

Dehydrodivanillin: Multi-dimensional NMR Spectral Studies, Surface Morphology and Electrical Characteristics of Thin Films

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The complete structural characterization of dehydrodivanillin, an important natural product of interest to the food, cosmetics and aroma industries, has been carried out using multi-dimensional NMR spectroscopic techniques, and its previously reported ¹³C-NMR values have been reassigned. Dense and granular thin films of dehydrodivanillin have been grown by sublimation under high vacuum and studied using Scanning Electron Microscopy (SEM), electrical and optical techniques. The transmittance spectra of the films indicate a wide optical band gap of more than 3 eV. Typical J-V characteristics of Glass/ITO/dehydrodivanillin/Al structure exhibited moderate current densities $\sim 10^{-4}$ A/cm² at voltages > 25 V with an appreciable SCLC mobility of the order of 10^{-6} cm²/V-s.

Key Words: Dehydrodivanillin, 2 D-NMR, J-V Characteristics, SEM, SCLC mobility

Introduction

Dehydrodivanillin (3,3'-Diformyl-6,6'-dihydroxy-5,5'-dimethoxybiphenyl) (Fig. 1) is a natural product isolated from lignins of several important plant species.^{1,2} It is commercially important in the cosmetics, pharmaceuticals and food stuffs industries^{3,4} as an antioxidant and a flavouring agent.⁵ Moreover, it has been used in the preparation of positive photoresists for microlithography.^{6,7} It has been synthesized by the oxidative coupling of vanillin using soyabean peroxidase⁷, FeCl₃⁸ or sodium/potassium persulfate⁹ as the oxidising agent. Dehydrodivanillin is of interest in the present study because such small organic molecules have gained importance in recent years for electronic device applications e.g. light-emitting diodes (LEDs) and solar cells. Furthermore, amorphous and polycrystalline films of such small organic molecules offer good charge transport and photovoltaic properties.^{10,11} A theoretical study on nonlinear optical properties of the title compound has indicated a π -electron exchange between the two rings due to conjugation¹² and this prompted us to carry out measurements of the electrical and optical characteristics and surface morphology of thin films of this compound. A detailed structural characterization of molecular dehydrodivanillin was also done using multi-dimensional NMR methods.

Experimental

Optical measurements were done on a CARY-5E UV-Vis-NIR spectrophotometer. IR spectrum was recorded on a Spectrum BX series spectrophotometer using KBr. The NMR Spectra were recorded on Bruker 500 MHz instrument. HMBC and HMQC were recorded on Bruker 400 MHz instrument. GC-MS studies were carried out using JEOL JMS600 instrument. For device preparation, indium tin oxide (ITO) coated glass substrates were cleaned thoroughly by a sequential orga-

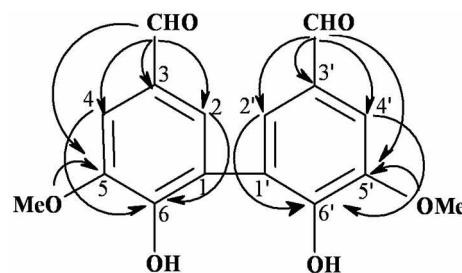


Figure 1. Key HMBC correlations of dehydrodivanillin.

nic wash procedure using acetone and iso-propanol. Devices were patterned using a resist followed by wet chemical etching. A thin film of Dehydrodivanillin (300 nm) was grown over ITO coated glass in a vacuum coating unit, under a base pressure of 2×10^{-6} mbar, at a rate of deposition < 0.5 Å/s. To form the metal contacts, aluminum (200 nm) was thermally evaporated, at deposition rate < 1 Å/s, over the film through a shadow mask. The active area of the resulting devices was 0.04 cm². SEM investigations were carried out on a LEO 1430 instrument. I-V measurements were performed, on samples immediately after deposition of electrodes under normal class 10000 clean room environmental conditions (25 °C and RH \sim 45 - 50%), using a Keithley 2410 sourcemeter.

Results and Discussion

NMR Studies. The expected meta-coupling in the ¹H-NMR spectrum of dehydrodivanillin has not been previously detected. We have observed this ($J_m = 3$ Hz) using a 500 MHz instrument.¹³ Further, the structural aspects of the molecule have also been investigated using 2D-NMR techniques. Based on results obtained, we conclude that previously the ¹³C-NMR values for this structure have been wrongly assigned.¹⁴ The Nuclear Overhauser spectrum (NOESY, Fig. 2), in addition to self correlations, showed the correlation of aromatic proton

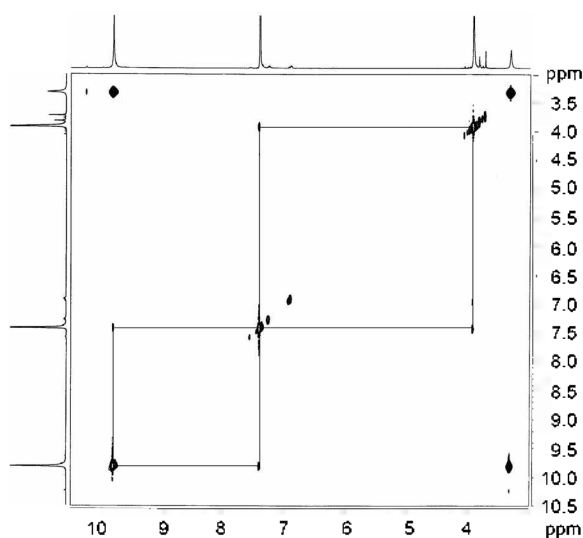


Figure 2. NOESY spectrum of dehydrodivanillin.

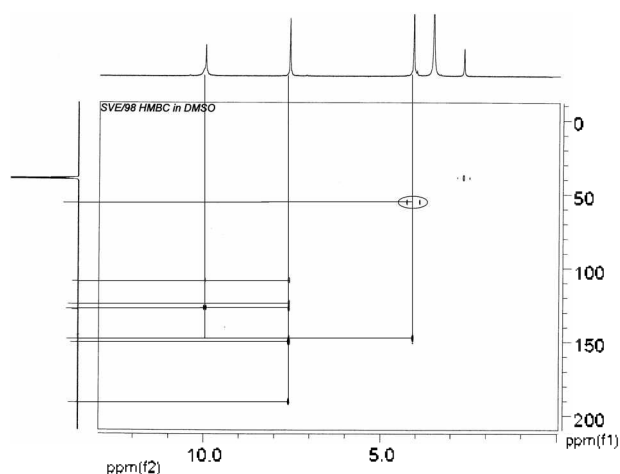


Figure 3. HMBC spectrum of dehydrodivanillin.

(δ 7.4) with the methoxyl protons (δ 3.9) and the aldehyde proton at δ 9.8. The spectrum showed the presence of an aromatic proton ortho to methoxy group at C-4. The aldehyde group correlated with two aromatic protons i.e. at C-2 and C-4, ortho to it. Key correlations from the Heteronuclear Multiple Bond

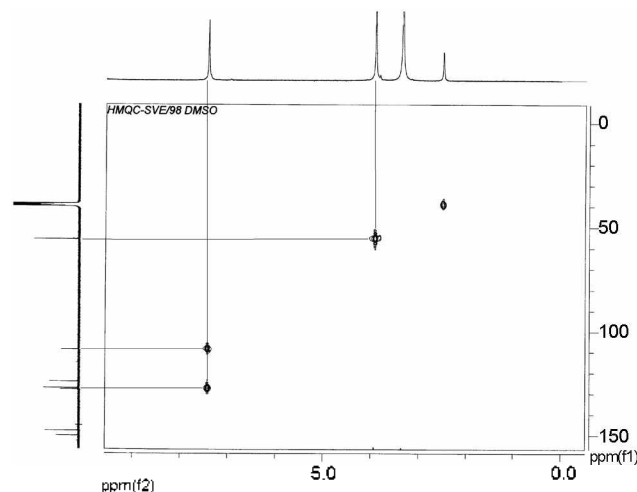


Figure 4. HMQC spectrum of dehydrodivanillin.

Correlation (HMBC) spectrum are shown in Figure 1. The HMBC spectrum (Fig. 3) shows a 3-bond cross peak between the methoxy protons at δ 3.9 and C-5 at 148 ppm. The two peaks for the methoxy protons, shown in circle, in the HMBC spectrum are the HSQC peaks that were not completely suppressed as they are not correlating with any ^{13}C peaks but instead are bisecting the actual carbon upon which those protons are sitting. A 2-bond cross peak was observed between the aldehyde protons at δ 9.8 and the C-3 & C-3' carbons at 127.6 ppm, with a resolved coupling of 23.4 Hz. The Heteronuclear Multiple Quantum Correlation (HMQC) spectrum (Fig. 4) shows a cross peak between the aromatic protons and the carbons at 109.20 and 127.97 ppm identifying them as either C-2 or C-4. A 3-bond coupling of \sim 6.4 Hz is resolved in the HMBC from the protons on C-2 / C-4 to hydroxyl bearing carbon C-6 at 150.66 ppm and C-4 is assigned as the most shielded aromatic carbon at 109.2 ppm. Consequently, the peak at 127.97 ppm has been assigned to C-2. The only remaining unassigned peak in ^{13}C NMR spectrum is a quaternary carbon at 124.6 ppm, which must belong to the C-1 carbons of the biphenyl linkage. The correlations of 2D-NMR have been summarized in Table 1.

Thin Film Studies. Transmittance of dehydrodivanillin films (over glass) was studied in the range 200 - 1000 nm. An absorption edge at 360 nm was obtained which indicated a wide energy band gap of 3.43 eV. A typical room temperature current density-voltage (J-V) curve for Glass/ITO/dehydrodivanillin/

Table 1. Assignment of 2D-NMR spectra of dehydrodivanillin

Position of H	^1H -NMR (δ)	^{13}C -NMR (ppm)	NOESY	HMQC	HMBC
1/1'		124.6			
2/2'	7.4	127.9	CHO	C-2	C-1, C-3, C-4, C-6, CHO
3/3'		127.6			
4/4'	7.4	109.2	CHO, OCH ₃	C-4	C-2, C-3, C-6, CHO
5/5'		148.2			
6/6'		150.6			
OCH ₃	3.9	55.9		OCH ₃	OCH ₃ , C-5
CHO	9.8	191			C-2, C-3, C-4, C-5

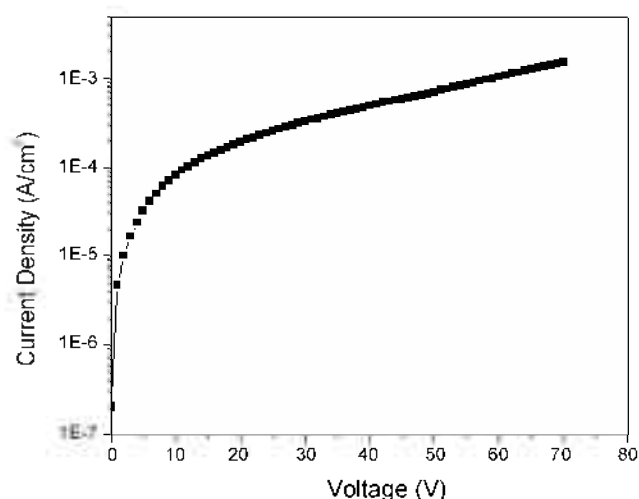


Figure 5. J-V Characteristics of Glass/ITO/dehydrodivanillin/Al thin film electronic devices.

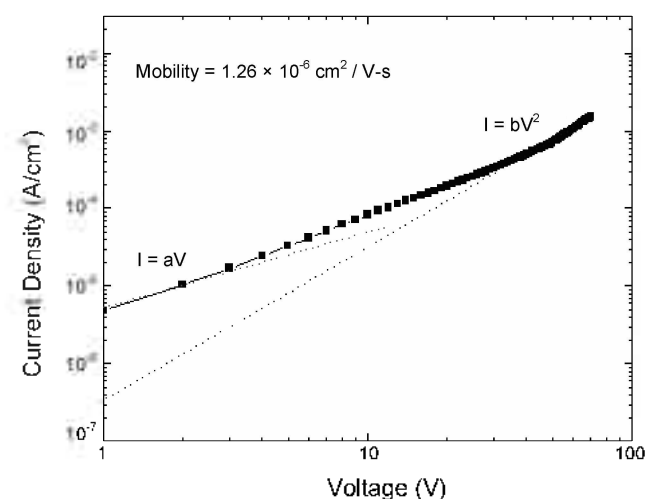


Figure 6. Mobility measurement from SCLC region.

Al device is shown in Fig. 5. In such devices ITO acts as anode and the hole injecting layer while the aluminum is used as the cathode. The current initially increases sharply in low voltage regime. After that, it increases steadily at a constant rate in the high voltage regime (> 25 V) with moderate current density of the order of 10^{-4} A/cm². In general, two separate voltage regions can be distinguished in Fig. 6. The device at low voltage demonstrates nearly ohmic I-V dependence. At higher voltage, a distinct region with $I \propto V^2$ was observed. Standard semiconductor theory predicts this type of I-V behaviour in case of space charge limited current (SCLC). Considering the present SCLC as the trap free limit, Child's Law can be applied,^{15,16} which states:

$$J = \frac{9}{8} \mu \epsilon \epsilon_0 \frac{V^2}{d^3}$$

where J is the current density, μ is the SCLC mobility of holes,

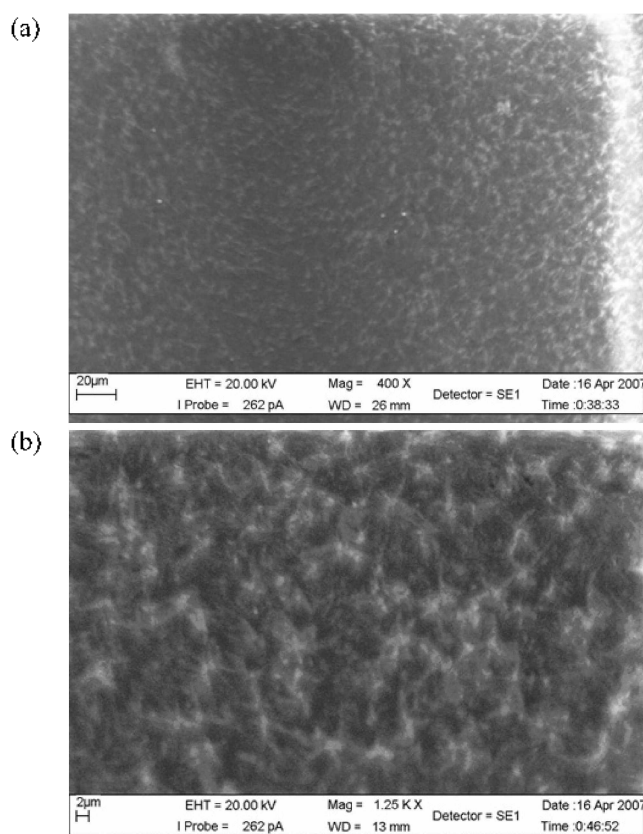


Figure 7. SEM image of the thermally grown film over ITO substrate [Resolution (a) 20 μ m (b) 2 μ m].

ϵ is the dielectric constant, ϵ_0 is the permittivity in a vacuum, V is the applied voltage and d is the film thickness.

Using the above J-V relationship, SCLC mobility was calculated to be of the order of 10^{-6} cm²/V-s (Fig. 6), which is in accordance with earlier reported values for such types of small molecules.¹⁷ The SEM images (Fig. 7) of the film grown over ITO substrate shows a reasonably uniform growth of the material with grain size of more than 1 μ m. The large grain size has been obtained due to reinforcement of π - π stacking of the biphenyl rings with intermolecular hydrogen bonding interactions. In this highly dense and granular crop of dehydrodivanillin, the grains are closely packed and uniformly distributed. Because of this regularity of grains in solid state, the intermolecular carrier transport by hopping is highly efficient and losses of carrier at grain boundaries by phonon scattering are minimum. This feature has been translated into appreciable electro-optical characteristics.

Synthesis & Characterization. Dehydrodivanillin was synthesized as described in the ref. 9, yield: 87.8%; m.p.: 306–307 °C (Lit.⁹ 305 °C); IR (KBr): 3247.46 (hydroxyl group), 1674.06 (carbonyl), 1587.31, 1504.97 (aromatic ring) cm⁻¹; ¹H-NMR (DMSO-*d*₆): δ 9.8 (2H, s, -CHO), 7.4 (4H, d, Ar-H, $J_m = 3$ Hz), 3.9 (6H, s, 2 \times OCH₃); ¹³C-NMR (DMSO-*d*₆): δ 55.95 (OCH₃), 109.20 (C4), 124.63 (C1), 127.61 (C3), 127.97 (C2), 148.20 (C5), 150.66 (C6), 190.95 (CHO); GC-EI-MS (di-TMS derivative): 445.9 (M⁺, 48%), 431 (M⁺-15, 100%) calcd. 446.6.

Conclusions

The commercial importance of dehydrodivanillin prompted us use it for as precursor for crosslinkers and polymers. For the complete characterization of molecule we carried out 2D-NMR studies. Based on which, ^{13}C -NMR values for dehydrodivanillin have been reassigned. Conjugation between two aromatic rings and efficient π - π stacking in the film has led to good film properties that is evident from SEM images and reflected in much better electrical and optical characteristics compared to earlier reports with SCLC mobility as high as $10^{-6}\text{ cm}^2/\text{V}\cdot\text{s}$. Dehydrodivanillin has shown immense potential to be used for the development of conducting polymers and crosslinkers for polymers, CNTs and biomolecules, in electronic applications.

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