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Application of Differential Scanning Calorimetry in an Organic Chemistry Laboratory Course: Development of a Binary Phase Diagram of Cis/Trans-1, 2-Dibenzoylethylene

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Abstract In organic chemistry lab it is important to give students hands-on experiences to help them further their understanding of important chemistry topics. Binary phase diagrams incorporate many of these topics into a single graph. Differential Scanning Calorimetry (DSC) has been shown to produce data to make binary phase diagrams for alloys; however, it is more difficult to produce these diagrams using non-metal organic compounds. The purpose of this experiment was to determine if the DSC could be used to give students a challenging, yet doable experiment to prepare a binary phase diagram and determine the eutectic composition for the mixture of cis/trans-1,2-dibenzoylethylene. The conclusions from this work are: (i) The eutectic composition for cis/trans-1,2-dibenzoylethylene is at the weight percent of 30% cis and 70% trans which corresponds to an onset melting temperature of 93.5°C; (ii) as the cis increased from a weight percent of 30% the melt temperature also increased; (iii) as the trans increased from a weight percent of 70% the melt temperature also increased; (iii) the DSC produced sufficient data necessary to develop a binary phase diagram of peak melt temperatures vs the weight percent of the cis isomer; (iv) the DSC could be incorporated into an organic chemistry lab to enhance student's knowledge of important topics while giving them an experience working with advanced laboratory thermal instruments.

Keywords: *upper-division undergraduate, laboratory instruction, organic chemistry, hands-on learning, instrumental methods, phases diagrams, eutectic, cis/trans 1,2 dibenzoylethylene, Differential Scanning Calorimetry*

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1. Introduction

Phase diagrams are usually introduced in general chemistry courses. They expose students to a simple graphical representation of the affects variables, such as temperature and pressure, have on simple phases of pure compounds [1,2,3]. These phase diagrams are often single substances such as water or carbon dioxide and are typically a plot of pressure versus temperature showing the equilibrium boundaries between the three phases of matter. In organic and physical chemistry classes, binary phase diagrams of eutectic and azeotropic mixtures of two components are often introduced. Phase diagrams of these binary systems are a plot of temperature versus the composition of the binary system under constant pressure. In a typical physical chemistry laboratory a eutectic alloy is often used to construct a classic binary phase diagram [4,5,6,7]. In a typical organic chemistry laboratory students are often taught how to make and understand azeotropic phase diagrams in which a fixed composition cannot be changed by either simple or fractional distillation [8]. In organic chemistry, students are also often taught how to develop and understand more advanced binary phase diagrams. Binary phase diagrams introduce students to the affects that mixing compounds have on their properties, such as melting/freezing and boiling points. In organic chemistry lab, it is important to give students hands on experience to further their understanding of certain aspects of the science. Binary phase diagrams incorporate many important aspects of organic chemistry, which makes it beneficial to incorporate into an organic chemistry lab.

The phase diagrams of many binary organic systems have been previously critically evaluated. Systems based on three isomers of 1, 2-, 1, 3- and 1, 4- diaminobenzenes or benzidine with a second component such as phenols, benzoic acid and several other aromatic compounds have been studied [9]. Erich C. Meister, et. al. [10] showed the results of a laboratory project in which a set of six substances were combined to yield a total of 15 binary phase diagrams. The six compounds were biphenyl, durene, diphenylmethane, napththalene, phenanthrene, and triphenylmethane. The results showed that the combination of any two of these compounds showed various eutectic compositions and phase diagrams.

Binary phase diagrams are used to explain the relationship between variables, such as temperature, pressure and composition of a binary system. Typically, a temperature-composition graph will be developed under constant pressure, or a pressure-composition graph will be developed under constant temperature. In organic chemistry, binary phase diagrams are often used to find the eutectic properties of a binary system. The eutectic composition is described as the homogenous mixture of two or more elements or compounds. In a temperature-composition diagram, the eutectic temperature will occur at a melting point which is below that of the individual pure substance as well as below the melting points of all other compositions. The composition at which the eutectic point occurs is termed the eutectic composition. The compositions of the mixtures can be determined by different means, such as weight percent, mole fraction or mass fraction.

Differential Scanning Calorimetry (DSC) is commonly used to determine many different thermal properties and used in a wide variety of applications ranging from polymer analysis to food analysis [11,12,13]. DSC has been used for general, organic, and physical chemistry experiments. A series of articles introducing Differential Scanning Calorimetry to the undergraduate chemistry curriculum have been published which show the broad use and applicability of the technique [14,15,16].

DSC is a common instrumental and thermoanalytical technique which can be used, among other uses, to build a binary phase diagram. The DSC can record the melting and crystalline properties of a binary system. A sample is placed into a pan and then inserted into the DSC. After parameters have been set, the DSC records the amount of heat which is required to change the temperature of the sample, compared to a reference which has a well-known heat capacity. As the sample undergoes a phase change, heat will flow into or out of the sample at different rates compared to the reference in order for both to maintain similar temperatures. This heat flow is recorded. Phase changes are represented in the DSC as deviations of thermal flow from the baseline, either endothermic (melting) or exothermic (crystallization). Usually, the heat flow associated with the melting point is used. The melting point observed from different compositions of the same binary systems are compared to produce the binary phase diagram and to determine the eutectic temperature and composition of the mixture.

Frequently, binary phase diagrams are built from metal alloys. This is due to their sharp melting points, easiness to obtain and predictability. Although it has been shown that the DSC can be used to determine thermal properties of organic compounds [9,10], the DSC has not been fully tested to its ability to determine the binary phase diagrams of nonmetal organic compounds such as cis and trans- 1, 2- dibenzoylethylene.

1.1. Learning Objectives

The purpose or goals of this experiment are:

(i) To determine if the DSC can properly and reliably be used to create a binary phase diagram of nonmetal organic compounds;
(ii) To study thermal properties of cis- and trans- 1,2-dibenzoylethylene at varying compositions;
(iii) To determine the eutectic properties of cis- and trans- 1,2-dibenzoylethylene mixtures;
(iv) To determine the liquidus and solidus lines of the cis- and trans- 1, 2- dibenzoylethylene binary phase diagram;
(v) To decide if developing a binary phase diagram using DSC could be beneficial to incorporate into an organic chemistry lab class.

2. Materials and Methods

2.1. Materials

Trans-1,2-dibenzoylethylene (trans-1,4-diphenyl-2-butene-1,4-dione) was purchased from Sigma-Aldrich as a 96% pure yellow crystalline solid, CAS # 959-28-4. A 95% ethanol solution was prepared by mixing by volume 95 ml of pure 100% ethanol purchased from Sigma-Aldrich with 5 ml of distilled/deionized water.

2.2. Procedure for Purification of Trans – 1,2 Dibenzolyethylene by Recrystallization from Ethanol

Trans-1, 2-dibenzoylethylene that was obtained from Sigma-Aldrich was dissolved in 95% (v/v) ethanol by slowing heating to produce a homogenous mixture. This mixture was allowed to slowly cool to room temperature and then placed in an ice bath. After cooling, using vacuum filtration, a purer yellow crystals of trans-1,2-dibenzoylethylene was collected. This method was repeated twice to produce nearly 99.9% pure trans-1,2-dibenzoylethylene with a 85% recovery. A capillary melting point of 110.5°C was obtained which compared with literature values. Also an FTIR spectrum was also obtained as a attenuated total reflectance (ATR) spectrum and the carbonyl peak of 1608 cm^{-1} compared to literature values.

2.3. Photochemical Isomerization of Trans-1,2-Dibenzoylethylene to Its Cis Isomer [17,18]

Dissolved 3.0 g of recrystallized trans 1, 2-dibenzoylethylene (trans-1, 4-diphenyl-2-butene-1,4-dione) in 120 ml of 95% ethanol in a 250-ml Erlenmeyer flask by gently heating on a hot plate until a homogenous mixture was formed. While still hot, covered with aluminum foil and irradiate with an unfiltered 150 watt sun lamp at a distance of 3-4 in for about 6-7 hours. A 93510 PV module bench – top open array EXE Solar Simulator system consisting of an EYE/IWASAKI proprietary Solar LUX solar refractorized lamp having a 1000w/m^2 intensity operating at 6.5A current. The unit was manufactured by Eyelighting Company. The irradiation level was set at 95% lamp power. Up to three flasks can be successfully irradiated simultaneously with one lamp if the lamp and flasks are surrounded with aluminum foil. The reaction flask was cooled in an ice bath to further induce crystallization. Collected the white crystals by vacuum filtration using a Buchner funnel. The yield was 78%. The cis isomer was air dried and a capillary melting point was taken which was 136.3^0 C as well as an ATR FTIR in which the carbonyl frequency of 1634 cm^{-1} was obtained which compared to literature values. Shown in Figure 1 below is a the stoichiometric equation for the photochemical isomerization reaction.

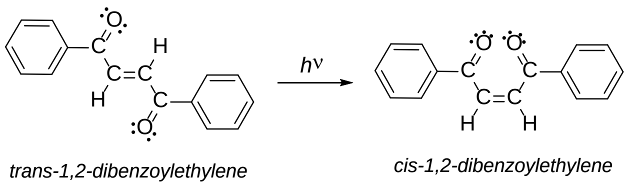

Figure 1. The stoichiometric chemical equation for the photochemical isomerization reaction

2.4. Equipment and Calibration

A Perkin-Elmer Power Compensated DSC model Pyris 1 was used to study the trans/cis- 1,2 – dibenzoylethylene binary system. Prior to beginning the experiment the DSC was calibrated for temperature, heat flow, and baseline linearity. This was done by first running empty cells in both the sample and reference compartments to produce a thermal baseline. Highly pure standards of tin, lead and indium were then run through 4 thermal cycles/ramps of two heats and two cools at a constant rate of 10.0°C/min. The onset melting and recrystallization temperatures for the standards were used for the temperature calibration. The onset melting/recrystallization temperatures are defined as the temperatures at the initial endothermic/exothermic change from the thermal baseline. The change in enthalpy (ΔH) was used to calibrate the heat flow. The ΔH is found by the peak area under the curve. The endothermic and exothermic transition temperatures as well as the enthalpies of fusion and crystallization were recorded by the Pyris 1 for windows software.

2.4.1. Binary Mixture Preparation

The proper mixtures of trans and cis- 1,2-dibenzoylethylene were prepared by manipulating the weight percent of each isomer. The amount of each isomer for a desired mixture was based off a total weight of 15mg. If, for example, 60% trans and 40% cis was the desired mixture then 9mg of the trans isomer would be combined with 6mg of the cis isomer. A mortar and pestle was then used to crush, grind and mix the two isomers. This was done in order to better mix and break down the trans/cis crystals which allowed for a greater amount to fit within the aluminum sample volatile pans. After thoroughly grinding and mixing the cis/trans isomers an aluminum volatile pan was filled with the mixture. Total weights of the mixtures ranged from 6.0 to 11.6 mg. The mass percent of the cis isomer used in each mixture are shown in Table 1.

2.4.2. Procedure

Each mixture underwent four (4) consecutive thermal cycles:

(i) First heating cycle from 30°C to 150°C
(ii) First cooling cycle from 150°C to 30°C
(iii) Second heating cycle from 30°C to 150°C
(iv) Second cooling cycle from 150°C to 30°C

The first round of heating and cooling was important for the mixture of the cis and trans isomers to melt, intertwine, and then recrystallize as one uniform homogeneous mixture. The second round of heating and cooling included the thermal cycle/ramps from which the data was recorded. Between each thermal cycle the temperature was kept constant for a minute. This allowed for the DSC to re-equilibrate prior to the following thermal ramp. Each thermal ramp underwent a heating/cooling rate of 10°C/min. The Pyris 1 software for Windows was used to record the thermograms. The data was analyzed using the Pyris 1 software.The melting and crystallizing points were determined by the onset temperatures, defined by the initial endothermic or exothermic change from the baseline. The enthalpies of fusion and crystallization were measured by the area under the curve which begins at the onset and ends once the thermal changes return to baseline. The peak temperature is considered the temperature at which the peak was the highest. All thermal cycles were done under a constant nitrogen flow of 20ml/min to keep the samples dry.

Table 1. Summary of the DSC thermal data for the second heating cycle for all the binary mixtures studied of the cis/trans isomers of 1,2-dibenzoylethylene

	First Peak[a]			Second Peak[a]		
Mass % of cis	**Onset (°C)**	**Peak (°C)**	**ΔH (J/g)**	**Onset (°C)**	**Peak (°C)**	**ΔH (J/g)**
0	107.7	110.9	124.4	--	--	--
10	94.9	99.9	92.3	101.1	104.1	2.6
20	94.4	98.4	97.8	99.3	100.2	0 .2
30[b]	93.5	95.1	100.1	--	--	--
40	94.4	97.6	83.1	100.8	103.2	22.8
50	95.8	99.9	75.1	103.5	108.5	35.9
60	93.1	96.4	51.3	107.1	112.5	59.6
70	92.9	96.3	38.0	111.9	117.6	71.2
80	92.5	96.1	20.9	120.7	125.7	102.7
90	91.3	93.9	1.8	125.8	132.1	28.3
100	132.1	136.5	139.4	---	---	---

[a]Thermo data for second heating cycle from 30°C to 150°C. [b]Eutectic composition.

2.4.3. Hazards

Ethanol is a highly flammable substance that should be used with care. Eye protection and a lab coat should be worn to limit contact with skin and the eyes. If the skin or eyes come into contact with ethanol the affected area should be immediately washed with water. Trans and cis-1,2-dibenzoylethylene do not have high risk factors. Nevertheless, proper lab safety practices should be observed. A lab coat and eye protection should be worn to limit contact with the skin and eyes. If contact does occur, the contaminated area should immediately be washed off with water. These isomers are considered nontoxic but should not be ingested or inhaled. The small amounts used in this experiment help to reduce any significant hazard effects. Proper disposal of ethanol and the cis/trans 1,2-dibenzoylethylene should be followed per local and OSHA regulations.

2.4.4. Statistical Analysis

Each of the DSC thermograms were analyzed multiple times. The data reported is an average of at least duplicated thermal cycles. The average relative standard deviation for all the samples ranged from 0.5% - 1.3%.

3. Results and Discussion

Figure 2 shows the DSC thermograms of the pure trans and cis isomers. The DSC thermogram for the trans isomer shows an endothermic peak having an onset melting point of 107.7^{o} C and an enthalpy of fusion (ΔH_{fusion}) of 124.4 J/g, The DSC thermogram of the cis isomer shows an endothermic peak having an onset temperature of 132.1^{o} C and the enthalpy of fusion (ΔH_{fusion}) of 139.4 J/g . A thermogram for the 30 wt % of the cis isomer mixture is shown in Figure 3. The sample containing 30% cis and 70% trans is the eutectic composition of the trans/cis-1,2-dibenzoylethylene binary system. This composition has an onset melting temperature of 93.5°C and a ΔH_{fusion} of 100.1 J/g. A summary of the thermal data obtained from the DSC second heating cycle for the samples studied is listed in Table 1. The weight percent of the cis isomer in the mixtures ranged from 10% to 90% with integrals of 10%. The weight percent of the trans isomer in the mixtures corresponded to 100% minus the percent of cis.

The binary phase diagram of the cis/trans isomers is shown in Figure 4. It is a plot of the peak temperatures (°C) versus wt % cis isomer. The binary phase diagram shows both the liquidus and solidus lines for the cis/trans mixtures studied. The point of intersection of the cis liquidus line and the trans liquidus line corresponds to the eutectic composition of 30% wt cis isomer. The liquid and solid phases as well as the corresponding mixed phases are labled in the phase diagram.This diagram plots the peak temperatures versus the weight % of cis-1,2-dibenzoylethylene. There are four areas within this graph:

(i) Liquid cis/trans isomers
(ii) Solid trans and liquid phase
(iii) Solid cis and liquid phase
(iv) Solid cis/trans isomer.

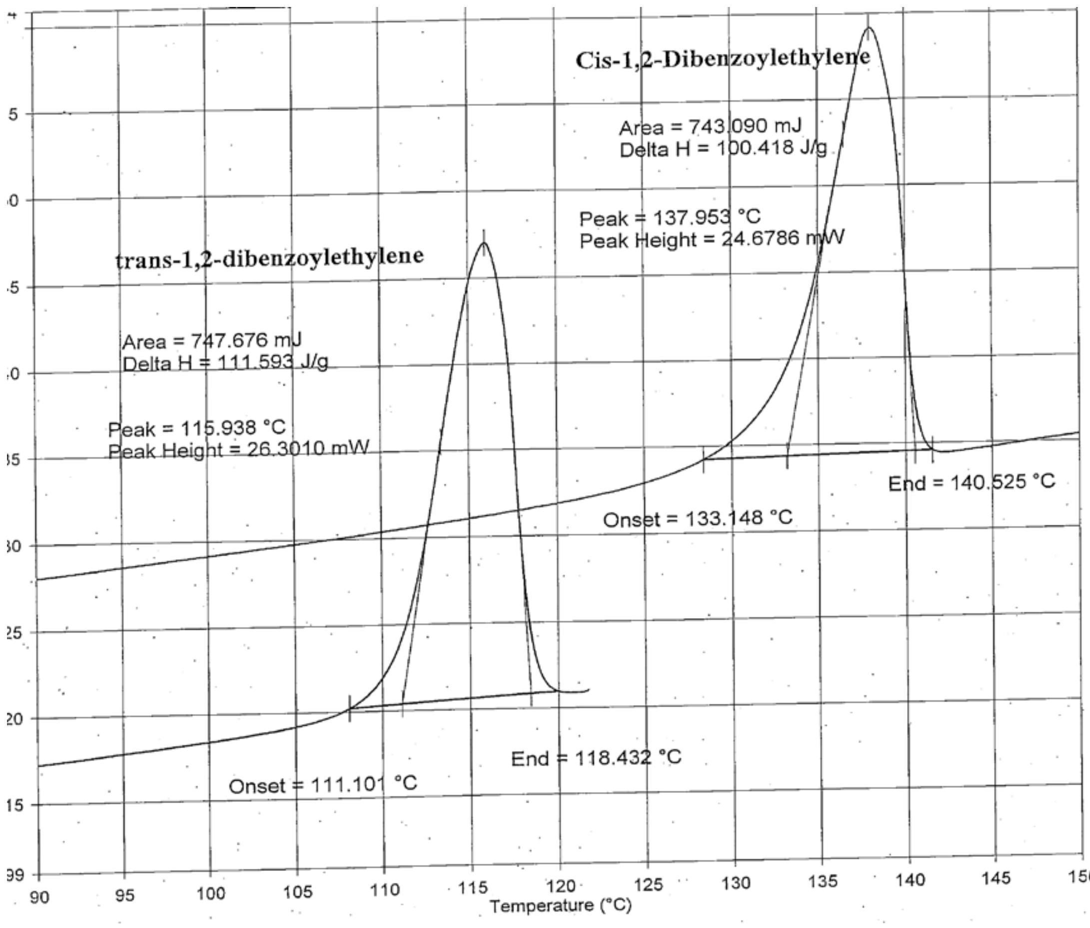

Figure 2. DSC thermogram of pure trans and cis isomer of 1,2-dibenzoylethylene showing the onset, peak, and end temperatures of melting and enthalpy of fusion

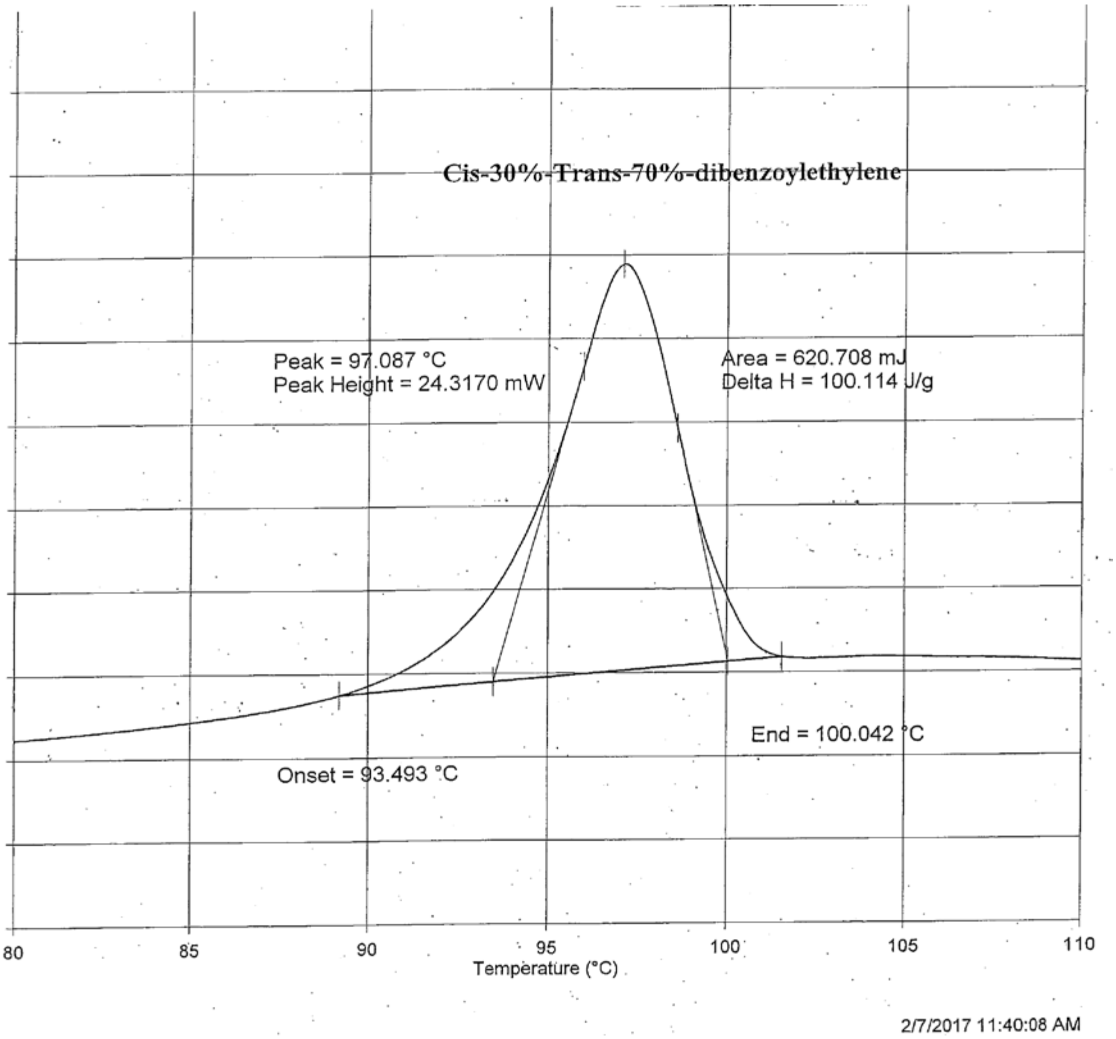

Figure 3. DSC thermogram of the eutectic mixture of 30% cis and 70% trans isomers of 1,2-dibenzoylethylene showing the onset, peak, and end temperatures of melting and enthalpy of fusion

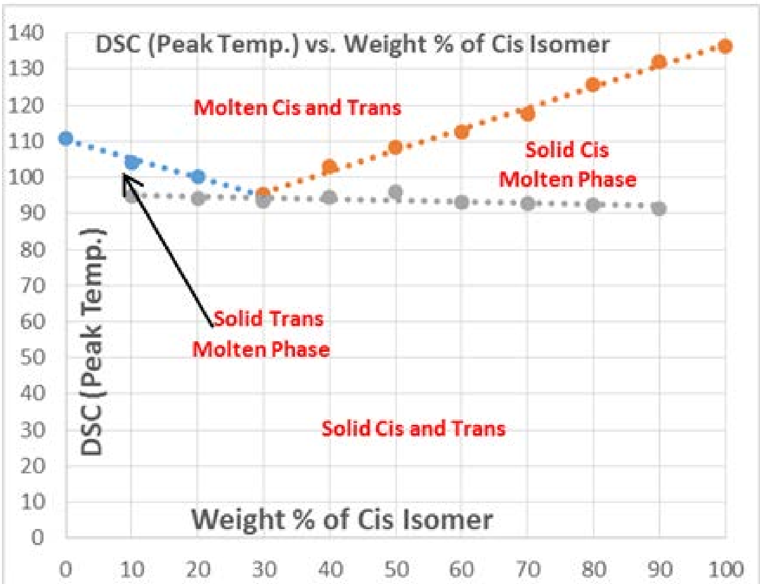

Figure 4. Phase diagram for the binary system of cis and trans isomer of 1,2 dibenzoyl ethylene. The binary phase diagram shows both the liquidus and solidus lines. The point of intersection of the cis liquidus and the trans liquidus line corresponds to the eutectic composition

A plot of ΔH_{fusion} for the eutectic component versus weight % cis is shown in Figure 5. As the wt% of the cis isomer increases ΔH_{fusion} first increases until it reaches the eutectic composition of 30 wt % at its highest enthalpy (ΔH_{fusion} = 100.1 J/g), and then it decreases. The point of intersection can be used as an additional method of dertmining the binary composition for the cis/trans mixtures.

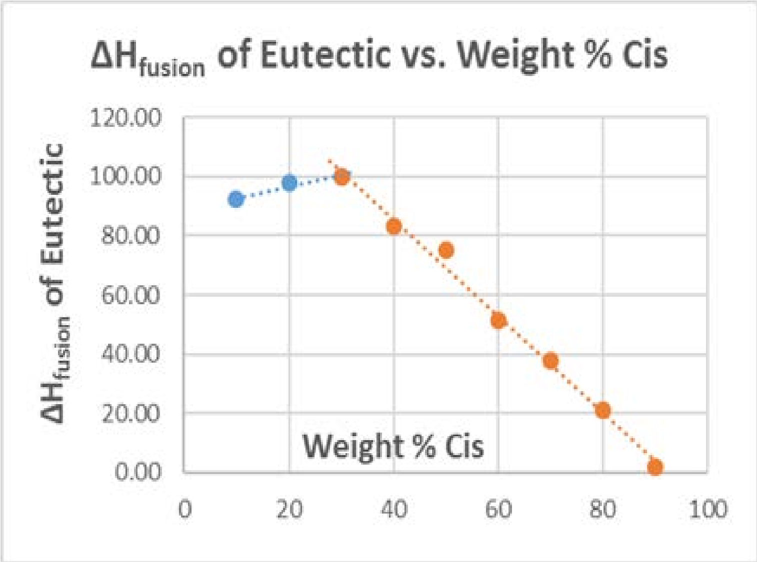

Figure 5. A plot of the eutectic peak enthalpy of fusion (ΔH) versus wt % cis isomer composition. The maximum corresponds to the eutectic composition (30 wt % cis isomer) having the maximum enthalpy of fusion of 100.1 J/g

4. Conclusion

The eutectic composition was observed to be 30% cis and 70% trans 1,2-dibenzoylethylene with a melting temperature of 94°C and a ΔH_{fusion} of 100 J/g. As the cis isomer increased from 30% to 90% of the total mass, the peak temperature of melting increased. As the trans isomer increased from 70% to 90% of the total mass, the peak temperature of melting increased. A eutectic point was found from various trends in the thermal properties of cis/trans-1,2-dibenzoylethylene mixtures, and therefore a binary phase diagram can be developed, indicating that the DSC can properly be used to produce a binary phase diagram for nonmetal isomeric organic compounds. This supports results of other type of experiments used to build a binary phase diagram of non-metal organic compounds. The DSC is an easy to use instrument that after a brief introduction could be quickly understood by students. Incorporating it into an organic chemistry lab class, in order to develop a binary phase diagram, could benefit students by exposing them to high tech lab equipment while simultaneously furthering their understanding of important chemistry topics.

Statement of Competing Interests

The Authors have no competing interests.

List of Abbreviations

All the abbreviations are defined in the body of the text.

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