

## Separation and Crystal Structure of Two Isomeric of 1,3,3-Trimethyl-5-nitro-3-(4-nitrophenyl)-2,3-dihydro-1*H*-indene and 1,3,3-Trimethyl-5-nitro-1-(4-nitrophenyl)-2,3-dihydro-1*H*-indene

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The isomers, 1,3,3-trimethyl-5-nitro-3-(4-nitrophenyl)-2,3-dihydro-1*H*-indene (**1**) and 1,3,3-trimethyl-5-nitro-1-(4-nitrophenyl)-2,3-dihydro-1*H*-indene (**2**), have been prepared and separated effectively. Their crystal structures can not be confirmed by the results of IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS studies, but determined by X-ray diffraction. The structure identity has explained the precise configurations of title compounds. DSC/TG analysis illustrate that the isomers **1** and **2** possess excellent thermal stability.

**Keywords:** Indene, Aromatic nitration, Single structure, X-Ray diffraction.

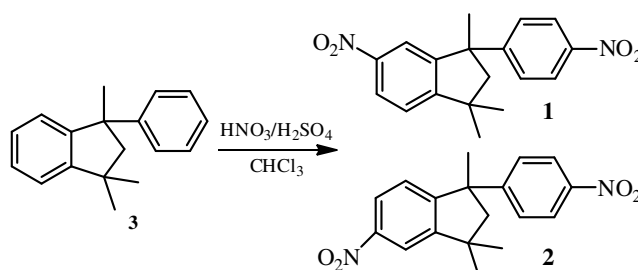
### INTRODUCTION

Bismaleimide (BMI) resins possess outstanding key properties such as high use temperature, thermooxidative stability, high mechanical strength, high modulus, excellent electrical properties and superior chemical resistance<sup>1,2</sup>. Recently, the indene fragment has been developed by Ciba-Geigy company<sup>3</sup> to design and synthesize novel bismaleimide resins. They indicated that indene fragment features a rigid structure, a chiral carbon atom and low melting point of the mixture of isomers after nitration. The new findings decrease the melting point and increase solubility of bismaleimide, not sacrifice their thermal stability. The novel bismaleimides also reflect incredible stability and mechanical properties. Terasaki *et al.*<sup>4</sup> also introduced the indene fragment into bisphenol A intermediates. However, they haven't supplied any compelling experimental evidence to illustrate those improvements of that designed fragment. The indene fragment also kindles our interest in design some other novel bismaleimides. Bismaleimides are usually obtained from condensation of anhydrides and diamines<sup>5,6</sup>. The title compounds described in this paper are precursors of diamines which are required for bismaleimides synthesis. However, elemental analyses, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS studies all failed to distinguish these two isomers (**Scheme-I**). Herein, we separate the title isomers effectively through general method and report the single crystal structure to reveal the precise configuration of the title compounds.

### EXPERIMENTAL

1,3,3-Trimethyl-3-phenyl-2,3-dihydro-1*H*-indene (**3**) was prepared according to reported procedure<sup>7,8</sup>. The other chemicals

were obtained from commercial sources and used without further purification. Crystal structure determination was carried out on a CAD4SDP 44 M/H diffractometer. IR spectra were recorded on NEXUS 670 spectrometer with KBr pellets in the 4000-400 cm<sup>-1</sup> region. C, H, N and O elemental analyses were performed with a Euro EA3000 apparatus. <sup>1</sup>H and <sup>13</sup>C spectra were recorded at room temperature of 400 and 100 MHz, respectively. DSC analysis was implemented on a TA Instrument DSC-Q100, TG on a TA Instruments TGA-Q500. The data were recorded from room temperature to 500 °C at a heating rate of 20 °C/min under N<sub>2</sub> atmosphere.



**Scheme-I:** Synthesis of compounds **1** and **2**

**General procedure:** Compound **3** (23.6 g, 0.1 mol) and chloroform (75 mL) were added to a 250 mL flask, after the mixture was stirred and cooled down to 2-8 °C, followed by slow addition of a previously prepared solution of mixed acid (HNO<sub>3</sub> 13.4 mL, H<sub>2</sub>SO<sub>4</sub> 39.6 mL). The process of the reaction was monitored by using TLC analysis. Upon completion, the reaction mixture was poured into ice water (300 mL). The

TABLE-1  
 CRYSTAL DATA AND STRUCTURE REFINEMENT FOR COMPOUND **1** AND **2**

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>
Formula weight	326.34	326.34
Temperature (K)	291(2)	113(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	P21/n
Unit cell dimensions (Å)		
(Å)	a = 9.501(4)	a = 8.0246(16)
(Å)	b = 16.660(4)	b = 29.435(6)
(Å)	c = 12.732(4)	c = 13.328(3)
(°)	β = 127.06(4)	β = 90.92(3) <sup>o</sup>
Volume (Å <sup>3</sup> )	1608.2(9)	3147.7(11)
Z	4	8
Density (calculated) (g/cm <sup>3</sup> )	1.348	1.377
Absorption coefficient	0.096	0.098
F <sub>(000)</sub>	688	1376
Crystal size (mm <sup>3</sup> )	0.46 × 0.42 × 0.38	0.20 × 0.18 × 0.12
Theta range for data collection (°)	2.35-25.52	2.06-25.02
Index ranges		
	-11 ≤ h ≤ 11	-9 ≤ h ≤ 9
	-20 ≤ k ≤ 0	-21 ≤ k ≤ 35
	-10 ≤ l ≤ 15	-15 ≤ l ≤ 15
Reflections collected	3,214	20,260
Independent reflections	2,985	5,540
Data/restraints/parameters	2985/0/220	2985/0/220
Refinement method	Full-matrix least-squares of F <sup>2</sup>	Full-matrix least-squares of F <sup>2</sup>
Goodness-of-fit on F <sup>2</sup>	0.975	1.077
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0509, wR <sub>2</sub> = 0.1462	R <sub>1</sub> = 0.0485, wR <sub>2</sub> = 0.1102
R indices (all data)	R <sub>1</sub> = 0.1005, wR <sub>2</sub> = 0.1679	R <sub>1</sub> = 0.0556, wR <sub>2</sub> = 0.1153
Δρ <sub>min</sub> /Δρ <sub>max</sub> (e Å <sup>-3</sup> )	-0.21/0.18	-0.22/0.25

organic extracts were successively washed with 5 % NaHCO<sub>3</sub> solution, dried over anhydrous MgSO<sub>4</sub> and then evaporated under reduced pressure. The yellow oil residue was purified through a silica gel column chromatography to produce 25.2 g (16.8 g + 8.4 g) (yield 77.3 %) of the title isomers **1** and **2**. Data of the two isomers are same unless specified (Table-1). (m.p. 138-140 °C) anal. calcd.(%) for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>: C, 66.25; H, 5.55; N, 8.58. Found (%): C, 66.15, 66.25; H, 5.65, 5.87; N, 8.58, 8.95. Main IR peaks (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3066 (C-H), 1592 (C=H), 2963, 2923, 2866 (C-H), 1013 (C-H), 1518 (N-O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ ppm): 1.11(s, 3H, Me), 1.43 (s, 3H, Me), 1.76 (s, 3H, Me), 2.34 (d, J = 12, 2H, -CH<sub>2</sub>-), 2.48 (d, J = 12, 2H, -CH<sub>2</sub>-), 7.22-7.32 (m, 3H, Ar-H), 8.09-8.19 (m, 4H, Ar-H). <sup>13</sup>C NMR for **1** (CDCl<sub>3</sub>, 100 MHz, δ ppm): 156.92, 154.76, 154.06, 148.46, 146.31, 127.38, 125.54, 123.64, 123.95, 118.58, 58.95, 51.40, 43.22, 30.43, 30.28, 30.27. <sup>13</sup>C NMR for **2** (CDCl<sub>3</sub>, 100 MHz, δ ppm): 159.62, 156.92, 149.17, 147.87, 146.31, 127.37, 123.81, 123.80, 123.67, 120.24, 58.85, 51.10, 43.44, 30.50, 30.23, 30.06.

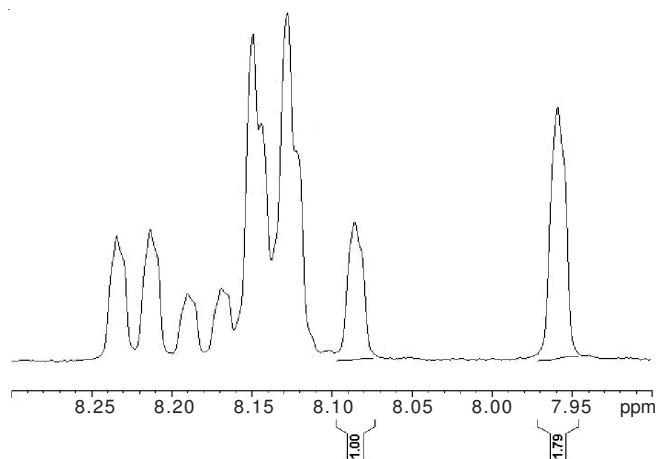
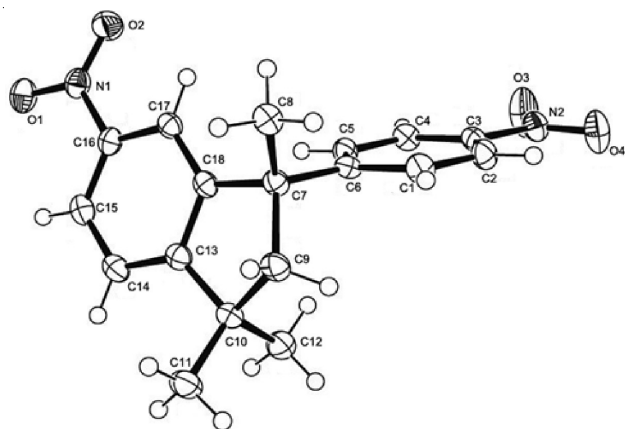
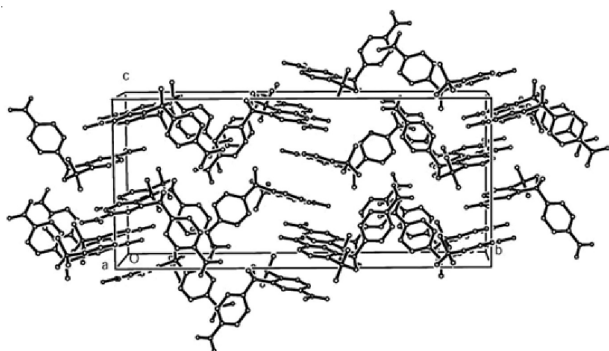
## RESULTS AND DISCUSSION

**Synthesis and separation:** Nitration of **3** was achieved with 2.2 equivalent of 65 % HNO<sub>3</sub> and 7 equivalent of 98 % H<sub>2</sub>SO<sub>4</sub> at 0-15 °C. Upon completion, the residue contains very small quality of mononitration compound. With the increase of the ratio of the HNO<sub>3</sub> and temperature, mononitration product decreases, but the total yield of the title compounds also decreases noticeably. Under the standard conditions, we obtained **1** and **2** in ratio 1:2 or 2:1 after purification by silica

gel column chromatography. We can not distinguish these two isomers. According to IR, <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **1** and **2**, there is no obvious difference between the two compounds. After analyzing the mixture's <sup>1</sup>H NMR spectrum (the residue before purification by silica gel column chromatography), there are two single-proton-peaks near the low field δ = 8 ppm and the other proton shifts are all the same compared with the <sup>1</sup>H NMR spectrum of **1** or **2**. By classifying the proton shifts of all the hydrogen atoms, it can be confirmed that the proton peaks δ = 8.09 ppm and δ = 7.96 ppm are located in C17-H (**1**, Fig. 2) or C14-H (**2**, Fig. 4). Mixture helps to increase the split between C17-H (**1**) and C14-H (**2**) under the detection of NMR. The ratio between the two proton peak areas is 1:1.79 (S<sub>δ = 8.09 ppm</sub>/S<sub>δ = 7.96 ppm</sub>), in Fig. 1, matching closely with the ratio of **1** and **2** after purification by silica gel column chromatography. However, those methods also can not help to distinguish which one is **1** or **2**. We turn to single-crystal X-ray diffraction for help at last.

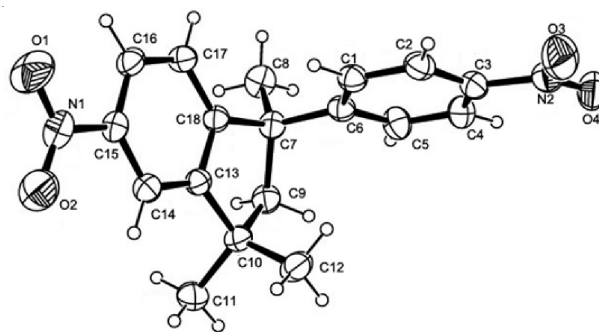
**Structure description:** Suitable crystals of **1** and **2** were obtained by slow evaporation from methanol/CHCl<sub>3</sub> solution at room temperature. After analyzing by X-ray diffraction, we can confirm that the major product is **2** finally. The molecular structures of **1** and **2** are revealed in Figs. 2 and 4 and their packing diagrams in Figs. 3 and 5.

As shown in Tables 2 and 3, the bond lengths and angles in the **1** and **2** have normal values. In the title molecules, the five-membered rings of the indene fragment adopt an envelope conformation, while the flap atoms deviate by 0.5177(19) Å (**1**) and 0.4329(30) Å (**2**) from the plane of the remaining

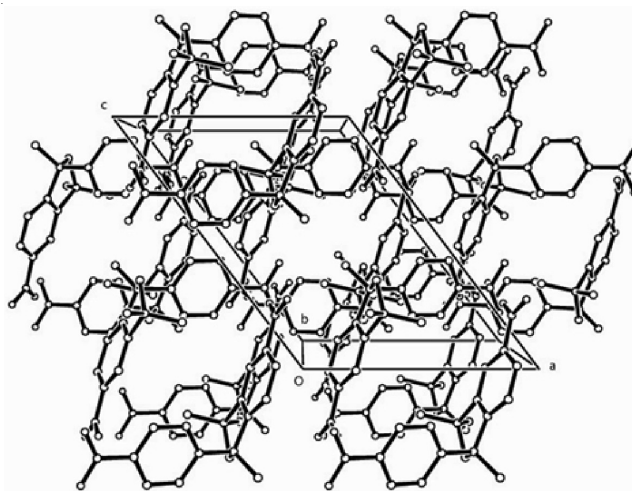
Fig. 1.  $^1\text{H}$  NMR data for mixture of **1** and **2**Fig. 2. Molecular structure of the title regioisomer **1**Fig. 3. Packing diagram of regioisomer **1**

four atoms (C10, C13, C18, C7), respectively. The dihedral angles between the phenyl ring (C1-C6) and the indene benzene ring (C13-C18) are  $59.68(19)^\circ$  (**1**) and  $81.16(51)^\circ$  (**2**), respectively. C7, the chiral atom connects the indene ring and phenyl ring, must be mentioned. Each angle of the four carbon atoms (C6, C8, C9, C18) attached to C7 ( $\angle\text{C6-C7-C9}$ ,  $\angle\text{C6-C7-C8}$ ,  $\angle\text{C8-C7-C9}$ ,  $\angle\text{C8-C7-C18}$ ) is near close to  $109.47^\circ$ , the standard angle of regular tetrahedron structure, which means C7 dominates the twisty configuration of the title compounds and enforces the molecules' rigidity. The indene benzene ring forms dihedral angle of  $-33.47(08)^\circ$  (**1**) and  $-29.14(20)^\circ$  (**2**) with the plane defined by the indene  $sp^3$ -hybridized carbon atoms C7, C9 and C10.

According to the Figs. 2 and 4, it can be seen that the C15-nitro is farther from the nitrophenyl (C1-C6) than C16-nitro. The dihedral angle of **2** between the phenyl ring (C1-C6) and the indene benzene ring (C13-C18)  $21.48^\circ$  is greater than that of **1**. It is the torsion of the nitrophenyl, which helps reduce the oppression of nitrophenyl on indene fragment and flap atom of **2** deviates shorter than that of **1**. In other words, we can speculate, in the fragment of **3**, that C16 holds greater steric hindrance than C15 from the geometrical parameters for the crystal structure of the title isomers<sup>9,10</sup>.

Fig. 4. Molecular structure of the title regioisomer **2**

From the crystal packing diagrams of **1** and **2**, in Figs. 3 and 5, the molecule crystals are composed of dispersive molecules hold together by van der Waals forces, without other obvious intermolecular interactions. These non-covalent interactions, in the title compound of **1** and **2**, mainly come from the dipole-dipole interaction of  $\text{NO}_2\text{-NO}_2$  and the dipole-induced dipole interaction of  $\text{NO}_2\text{-phenyl}$ <sup>11</sup>.

Fig. 5. Packing diagram of the title regioisomer **2**

**DSC-TG analysis:** The thermal properties of the two isomers, **1** and **2**, have been investigated by DSC and TG methods. Experimental data are shown in Table-4. The absorption peaks of isomers **1** and **2** are all matched with their melting-point. Especially, there are no any other absorption peaks existing under  $300^\circ\text{C}$ , which means no polymerization or decomposition carrying out below  $300^\circ\text{C}$ . The TG data show that the isomers, **1** and **2** have excellent initial decomposition temperature ( $T_{5\%}$ ),  $221.2^\circ\text{C}$ ,  $234.1^\circ\text{C}$  and  $234.1^\circ\text{C}$ , respectively.

TABLE-2  
SELECTED BOND LENGTHS (Å)  
AND ANGLES (°) BY X-RAY FOR **1**

Bonds	Dist.	Angle	(°)
O1-N1	1.210(3)	O1-N1-O2	123.22(17)
O2-N1	1.204(3)	O1-N1-C16	118.37(16)
O3-N2	1.225(3)	O2-N1-C16	118.39(16)
O4-N2	1.216(3)	O3-N2-C3	118.68(16)
C3-N2	1.469(3)	O3-N2-O4	122.50(17)
C3-C4	1.374(3)	O4-N2-C3	118.82(18)
C6-C7	1.532(3)	C6-C7-C9	111.67(15)
C7-C9	1.548(3)	C6-C7-C8	108.79(15)
C7-C18	1.514(3)	C7-C9-C10	107.52(15)
C9-C10	1.547(3)	C7-C18-C17	128.06(16)
C10-C13	1.524(3)	C8-C7-C9	111.18(15)
C14-C15	1.375(3)	C8-C7-C18	110.44(15)
C15-C16	1.372(3)	C9-C10-C13	101.34(15)
C15-N1	1.471(3)	–	–

TABLE-3  
SELECTED BOND LENGTHS (Å)  
AND ANGLES (°) BY X-RAY FOR **2**

Bonds	Dist.	Angle	(°)
O1-N1	1.210(3)	O1-N1-O2	122.6(2)
O2-N1	1.204(3)	O1-N1-C15	118.7(2)
O3-N2	1.225(3)	O2-N1-C15	118.6(2)
O4-N2	1.216(3)	O3-N2-C3	117.8(3)
C3-N2	1.469(3)	O3-N2-O4	123.7(3)
C3-C4	1.374(3)	O4-N2-C3	118.5(3)
C6-C7	1.532(3)	C6-C7-C9	111.52(19)
C7-C9	1.548(3)	C6-C7-C8	109.14(19)
C7-C18	1.514(3)	C7-C9-C10	107.62(17)
C9-C10	1.547(3)	C7-C18-C17	127.6(2)
C10-C13	1.524(3)	C8-C7-C9	111.98(19)
C14-C15	1.375(3)	C8-C7-C18	112.34(19)
C15-C16	1.372(3)	C9-C10-C13	100.42(19)
C15-N1	1.471(3)	–	–

TABLE-4  
DSC AND TG DATA OF ISOMERS, **1** AND **2**

Compound	DSC		TG	
	m.p. (°C)	T <sub>m</sub> (°C)	T <sub>5%</sub> (°C)	T <sub>max</sub> (°C)
<b>1</b>	138-140	143.8	234.1	304.2
<b>2</b>	138-140	143.8	234.1	304.2
Isomers	108-126	121.3	221.2	287.6

They also perform well in the maximal decomposition temperature (T<sub>m</sub>), 287.6, 304.2 and 304.2 °C, respectively. Those data cited above illustrate that the isomers **1** and **2** possess excellent thermal stability. It is concluded that the thermal properties of material, in this paper, are mainly controlled by the rigidity or configuration of the molecules and the existence of isomer molecule.

### Conclusion

1,3,3-Trimethyl-5-nitro-3-(4-nitrophenyl)-2,3-dihydro-1*H*-indene (**1**) and 1,3,3-trimethyl-5-nitro-1-(4-nitrophenyl)-2,3-dihydro-1*H*-indene (**2**) were separated successfully through general method and characterized. Crystal structure of **1** and **2** were determined by the X-ray single crystal diffraction analysis. In addition, the DSC-TG data show that the title compounds have good thermal stability. These evidences conduct us to design some other novel bismaleimide resins containing the attractive indene fragment in the following work.

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