the C7–H₂ rocking in the β -isomer. The C4–H₂ rocking can be the dominant vibrational mode in the α -isomers under the thermal stress of the applied temperature gradient, because the C4 site is clearly far more elastic than the C7 site. Sites of elasticity cannot be detected under steady state conditions because elasticity/inelasticity is always a differential response to stress. At a constant temperature, no molecular response to thermal stress can or would be observed.

The two CH₂ rocking wavenumbers in β -isomer (763 cm⁻¹ and 734 cm⁻¹) are spectroscopic evidence that in a thermal gradient, C7 rocking and C4 rocking occur at different wavenumbers in the β -isomer as well as in the α -isomer. One of the two C7 rocking wavenumbers in the α -isomer (777 cm⁻¹) appears to overlap with one of the C7 rocking wavenumbers in the β -isomer (763 cm⁻¹). Ring expansion at C7–H₂ site is occurring in the α -isomer, whereas ring compression occurs at C7–H₂ in the β -isomer under the same thermal gradient. When both isomers are concurrently present (in a melt), ring expansion at C7 in the α -isomer and ring compression at C7 in the β -isomer will occur. A molecular pathway by which the β -isomer converts to the α -isomer on heating is clear. Compression at C7 in the β -isomer which results in ring expansion at C4 would generate the CH₂ rocking modes present in the α -isomer.

3.3.5. Ring expansion and compression

The two ring vibrational modes ω_7 (683 cm⁻¹) and ω_5 (476 cm⁻¹) for 1,3-dioxepane have been published using Density Function Theory parameters [31]. In ω_7 mode, C7 and C4 sites move outward resulting in ring expansion across C7 to C4 (Fig. S4) [20]. The ω_5 vibrational mode results in C7 and C4 ring compression between C7 to C4; concurrent with ring compression, S2 moves outward from the ring resulting in elongation as well. Interestingly, ω_5 requires all seven ring atoms, and ω_7 involves only six. These two vibrational modes dominate the GTRS of the β -isomer and are about eight times larger than in the α -isomer. In the α -isomers, the large increase in C7–H₂ rocking occurs at the same C7 site at which the ring is expanding.

The weak intensity of C7–H₂ and C4–H₂ rocking in the β -isomer can be due to the close balance between ω 7 ring expansion and ω 5 ring compression modes.

In the ω 8 asymmetrical ring vibrational mode (616 cm⁻¹), site C7 expands and site C4 contracts. The wavenumber is identical between the α - and β -isomers and about 30% more intense in the α -isomer. Half the vibrational modes in ω 8 and in ω 7 are identical in site (at C6, C7, O1) and in direction (rc, re, rc). The other half of the modes are identical in site (O3, C4, C5) and in opposite direction (rc, re, rc in ω 7 versus re, rc, re in ω 8). In contrast comparing the vibrational modes ω 5 and ω 8, three of the seven vibrational modes in ω 5 and in ω 8 are identical in site (at O1, C4, C5) and in direction (rc, rc, re). Another three vibrational modes are identical in site (C6, C7, O3,) and opposite in direction (rc, re, re in ω 7 versus re, rc, rc in ω 8). The seventh mode in this correlation is ring expansion at the S site and occurs in ω 5; however in ω 8 and ω 7, S2 site neither expands nor contracts.

4. Discussion

4.1. Spectral Interpretation

The differences in the vibrational modes corresponding to the hydrogens on C7, C6, C5, and C4 sites fully describe the curvature, torsion, and torque for each of the endosulfan isomers. The hydrogens on H–C6–C5–H are roughly perpendicular to the backbone of the seven-membered ring in both the α - and β -isomers. The spectral regions of 1080 cm⁻¹ to 880 cm⁻¹ (Fig. 3) correspond to the C6–H and C5–H out of plane (op) wagging. Because of curvature, in parallel CH site wagging in one direction results in ring expansion; wagging in the opposite

direction results in ring compression. Ring compression requires more energy and occurs at the higher wavenumber (α : 1027 cm^{-1} ; β : 1022 cm^{-1}), whereas the wavenumber for ring expansion is 119 cm^{-1} lower (α : 908 cm^{-1} ; β : 903 cm^{-1}). With anti-parallel wagging at C6–H and C5–H, in the α -isomers, out of plane wagging occurs at halfway between the two. In a temperature gradient, the specific sites and vibrational modes which correspond to more elasticity, i.e., ring expansion, require less thermal energy than the sites and vibrational modes which correspond to more rigidity, i.e., ring compression, whether in the α -isomer or the β -isomer. As a result, torque increases from compression and decreases from expansion at this site and is virtually identical between the β - and α -isomers.

Perhaps unexpectedly in the β -isomer, the wagging vibrational mode for C6 and C5 is not a single value (not at 963 cm^{-1} as is observed in the α -isomer), but is two discretely-different wavenumbers (976 cm^{-1} and 952 cm^{-1}). The wagging due to ring expansion followed by wagging due to ring compression appears to take less energy than wagging due to ring compression followed by wagging due to ring expansion. In the absence of a temperature gradient, no difference between the two would be expected. Nevertheless, torque from expansion followed by compression is not equal to torque from compression followed by expansion. Compressed curvature increases rigidity and expanded curvature increases elasticity.

The spectral region 900 cm^{-1} and 720 cm^{-1} (Fig. 4) corresponding to C7–H₂ and C4–H₂ rocking is markedly different among the β - and the α -isomers. The signal for C4–H₂ rocking in the α -isomer (745 cm^{-1}) is greater and more elastic than the corresponding rocking in the β -isomer. The two C7–H₂ rocking wavenumbers in the α -isomer correspond to rocking resulting in ring compression (848 cm^{-1}) or ring expansion (777 cm^{-1}) depending upon the relative direction of rocking. A wavenumber difference from ring compression at C7–H₂ site in the α -isomer

versus from ring compression at the C4–H₂ in the β -isomer (114 cm⁻¹) is quite similar to the difference in wavenumber between ring expansion and ring compression at H–C6–C5–H in both isomer sites due to out-of-plane wagging (119 cm⁻¹). This suggests that these movements are not independent of each other.

The C4–H₂ rocking site in α -isomer appears to neither expand nor contract the backbone ring. Two C7–H₂ rocking vibrational modes occur concurrently; ring compression makes the conformation more rigid, whereas ring expansion makes the ring less rigid. Torque in opposite directions between C7 and C4 explains the molecular elasticity and the molecular asymmetry in the α -isomers (Fig. 4). In contrast for the β -isomer, C7–H₂ rocking and C4–H₂ rocking are both weak and are much more closer in wavenumber (α : 848 cm⁻¹ and 777 cm⁻¹ versus β : 763 cm⁻¹ and 734 cm⁻¹). The simplest interpretation of these two wavenumbers is the vibrational modes for C7–H₂ and C4–H₂ are rocking out-of-phase: ring compression at one site is concurrent, i.e., in phase, with ring expansion at the other site. The torsion contained in the β -isomer is very similar in the α -isomers, except it is centered between S2 and half-way between C6 and C5 versus between C7 and C4 in the α -isomers.

4.2. Isomerization β -endosulfan to α -endosulfan

Increasing the temperature of a curved surface can relax bending, and therefore increase the curved radius. Concurrently, twisting stress can progressively increase with temperature. Sufficient stress localized at one particular molecular site can then trigger a major conformational change. GTRS is useful in identifying the molecular sites and temperature at

which torque can result in major conformational changes, such isomerization of β -endosulfan to α -endosulfan.

The GTRS data support that torsion in the left half (clockwise) and the right half (counterclockwise) in the β -isomer is in the opposite direction. The structural consequence of torsion in opposite directions is the bending/flattening/compression of the ring. The same torque can be present over the same set of four atoms in both isomers. With the β -isomer, torque at S2–O3–C4–C5 can equally be balanced with torque at C6–C7–O1–S2. Balanced torque results in molecular rigidity at some sites and ring expansion at other sites. The β -isomer is thermally stable as a solid by 100 °C more than the α -isomer, reflecting the higher free energy of the β -isomer and the greater flexibility of the α -isomers.

The assigned vibrational modes in the 720 cm^{-1} to 420 cm^{-1} range enables two additional molecular mechanisms by which β -endosulfan can convert to α -endosulfan to be identified. The asymmetrical vibrational mode ω_8 can disrupt half of the symmetrical modes in the ω_7 mode at O3, C4, and C5 sites. The C4 site, where C4H₂ rocking occurs, is the most elastic site as is evidenced in the signal intensity; this vibrational mode at 745 cm^{-1} is twice the intensity as the next largest vibrational mode at 1600 cm^{-1} . Second, since ω_5 includes a ring expansion at the S2 site, disruption of symmetry at the S=O site would allow for the regular length at S2 to return [20]. No simple or straightforward molecular pathway is apparent in the spectral data by which α -endosulfan can convert to β -endosulfan.

Rocking from ring expansion occurs at (777 cm^{-1}) in the α -isomer, which can be absorbed at the C7–H₂ ring expansion vibrational mode (763 cm^{-1}) in the β -isomer. Ring compression and expansions occurs at the same molecular sites in both rings. In the presence of the α -isomer or some other asymmetric molecule in the environmental matrix, C7–H₂ and C4–H₂ progressively

become sufficiently dissimilar in the β -isomer. With sufficient activation energy and once C7–H₂ and C4–H₂ are sufficiently unequal in elasticity, the β -isomer irreversibly changes conformation and becomes the α -isomer.

In α - and β -endosulfan, C7–H₂ rocking and C4–H₂ rocking are not identical in a small thermal gradient. Under the resulting thermal stress, torsion between sites most elastic and least elastic can be detected. At steady state, torsion between sites most elastic and least elastic will always appear to be zero. Curvature, torsion, and torque can also be present in the middle of a two four atom sequence as well as any particular atomic site. In β -endosulfan, curvature at the planar sequences C7–C6–C5–C4 and H–C6–C5–H resulted in torque at the bond between C6 and C5 as well [20]. Bending above the plane that include C5, C6 and S2 occurs at both C4 and C7 sites, and unequal bending above and below the same plane results in twisting and conversion to the α -isomer

4. Conclusion – use of GTRS

GTRS enables identification the molecular sites at which bending vibrational modes becomes twisting or wagging vibrational modes. The temperature at which a glass or phase transition occurs can be correlated with the temperature at which vibrational modes change with temperature.

Molecular sites at which the most torque is observed are most likely the sites which are the most elastic. In the presence of curvature, bending and twisting [due to torsion] cannot change independently [24]. Especially interesting is the evidence bending mode and twisting

mode are mathematically orthogonal. Thus, compression of a curved space increases twisting, and stretching a curves space decreases bending. Present models on torsion may assume [incorrectly] that bending and twisting on curved surfaces can change independently. Of course in the absence of curvature, bending and twisting are fully independent variables.

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Figure legends

Figure 1. Structure of α_1 -endosulfan, its mirror image (α_2 -endosulfan), and β -endosulfan. The numbering of sites on ring follows the literature for cyclo-1,3-dioxepanes [31]. Positions of α_1 -endosulfan hydrogens: C4–H axial up, C4–H equatorial, C5–H axial up, C6–H axial up, C7–H axial down, C4–H equatorial. Planar atoms for α_1 -endosulfan: C5–C6–C7–H_{eq}. Positions of β -endosulfan hydrogens: C4–H axial up, C4–H equatorial, C5–H axial up, C6–H axial up, C7–H axial up, C4–H equatorial. Planar atoms for β -endosulfan: C5–C6–C7–H_{eq} and C6–C5–C4–H_{eq}.

Figure 2. Seven member ring in endosulfan isomers: turquoise = carbon, red = oxygen, yellow = sulfur.

Figure 3. Raman spectra from 1060 cm⁻¹ to 880 cm⁻¹ acquired at 1 °C intervals from 50 to 102 °C for α -endosulfan and β -endosulfan. Relative intensities of each vibrational mode in the individual isomers were essentially temperature independent.

Figure 4. Raman spectra from 900 cm⁻¹ to 720 cm⁻¹ acquired at 1 °C intervals from 50 to 102 °C for α -endosulfan and β -endosulfan. Relative intensities of each vibrational mode in the individual isomers were essentially temperature independent.

Figure(s)

α -endosulfan (twist chair forms)

β -endosulfan (symmetrical)

Figure(s)

Twist at C4 and C7 Counterclockwise

Twist at C4 and C7 Clockwise

Twist C4 Clockwise
Twist C7 Counterclockwise
(twist is relative to O1-S2-O3)

Figure(s)

Figure(s)

β -endosulfan

α -endosulfan

Table 1. Four atom torsion angles in α_1 -, α_2 -, and β -endosulfan isomers

Torsion site	α_1 -endosulfan torsion angle ($^\circ$)	α_2 -endosulfan torsion angle ($^\circ$)	β -endosulfan torsion angle ($^\circ$)
Backbone atoms			
C4–C5–C6–C7	7	-3	1
O1–S2–O3–C4	-66	71	104
C7–O1–S2–O3	-35	33	-103
S2–O3–C4–C5	110	-111	-82
C6–C7–O1–S2	95	-95	82
C5–C6–C7–O1	-49	48	-30
O3–C4–C5–C6	-44	39	29
$\Sigma+$	212	191	215
$\Sigma-$	-194	-209	-215
Total	18	-18	0
C7–H atoms			
H _{eq} –C7–C6–C5	121	-128	-150
H _{eq} –C7–C6–H	5	7	86
H _{ax} –C7–C6–C5	-119	117	95
H _{ax} –C7–C6–H	126	-123	-32
$\Sigma+$	252	-251	181
$\Sigma-$	-119	126	-182
Total	133	-125	-1
C4–H atoms			
H _{eq} –C4–C5–C6	-175	176	149
H _{eq} –C4–C5–H	-56	61	-86
H _{ax} –C4–C5–C6	58	57	-94
H _{ax} –C4–C5–H	-60	-58	31
$\Sigma+$	58	57	180
$\Sigma-$	-291	294	-180
Total	233	237	0
C5–H and C6–H atoms			
H–C5–C6–C7	-115	119	-122
H–C6–C5–C4	127	-132	124
O3–C4–C5–H	78	-89	153
O1–C7–C6–H	-170	-178	-154
$\Sigma+$	205	297	276
$\Sigma-$	-285	-221	-277
Total	-80	76	-1

GTRS Vibrational Modes ν (cm ⁻¹) *					Assignment**
α -endosulfan	β -endosulfan	$\Delta\nu$ (α - β)	$\Delta\nu$ (C7 - C4)	$\Delta\nu$ (C6 - C5)	
1600	1602	-2			ν (C-C6) + ν (C6C5) + ν (C5-C) + ρ (C6H) _{ip} + ρ (C5H) _{ip}
1473		19	24		δ (C7H ₂)
1449	1454	-5	0		δ (C7H ₂), δ (C4H ₂)
1380	1377	3	-54		γ (C6-C5-C4-H _{ax})
1326	1326	0	24 51		γ (H _{eq} -C7-C6-C5) γ (C6-C5-C4-H _{eq})
	1302	-78			γ (H _{ax} -C7-C6-C5)
1233 w	1241	-8	-125		ω_{HH} (H _{ax} -C7-C6-H)
1191	1186	5			ω_{HH} (H _{ax} -C5-C4-H _{eq}) ω_{HH} (H _{eq} -C7-C6-H _{ax})
1151		35			ω_{HH} (H _{ax} -C5-C4-H _{ax})
	1116				ω_{HH} (H _{ax} -C5-C4-H _{ax})
1096		-145	-137		ω_{HH} (H _{ax} -C7-C6-H _{ax})
	1022			-59	ω_{HH} (H-C6-C5-H) _{re}
1027		5		-59	ω_{HH} (H-C6-C5-H) _{rc}
	976	-8		-12	ω_{HH} (H-C6-C5-H) _{asym}
968	(963)			0	ω_{HH} (H-C6-C5-H) _{equal}
	952	16		12	ω_{HH} (H-C5-C6-H) _{asym}
908		5		60	ω_{HH} (H-C6-C5-H) _{re}
	903			60	ω_{HH} (H-C6-C5-H) _{re}
848		-85	-38		ρ (C7H ₂) _{rc}
(810)		0			ρ (C7H ₂) _{equal}
777		38	38		ρ (C7H ₂) _{re}
	763 w	-18	-15		ρ (C7H ₂) _{rc}
745	(748)	3	-103		ρ (C4H ₂)
	734 w	12	15		ρ (C4H ₂) _{re}
678 w	683	-5	67		$\omega 7_{re}$
616	616	0	0		$\omega 8_{asym}$
460 w	479	-19	-137		$\omega 5_{rc}$
398	399	1			$\omega 3$

* w = weak

** δ = bending, γ = twisting, ν = stretching, ρ = rocking CH₂, ω = wagging
 asym = asymmetrical, rc = ring compression, re = ring expansion, ip = in plane