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SYNTHESIS AND CHARACTERIZATION OF A NOVEL NON-LINEAR OPTICAL (NLO) MATERIAL

Endo anthracene maleic anhydride – Diel's–Alder adduct of anthracene

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Anthracene is one of the organic molecular crystals, which exhibits peculiar optical and electronic properties. Since the 9, 10 positions are very reactive in anthracene, it undergoes the Diel's–Alder reaction with maleic anhydride in 99% yield. The synthesis of Diel's–Alder adduct has been carried out by adopting standard procedure. The product was subjected to various characterization studies such as FTIR, UV and ^{1}H NMR spectroscopy, and thermal studies to check its purity and determine the applicability of adduct in various applications. The second harmonic generation (SHG) efficiency of the adduct has been observed using Nd:YAG laser.

Keywords: *anthracene, characterization studies, Diel's–Alder adduct, SHG efficiency*

Introduction

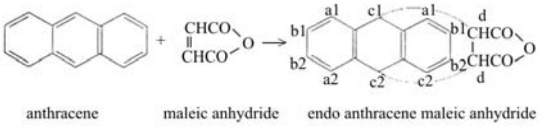
Organic materials are in increasing demand, as they are the better candidates for non-linear optical (NLO) and electro-optic device application than those of inorganic materials. Therefore, various organic-inorganic materials were developed and studied to improve the properties of inorganic materials [1–30]. Organic materials have been known for their applications in semi-conductors [31], super-conductors [32] and NLO devices [33, 34].

Many new organic crystals have been found based on the predictive molecular engineering approach and have been shown to have potential applications in non-linear optics. Some interest has been shown in the search for ultraviolet laser materials [35]. The overwhelming success of molecular engineering in controlling NLO properties in the last decade has prompted better initiatives in crystal engineering. This aims at regulating properties at a macroscopic level combining bonding and crystallization conditions [36, 37].

There are several reports on the growth and characterization of anthracene [38–40]. But there are no reports available in the literature on the synthesis and characterization of Diel's–Alder adduct of anthracene, which has good SHG efficiency.

Experimental

By using Analar samples of anthracene, maleic anhydride, xylene, an addition product of anthracene was synthesized by adopting standard procedure. Since it is a 4+2 cyclo addition reaction, this takes place during heating. Anthracene act as a diene and maleic anhydride behaves as dienophile. About 0.16 g of anthracene and 0.8 g of maleic anhydride with 2 mL of xylene were boiled with porcelain tips in a large boiling test tube. The test tube was clamped in ring stand and the reaction mixture was heated in a sand bath for 40 min. The crystals were filtered using ethyl acetate as washing solvent. The adduct *endo* anthracene maleic anhydride was obtained. Its theoretical melting point is 261–262°C.



Scheme 1

Measurements

NMR spectroscopy was recorded in JEOL instrument; model GSX using $CDCl_3$ as solvent.

TG-DTA of adduct was recorded on a STA409C Instrument in nitrogen atmosphere using Al_2O_3 crucible.

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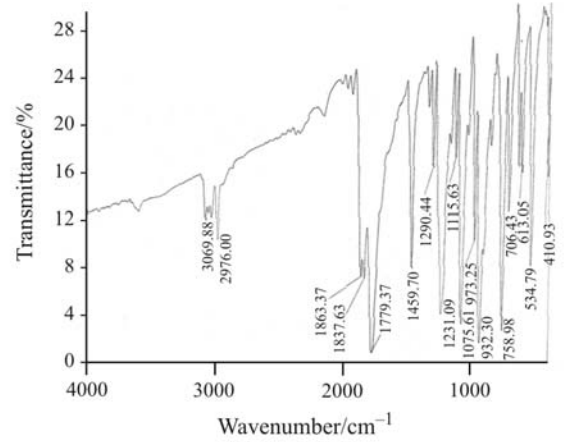

Fig. 1 FTIR spectrum of Diel’s–Alder adduct

The IR spectrum has been recorded on a PerkinElmer 283 Spectrophotometer using KBr pellet technique.

Results and discussion

The synthesized adduct was subjected to various characterization studies such as FTIR, UV, ^{1}H NMR spectroscopy and thermal analysis to check its purity and to determine the applicability of adduct in various applications.

FTIR spectrum of adduct

The FTIR spectrum of adduct was also recorded and has been shown in Fig. 1, which provides information of the structure of adduct. Usually an acid anhydride can be easily detected due to the appearance of two frequency bands in the region 1850–1750 cm^{-1}. The doublet appears because of the coupled vibrations of two C=O groups. The high frequency band is assigned to symmetrical vibrations and lower frequency band to asymmetric vibrations. The splitting of the band is due to Fermi Resonance. In the FTIR spectrum of Diel’s–Alder adduct, the doublet appears at 1837.63 and 1863.37 cm^{-1}. The absorption bands at 1231.09 and 1290.44 cm^{-1} are assigned to C–O stretching. The absorption band at 3069.88 cm^{-1} is characteristic of C=C–H stretching. The absorption bands between 900 and 700 cm^{-1} are characteristic of C–H deformation. The absorption band at 1779.37 cm^{-1} is due to C=O stretching.

UV spectral studies of D–A adduct

UV-visible spectral analysis was also used to measure the range of transmission of the adduct crystal, which is shown in Fig. 2. It was found that adduct was conveniently transparent from 400–1200 nm with about 75% of transmission. It indicated that adduct is suitable for modulation purposes.

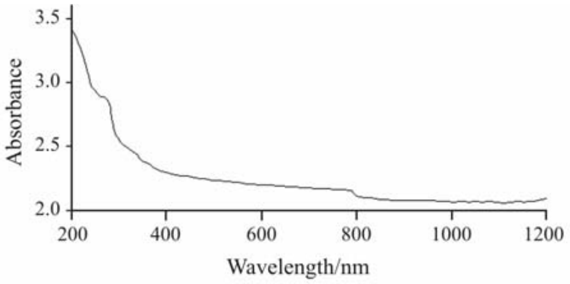

Fig. 2 UV visible spectrum of adduct

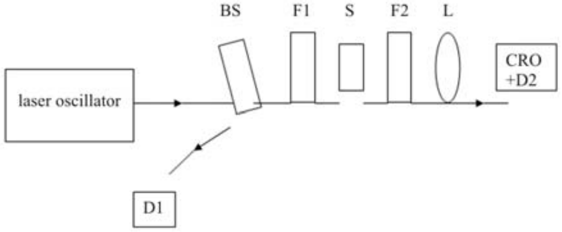

Fig. 3 Experimental arrangement of Kurtz powder technique

NLO property

The NLO property of Diel’s–Alder adduct was determined by Kurtz powder technique. The second harmonic generation developed in the pure Diel’s–Alder adduct has been confirmed from the emission of green radiation from the powder sample.

For comprehensive analysis of the second order non-linearity, Kurtz powder technique was used. The schematic diagram of Kurtz powder technique is shown in Fig. 3. In this technique the sample was prepared by sand-witching the graded crystalline powder with average particle size of about 90 μm between two quartz slides using copper spacers of 0.4 mm thickness. The powdered sample (S) was illuminated using a Q-switched Nd:YAG laser emitting 1.06 μm 40 ns laser pulses with spot radium of 1 mm. The energy meter D1 served as a reference to monitor the fluctuation in the input pulse. Filter F1 that transmits the fundamental laser emission was used to cut off the fundamental laser radiation and to pass the generated second harmonic. The second harmonic signal generated in the sample was collected by the lens and detected by the cathode ray oscilloscope (CRO) coupled with the photo multiplier tube D_2.

The SHG efficiency of Diel’s–Alder adduct was tested by using Nd:YAG laser source. The SHG signal of Diel’s–Alder adduct was found to be 66. It indicates that the SHG efficiency of Diel’s–Alder adduct is 66/149.5=0.44. That is Diel’s–Alder adduct is found to be 0.44 times SHG efficient than KDP crystals. Nd:YAG laser of fundamental wavelength 1064 nm was allowed to focused on capillary densely packed with the sample.

The signal was collected at 90° to the incident beam using Aczerny Turner monochromator and a visible photomultiplier tube (Hamamatsu R2059) and recorded on a digital storage oscilloscope (Tektronix TDS 3000B).

^{1}H NMR spectrum of Diel's–Alder adduct

The Diel's–Alder adduct of anthracene is subjected to ^{1}H NMR analysis. The ^{1}H NMR spectrum of D–A adduct was recorded using a JEOL instrument-model GSX400 using acetone as solvent and has been shown in Fig. 4. The Diel's–Alder adduct having non-equivalent protons. So they have different signals due to molecular arrangements. The double doublets at 7.5 and 7.35 δ are assigned to phenyl protons present in b1 and b2 positions, respectively. The multiplet at 7.2 δ is assigned to phenyl protons present in positions a1 and a2. The singlet at 4.9 δ is assigned to benzylic protons present in position c1 and other benzylic proton present in position c2 gives a singlet at 3.00 δ. The triplet at 3.78 δ is assigned to protons present in d position. We expect the benzylic protons present in c and c1 to give doublet. But they give two singlets at 4.9 and 3.00 δ, due to more electronegative phenyl group is present adjacent to each protons.

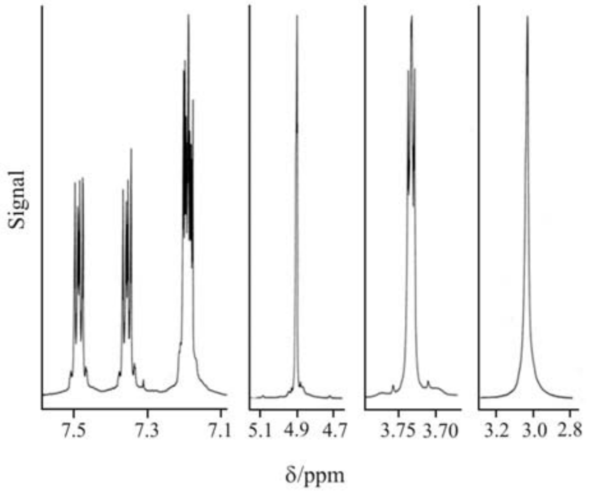

Fig. 4 ^{1}H NMR spectrum of Diel's–Alder adduct

Thermal studies of adduct

The anthracene and Diel's–Alder adduct was subjected to thermogravimetric (TG) analysis and differential thermal analysis (DTA). Diel's–Alder adduct exhibited higher thermal stability compared to anthracene.

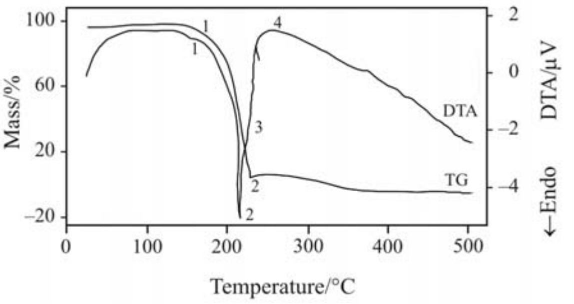

Fig. 5 TG and DTA curves of anthracene

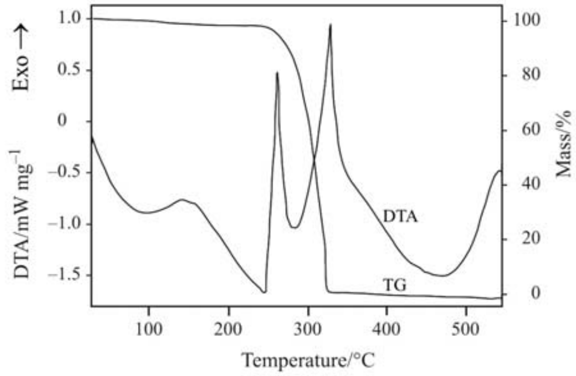

Fig. 6 TG and DTA curves of Diel's–Alder adduct

The TG and DTA curves for the decomposition of anthracene have been shown in Fig. 5. The TG curve indicates that it is thermally stable up to 150°C. Afterwards, the TG curve shows a major mass loss step corresponding the decomposition of anthracene. The DTA curve for anthracene (Fig. 5) shows an intensive endothermic peak at 215°C ascribed to the decomposition of anthracene.

TG and DTA curves for the decomposition of Diel's–Alder adduct are given in Fig. 6. The TG curve exhibits that it is thermally stable up to 260°C. Afterwards, the TG curve indicates a major mass loss step corresponding to the decomposition of Diel's–Alder adduct. DTA curve for Diel's–Alder adduct (Fig. 6) exhibits two intensive exothermic peaks at 261 and 350°C. The observed first exothermic peak corresponds to the melting point of Diel's–Alder adduct (Fig. 6), which is in good agreement with the theoretical melting point 261–262°C. This shows the high purity of the Diel's–Alder adduct which is suitable for fabrication. The second intensive exothermic peak is ascribed to the decomposition of Diel's–Alder adduct.

Conclusions

A novel NLO material – Diel's–Alder adduct of anthracene was synthesized by adopting standard procedure. Adduct was subjected to various characterization studies such as FTIR, UV and ^{1}H NMR spectroscopy, SHG efficiency and thermal analysis. FTIR and ^{1}H NMR spectral studies reveal the presence of functional groups and support the structure of adduct. UV spectral studies show that it is suitable for modulation purposes. The SHG efficiency of anthracene was found to be zero. The SHG signal of Diel's–Alder adduct was found to be 66. It indicates that the SHG efficiency of Diel's–Alder adduct is 66/149.5=0.44. This shows that Diel's–Alder adduct is found to be 0.44 times SHG efficient than potassium dihydrogen phosphate (KDP) crystals. This adduct can be used to modify the NLO property and scintillation property of anthracene.

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