

Thermochemical studies of twist–twist pi conjugated, sterically crowded stilbenes using simultaneous TG–DTA

C. O’Connell, P. Sekher, E.D. Luzik, J.E. Gano*

Department of Chemistry, University of Toledo, 2801 W. Bancroft St., Toledo, OH 43606-3390, USA

Accepted 06 August 1999

Dedicated to Professor David Dollimore on his 70th Birthday

Abstract

The thermal transformations of three twist–twist pi conjugated, sterically crowded stilbenes were monitored using simultaneous TG–DTA with a rising temperature program. The simplest compound, di-*tert*-butylstilbene, **1**, was shown to melt and then completely evaporate. Compound **2**, an extended version of **1** with three rings, melted and then partially evaporated, forming an intermediate, which evaporated at a higher temperature. An endothermic peak was observed in both **1** and **2** prior to the main melting point. This peak corresponds to a solid/solid or solid/liquid crystal phase transition. Compound **3**, an extended version of **1** with four rings, completely sublimed. The activation energies and frequency factors were calculated for evaporation or sublimation, using the Arrhenius method. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Twist–twist pi conjugated stilbenes; TTPC; Phase transitions; Thermogravimetry; Rising temperature kinetics; Arrhenius equation

1. Introduction

Thermal analysis can be used to characterize a wide variety of materials. Stilbene compounds have been studied in the past, using thermal analysis. Santoro et al. observed the transition of *cis*-stilbene to the *trans* form, using DTA [1]. Kwatra et al. used DTA and dielectric studies of *trans*-stilbene to determine the lack of a pre-melting phenomenon in the solid–solid crystal transition [2].

In this study, simultaneous TG–DTA was used to study the solid state transformation of three novel *trans*-stilbenes, which were synthesized at the University of Toledo. Phase changes, such as evaporation

and sublimation, were observed using TGA to record the amount of mass lost, as the samples were heated at a fixed rate. DTA was used to provide information about processes that did not involve a mass change, such as melting and crystal transition. The DTG plots were used to calculate the specific rate constants and Arrhenius constants of evaporation or sublimation.

Stilbenes possess a novel feature. In contrast to normal *trans*-stilbene, which is planar, have their benzene rings rotated perpendicular to the planes of the attached double bonds, $\theta \approx 90^\circ$ [3–5]. The structures of compounds are shown in Fig. 1. These compounds are oligomers of poly(phenylene 1,2-di-*tert*-butylvinylene). Since the discovery of poly(phenylene vinylene) electroluminescence [6], such materials have taken on a growing importance. An understanding of the thermal properties of these materials is significant for further work.

*Corresponding author. Tel.: 419-530-7847; fax: 419-530-4033.
E-mail address: jgano@uoft02.utoledo.edu (J.E. Gano)

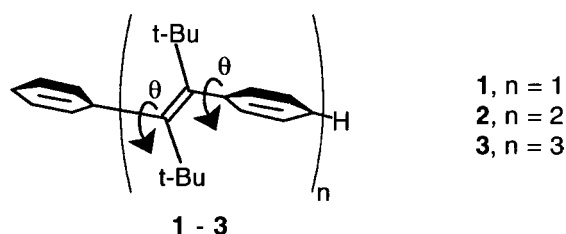


Fig. 1. Structures of compounds **13**.

2. Experimental

The synthesis of compounds is reported elsewhere [7,8]. The thermal analysis equipment consisted of a simultaneous TG–DTA unit, TA Instruments, Model Number 2960. The data were analyzed with TA Instruments Universal Analysis software, V1.10B. The

samples were analyzed in a platinum crucible, with an empty platinum crucible as a reference. The sample size and analysis time varied with each compound. All samples were analyzed at 10°C/min. The purge gas was dry nitrogen at 100 ml/min. The gas flow was monitored with an electronic flowmeter. Plots of temperature difference and weight percentage versus temperature were obtained for each sample. All endothermic temperatures are peak temperatures. Plots of the fraction reacted (α) versus temperature were sigmoidal.

3. Results and discussion

3.1. *E*-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene, **1**

Compound **1** was analyzed at 10°C/min to 400°C. A representative TGA and DTG plot can be found in

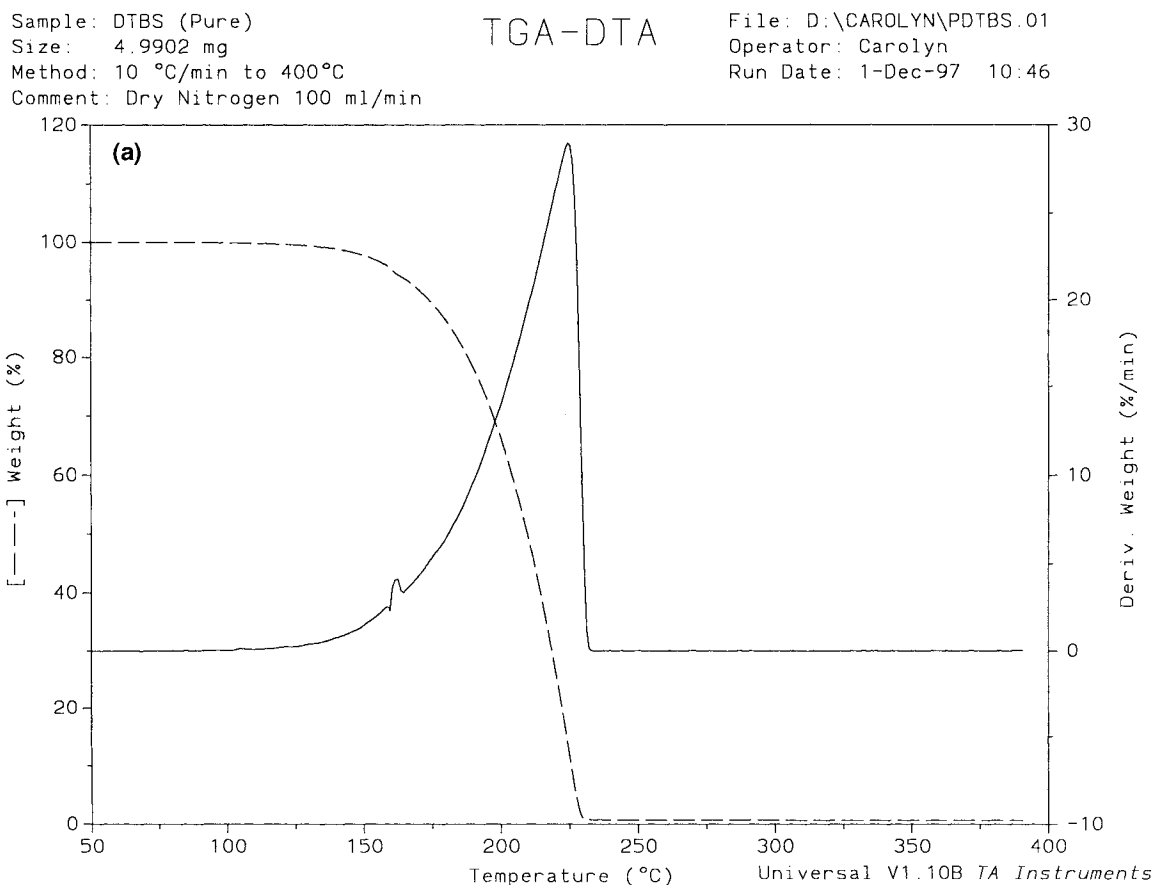


Fig. 2. (a) Representative TGA and DTG plots of compound **1**, heated 10°C/min to 400°C in dry N₂ at 100 ml/min. (b) Representative DTA plot of compound **1**, heated 10°C/min to 400°C in dry N₂ at 100 ml/min.

Sample: DTBS (Pure)
 Size: 4.9902 mg
 Method: 10 °C/min to 400°C
 Comment: Dry Nitrogen 100 ml/min

TGA-DTA

File: D:\CAROLYN\PD TBS.01
 Operator: Carolyn
 Run Date: 1-Dec-97 10:46

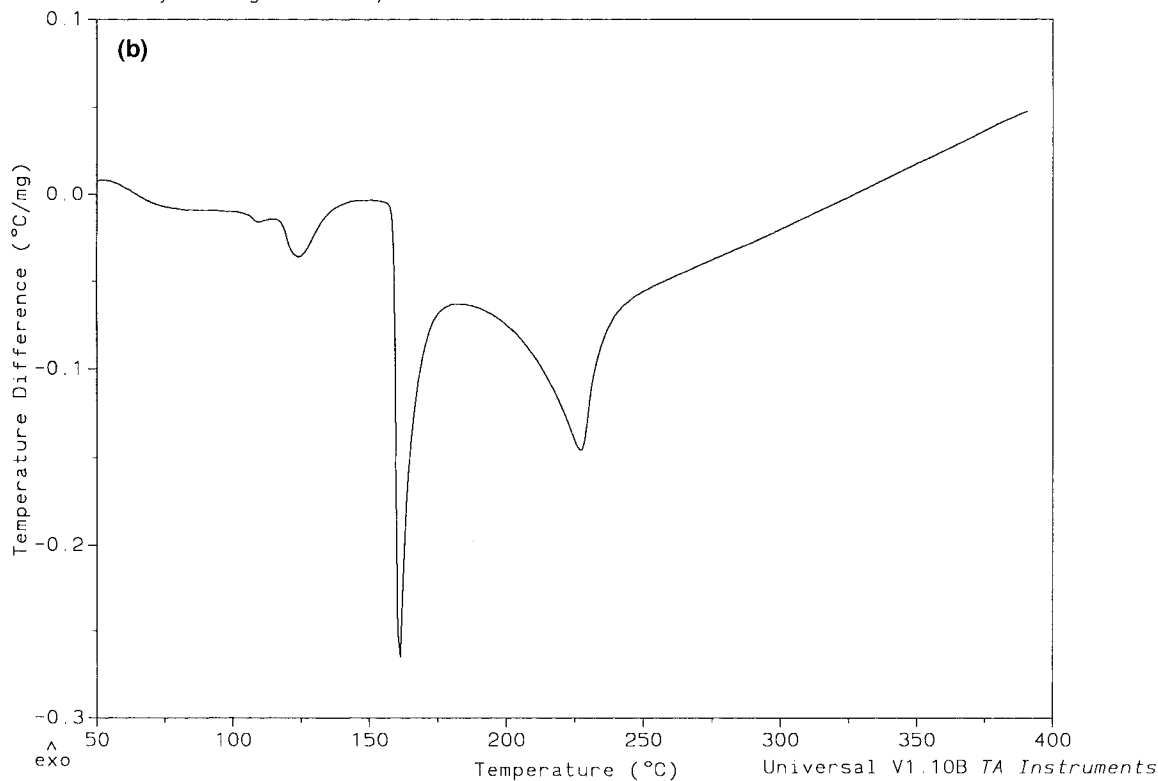


Fig. 2. (Continued)

Fig. 2(a). A representative DTA plot can be found in Fig. 2(b). The sample size varied from 3.1363 to 5.9374 mg. A small endotherm was noted at 125°C. This endotherm was preceded by a small, poorly resolved peak at 111°C, which disappeared on a later run. These peaks may represent a solid/solid transition or a solid/liquid crystal transition. Endotherms were observed at 160°C and an average temperature of 222°C, corresponding to melting and evaporation, respectively. Minimal mass loss was noted prior to the melting point. Complete mass loss was observed after the melting point in all runs. Two of the runs were completed, using the same sample. An unexpected endotherm was noted at 149°C in both runs. The third run was completed with a known pure sample. The endotherm at 149°C was not present in this run. It was concluded that the first sample contained an impurity,

which was probably 2,2,5,5-tetramethyl-3,4-diphenylhexane. Another run was completed, heating the sample 10°C/min to 162°C and stopping the run at the melting point. The usual endotherm observed at 124°C was due to a reversible process. The endotherm at 124°C was observed again when the run was repeated with a sample which was slowly cooled to ambient temperature from its melting point. A small mass loss was noted, as a result of evaporation.

The DTG plot exhibited a large, sharp peak after the melting point at 225°C, characteristic of a zero order process, [9-11] such as evaporation. For the pure sample, the maximum rate of mass loss was 1.528 mg/min at 225°C. This peak was preceded by a very small peak at about 161°C, which is the result of a buoyancy correction as air or vapor between the particles escapes once the liquid is formed.

Table 1
Summary of Arrhenius parameters

Compound	Melting point (°C)	Vaporization temperature (°C)	E_a (KJ/mol)	A (mg/min/cm ²)	R^2
1	160	228	65.72	4.3×10^7	0.9990
2	286	340	87.80	1.7×10^8	0.9973
3	–	427 ^a	172.25	4.2×10^{13}	0.9996

^a Sublimed.

The specific rate constants of evaporation were calculated by dividing dm/dt by the cross sectional area of the sample crucible (0.2951 cm²) [12]. Data points were taken for every 2°C. Plots of $\ln k$ versus $1/T$ were linear. The activation energies and the frequency factors were calculated from the slopes and the intercepts of the lines, respectively [12]. The results are summarized in Table 1.

3.2. (All-E)-1,1'-(1,4-benzenediyl)bis[1-(1,1-dimethylethyl)-3,3-dimethyl-2-phenyl-1-butenyl], 2

Compound 2 was analyzed 10°C/min to 500°C. The sample size varied from 5.0985 to 6.0154 mg. The sample consists of a 1 : 1 mixture of its *syn* and *anti* atropisomers. The *syn* atropisomer crystals are in a benzene solvate which slowly desolvates upon stand-

Sample: 3 RING
Size: 6.0154 mg
Method: 10°C/min to 500°C
Comment: Dry Nitrogen 100 ml/min

TGA-DTA

File: D:\CAROLYN\3RING.01
Operator: Carolyn
Run Date: 16-May-97 15:10

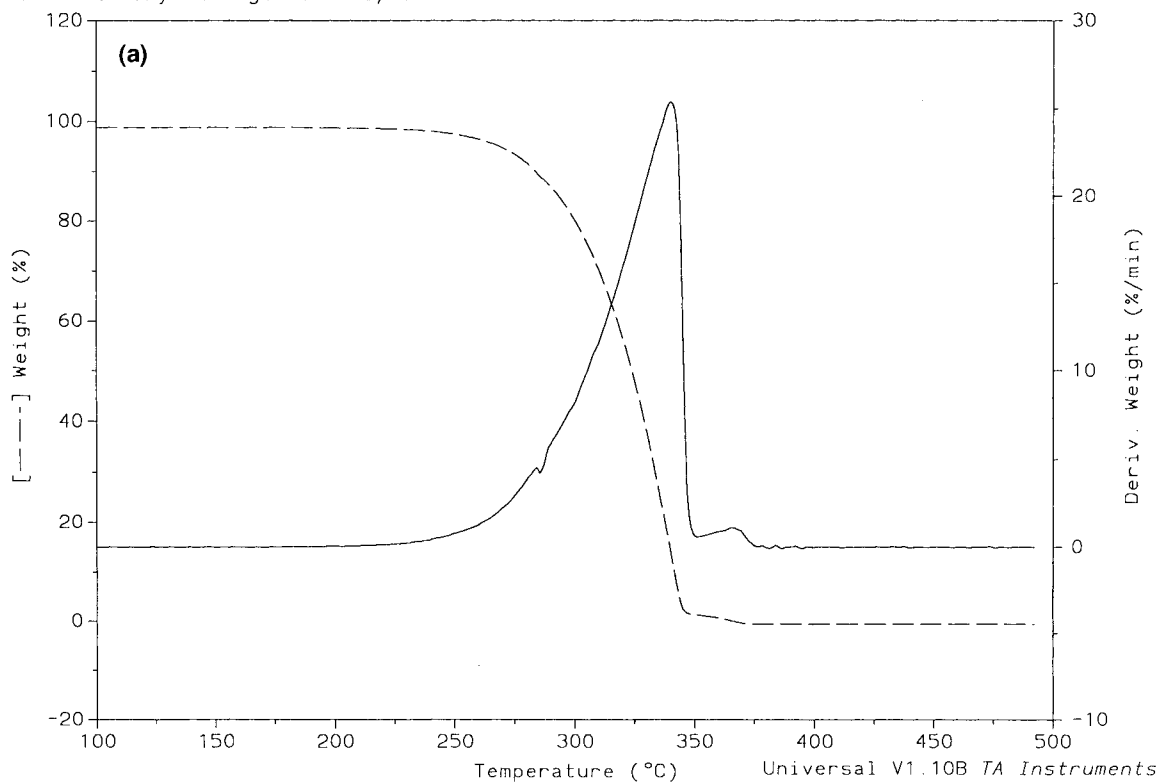


Fig. 3. (a) Representative TGA and DTG plots of compound 2, heated 10°C/min to 500°C in dry N₂ at 100 ml/min. (b) Representative DTA plot of compound 2, heated 10°C/min to 500°C in dry N₂ at 100 ml/min.

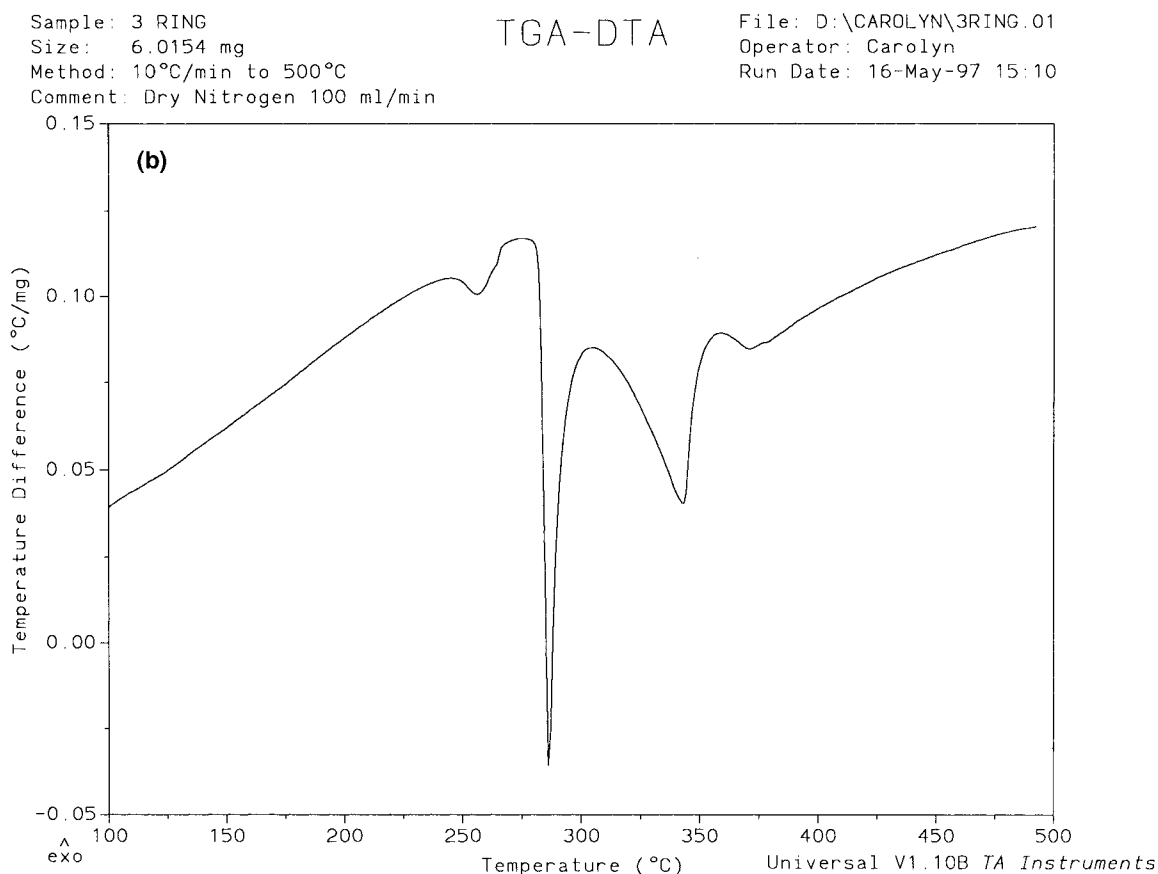


Fig. 3. (Continued).

ing in air. A representative TGA and DTG plot can be found in Fig. 3(a). A representative DTA plot can be found in Fig. 3(b). A small endotherm was noted at about 255°C. Another run was completed with a heating rate of 10°C/min to 280°C. The sample was held isothermally at 280°C for 10 min and then allowed to slowly cool to ambient temperature. It was then heated 10°C/min to 500°C. The DTA plot is presented in Fig. 4. The endotherm at 255°C was no longer present. No significant mass loss was observed at 255°C. It could be the result of a solid/solid or solid/liquid crystal transition involving the atropisomers [11]. The melting endotherm of the compound was observed at 286°C, followed by almost complete mass loss. An endotherm, corresponding to evaporation, was observed at an average temperature of 340°C. A residue (1% of the initial mass) was present at

350°C, *vide infra*, but disappeared by 380°C. Another small, poorly resolved endotherm was observed at 370°C.

The DTG plot contained a very small peak immediately before the melting point, which is the result of the buoyancy correction. A large, sharp peak was then observed, corresponding to mass loss due to the evaporation of the compound. The maximum rate of mass loss was 1.519 mg/min at 339°C. A small peak was also noted at 365°C, which represents the evaporation of the residue. Another run was completed at 10°C/min to 250°C and held isothermally at 250°C. The sample was cooled to ambient temperature and then heated 10°C/min to 500°C. The percentage of residue increased with the isothermal temperature, suggesting that this may be due to slow decomposition of **2** in the melt.

Sample: PURE 3 RING STILBENE
 Size: 12.0647 mg
 Method: 10°C/min to 500°C
 Comment: Dry Nitrogen 100 ml/min

TGA-DTA

File: D:\CAROLYN\PTRS.06
 Operator: Carolyn
 Run Date: 15-Jan-98 17:12

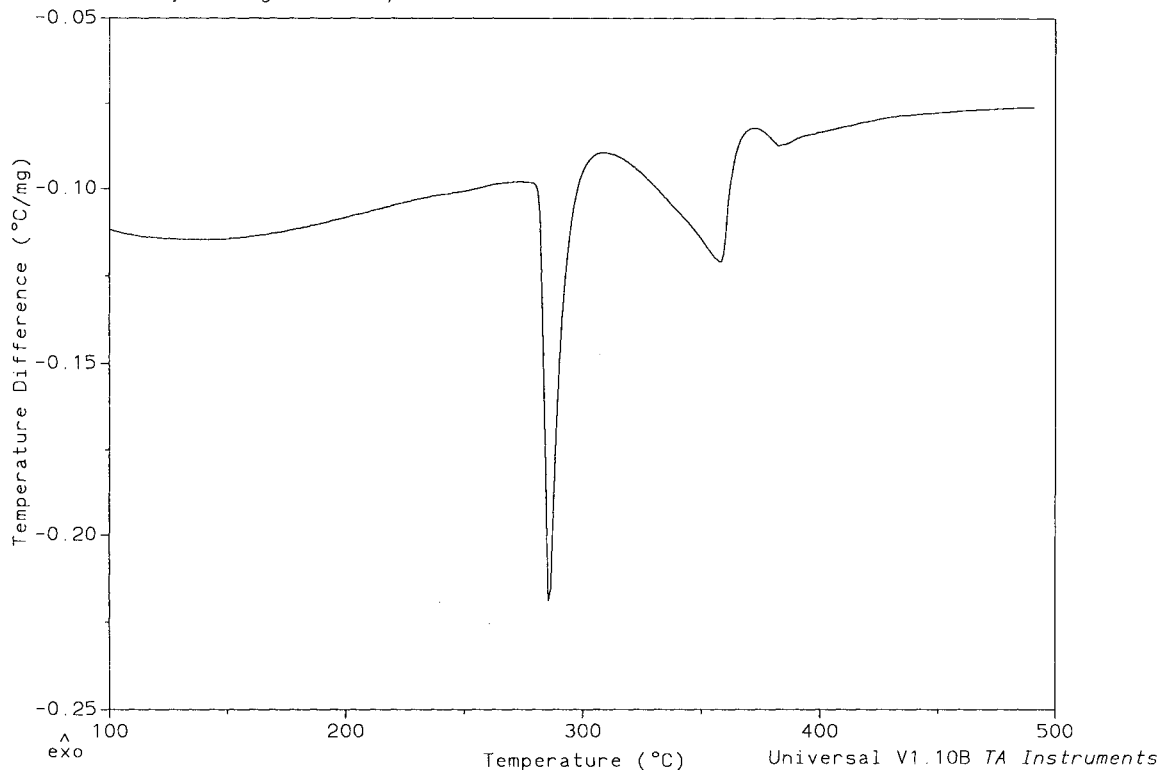


Fig. 4. DTA plot of compound **2** heated 10°C/min to 500°C, after heating to 280°C, holding isothermally at 280°C and cooling at ambient temperature.

The specific rate constants for the evaporation of the compound were calculated, using data obtained from the large DTG peak. Data points were taken every 2°C/min. The Arrhenius constants were calculated, using the method described previously. The results are summarized in Table 1.

3.3. (All-E)-1,1'-[1,2-bis(1,1-dimethylethyl)-1,2-ethenediyl]bis[4-[1-(1,1-dimethylethyl)-3,3-dimethyl-2-phenyl-1-butenyl]benzene], **3**

Compound **3** was analyzed at 10°C/min to 700°C. The sample size varied from 2.6376 to 5.7622 mg. The mass was stable until about 325°C when it began to rapidly decrease. A single endotherm was observed at

427°C during all runs. Complete mass loss was noted after this peak. It was concluded that sublimation occurred as no melting endotherm was observed.

The DTG plot contained only one large, sharp peak, corresponding to total mass loss. The DTG plots were indicative of a zero order kinetic mechanism as the baseline abruptly returned to zero. The maximum rate of mass loss was 1.704 mg/min at 430°C. The specific rate constants and Arrhenius parameters for sublimation were calculated from the DTG plot using the method described previously. The results are summarized in Table 1.

When the Arrhenius constants are compared, it can be noted that the activation energy for the sublimation of compound **3** is much higher than the activation energies for the evaporation of compounds **1** and **2**.

This is expected because more energy is required to change directly from the solid phase to the vapor phase than from the liquid phase to the vapor phase, due to increased intermolecular forces in the solid state. Compound **3** is also a much larger molecule than the others, and it can be observed that the activation energy increases as the number of phenyl rings increases. The frequency factor also increases as the number of rings increases.

4. Conclusions

Thermal analysis is a useful technique to examine the thermal transformations of various stilbene related compounds. The kinetic mechanism and Arrhenius parameters can be determined. The DTA plot can be used to determine the melting points and the presence of impurities. Solid–solid and solid–liquid crystal transitions can also be detected using DTA. It was shown that both compounds **1** and **2**, but not **3**, undergo a transition prior to melting and evaporation. The transition is reversible for **1** but not **2**. Whereas compounds **1** and **3** vaporized cleanly, compound **2** formed an intermediate compound in the melt, which evaporated at a higher temperature. Compound **3** sublimed as no melting point was observed. Melting/sublimation points increase about 135°C per ring as compound **1** was extended to **2** and **3**. All compounds ultimately evaporated readily, demonstrating their utility in vapor deposition applications.

Acknowledgements

We acknowledge the useful discussions of extended ring nomenclature with Bill Bigard and financial support from the OBOR and Research Challenge Program.

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