

Research Article

Synthesis and Electrical and Gas Sensing Properties of Some 5-(Quinolinylmethylene)-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione and 5-(Quinolinylmethylene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione Derivatives

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Eight new 5-(quinolinylmethylene)barbituric acid derivatives were synthesized by the reaction of 1,3-dimethylbarbituric acid and 1,3-diethyl-2-thiobarbituric acid with quinoline-4-carboxaldehydes and several quinoline-2-carboxaldehydes via Knoevenagel condensation. The novel compounds were characterized by ¹H NMR, ¹³C NMR, mass, IR, and UV-visible spectral data and elemental analyses. d.c. and a.c. conduction properties of the compounds were investigated in the frequency range of 40–10⁵ Hz and temperature range 295–440 K. The d.c. results showed an activated conductivity dependence on temperature for all films. Obtained data reveal that a.c. conductivity obeys the relation $\sigma_{ac}(\omega) = A\omega^s$ and exponent *s* is found to decrease by increasing temperature. The analysis of the a.c. conduction data showed that the CBH model is the dominant conduction mechanism for the electron transport in the films. Gas sensing properties of the films for the volatile organic compounds (VOCs) were also investigated in the same temperature range. Maximum sensitivity to VOCs was observed at around 360 K for compound **6**.

1. Introduction

Heterocyclic compounds and their derivatives, which are developing quite rapidly and becoming more important day by day, constitute a very important branch of organic chemistry. These compounds containing nitrogen, sulfur, and oxygen as ring members are commonly used in various fields of industry as analytical reagents, ligands, dyestuffs, pharmaceuticals, and bioindicators. In addition to these, barbituric and thiobarbituric acid derivatives are well known as antibacterials [1], sedatives [2], herbicides [3], fungicides [4], and antiviral agents with their specific properties [5]. On the other hand, barbiturates having heterocyclic moieties have attracted considerable attention due to their potential pharmacological activity, and have become valuable alternatives in drug design [6, 7].

The electrical characterizations (d.c. and a.c.) of the materials are crucial in order to study relevant mechanisms of conduction and to realize its future applications. For example, to produce any device whose active layer is made of this kind of material, we need to know the effect of the temperature on both a.c. and d.c. electrical properties of the film, so as to carry out the accurate design. Measurements of d.c. and a.c. conductivity is also a reliable method to study the localised states near the band edges below the conduction and above the valance bands produced by the substitutional disorders which control many of the optoelectronic properties. Hence, a study of d.c. and a.c. conductivity in these materials will throw light on the nature of these levels. There is an increasing demand for the detection of volatile organic solvents in the field of environmental analysis, industrial process control, and work-place monitoring. A number of materials, for

example *Pc* [8, 9], PVC blended lipid membrane [10], ω functionalized alkanethiols [11], substituted azacyclophanes [12], and tetradeятate dithioglyoximes [13] have been used as sensitive coating for the recognition of the organic solvent molecules.

In this study, eight new 5-(quinolinylmethylene) barbituric acid derivatives were synthesized via Knoevenagel reaction of quinoline-2-, quinoline-4-, 6-methylquinoline-2-, and 4,6-dimethylquinoline-2-carboxaldehyde with 1,3-dimethylbarbituric acid and 1,3-diethyl-2-thiobarbituric acid, respectively [14, 15] (Scheme 1). The temperature dependence of both d.c. and a.c. electrical conductivity of the *Pc* films were assessed in temperature range of 295–440 K to determine the carrier transport mechanism in the films. Sensing properties of the films towards VOC vapors were also explored as a function of temperature.

2. Results and Discussion

2.1. Synthesis and Characterization. Structural assignments of the obtained products were based on their spectral properties and elemental analyses. The IR spectra of all compounds **1–8** showed the presence of the C=O stretching of N-C=O groups. In addition, the IR spectra of **5–8** also indicated the presence of C=O stretching of N-CO-N group of pyrimidinetrione ring. But **1–4** showed the absence of any C=O stretching absorption of N-CO-N, while they showed the presence of C=S group stretching of 2-thioxopyrimidine-4,6-dione. The molecular masses and the fragments determined for **1–8**, rule out the possibility of the existence of the bispyrimidinylmethane structure and indicated that their formation was only accompanied by the elimination of one water molecule.

¹H NMR spectra of **1–4** revealed a triplet and a quartet for the protons of N-CH₂CH₃ groups. Besides, the singlets for the N-CH₃ protons of **5–8** appeared at their spectra. On the other hand, ¹H NMR spectra of **3**, **4**, **6**, and **7** showed a singlet for the **6** CH₃ group of the quinolinyl ring. Similarly, compound **4** revealed an additional singlet for the **4** CH₃ group of the ring. Moreover, PMR spectra of **1–8** indicated a singlet due to the methine proton. The ¹³C NMR data were in accordance with the expected structures of the compounds and they showed the carbon atoms of the C=O groups and the carbon atom of the C=S group at their special regions. On the other hand, the signals for the N-CH₃ carbon atoms of the barbiturate structures **5–7** and the carbon atoms of N-CH₂CH₃ groups of 2-thiobarbiturate moiety of the compounds appeared in their spectra. Furthermore, the ¹³C NMR spectra of **1–8** showed the typical signals of vinylic carbon atoms.

3. Electrical and Gas Sensing

The study of the temperature dependence of the electrical conductivity during heating may provide valuable information on process taking place in the film. In this connection, direct current (d.c.) conductivity studies were done on the film of **1–8**. These studies were carried out in the temperature range 295–440 K in vacuum of $\leq 10^{-3}$ mbar to avoid

contamination. Conductivity values were calculated from the measured current-voltage (*I*-V) characteristics by using the following relation (1):

$$\sigma_{\text{d.c.}} = \frac{I}{V} \frac{d}{(2n - l)l \cdot h}, \quad (1)$$

where *I* is the measured current, *V* is the bias voltage, *d* is the electrode spacing, *n* is the number of electrode finger pairs, *l* is the overlap length of the electrode fingers, and *h* is the thickness of the electrodes. Current-voltage measurements were carried out after the film deposition and as the temperature was increased, so that conduction arising from impurity levels are not expected. Figure 1 shows the variation of d.c. conductivity of compounds **1–8** as a function of reciprocal temperature in the temperature range 295–440 K. The order of electrical conductivities obtained is **7 > 3 > 8 > 4 > 6 > 2 > 1 > 5** for all temperatures investigated. The well defined straight line obtained from the Arrhenius plot suggests the presence of only one conduction mechanism, assuming that the dominant levels are the conduction and valence bands, in the temperature range of 295–440 K for all films. In this case, the temperature dependence of conductivity can be represented by the well known expression

$$\sigma_{\text{d.c.}} = \sigma_0 \exp\left(\frac{-E_A}{kT}\right), \quad (2)$$

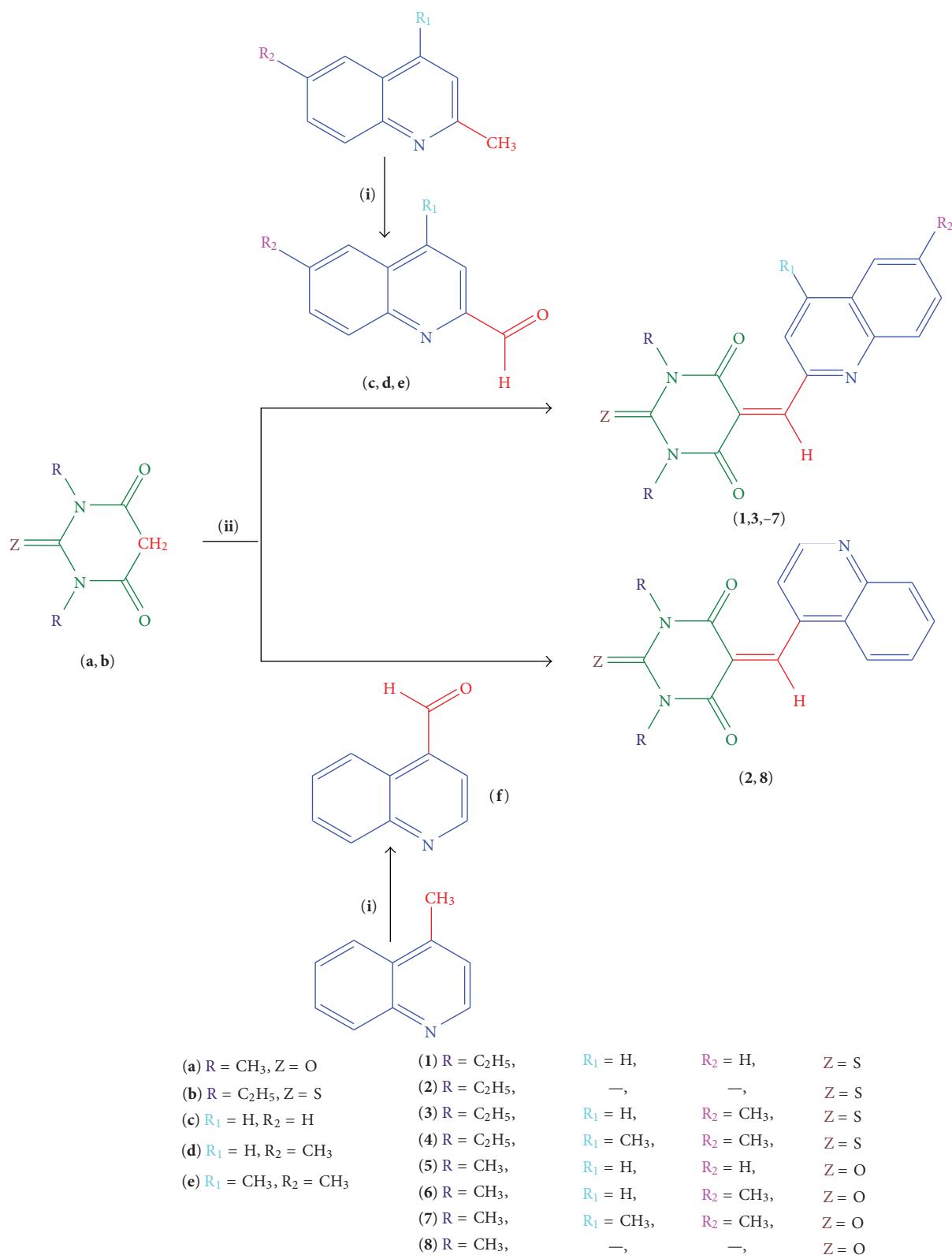
where *E_A* is the thermal activation energy of the electrical conduction, *T* is temperature, *k* is Boltzmann's constant, and σ_0 is a parameter depending on the semiconductor nature. The value of activation energy was derived from the slope of the ln ($\sigma_{\text{d.c.}}$) versus 1/*T* graph is 0.70, 0.74, 0.85, 0.82, 0.68, 0.77, 0.90, 0.84 eV for the compounds **1–8**, respectively.

It is known that the electrical conductivity of the compounds strongly depends on the interplanar spacing and the stacking direction of the molecules. The difference between the electrical behavior of compounds can be attributed to the differences in the stacking arrangements.

The a.c. electrical conductivity measurements were also performed on thin films of compounds in the frequency range 40–10⁵ Hz. at temperatures between 295 K and 440 K. Figure 2 shows the frequency dependence of the measured a.c. conductivity at 385 K for the films of **1–8**. A considerable number of experimental data concerning the frequency dependent conductivity of a large variety of materials can be found in the literature. There is a generally accepted view that the relation between the measured a.c. conductivity and frequency is given as

$$\sigma_{\text{a.c.}} = A\omega^s, \quad (3)$$

where *A* is constant and *ω* is the angular frequency. In spite of the absence of a satisfactory model describing a.c. transport in organic films, quantum mechanical tunnelling (QMT) and hopping models for the frequency response still appear to be adequate. In the QMT model an electron passes through a potential energy barrier without acquiring enough energy to pass over the top of the barrier. This model suggest



SCHEME 1: Synthesis of compounds **1–8**. **(i)** Dioxane, SeO_2 , 2 h, reflux. **(ii)** MeOH, 3 h, reflux.

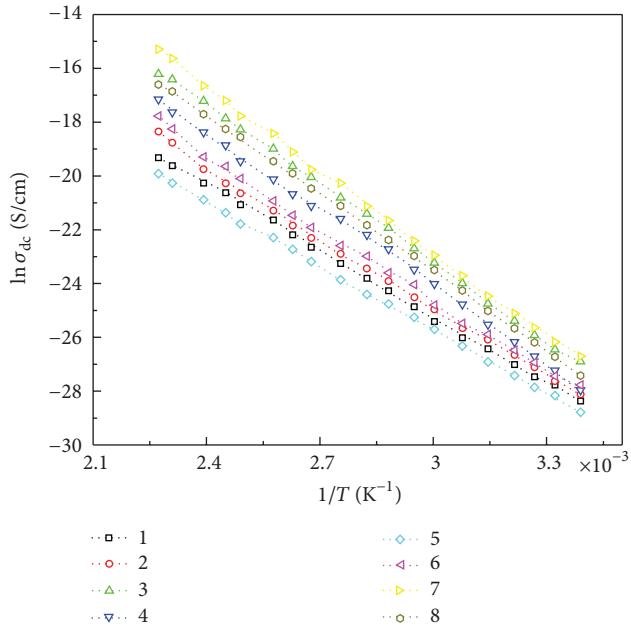


FIGURE 1: Temperature dependence of d.c. conductivity for spin coated film of compounds **1–8**.

a temperature independent frequency exponent s which is given by

$$s = 1 - \frac{4}{\ln(\omega\tau_0)}, \quad (4)$$

On the other hand, the hopping model predicts a temperature dependent frequency exponent s which is given by

$$s = 1 - \frac{6kT}{W_{OB} + kT \ln(\omega\tau_0)}, \quad (5)$$

where W_{OB} is the optical band gap, τ_0 a characteristic relaxation time, and k Boltzmann's constant.

To investigate the conduction mechanism involved the variation of the exponent s with temperature were examined. Values of the frequency exponent s were calculated from the straight-line fits in the logarithmic conductivity versus frequency plot. The obtained results showed that s is definitely a function of temperature for all samples measured and shows a general tendency to increase with decreasing temperature. The temperature dependence of the calculated s values is an indication of hopping conduction.

In order to determine the optimum operating temperature and the additive amount, responses of the films of **1–8** sensors to VOC vapors in dry nitrogen were examined as a function of operating temperature. It is well known that the adsorption of the gas molecules on the surface of a film plays an important role in the change of physical or chemical properties of these materials.

The effect of the various concentrations (200 to 1000 ppm) of toluene vapors on the conductivity of the **6** coated interdigital transducer (IDT) is shown in Figure 3 at indicated temperatures. During the gas sensing

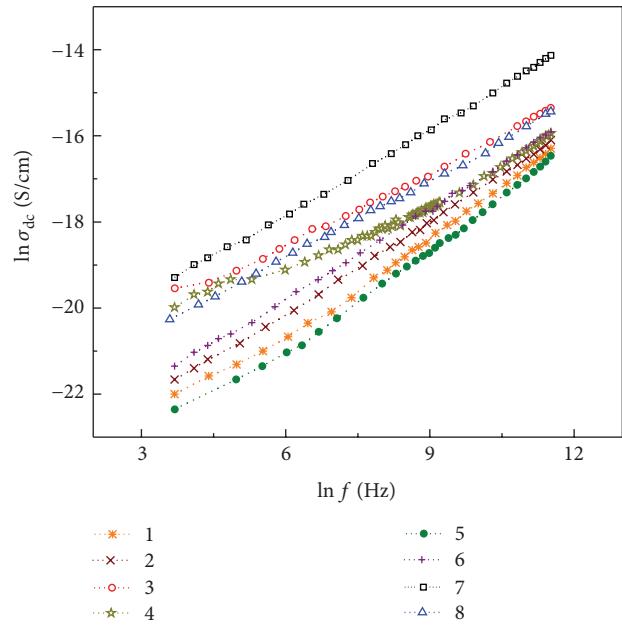


FIGURE 2: Frequency dependent conductivity of the spin coated films of compounds at 385 K.

measurements, the film was exposed to toluene vapors repeatedly. Each cycle of exposure lasted for 10 min, followed by recovery in dry nitrogen for another 10 min. It is clearly seen that the current increased sharply in the initial doping stage for a few minutes and the rate of increase slowed down. Although a complete steady-state current cannot be approached during a period of 10 min, the increase in current is adequate to indicate the presence of toluene gas in the atmosphere. After several minutes' exposure to toluene vapors, purging with dry nitrogen leads to an initial fast decrease followed by a slow drift that the current reaches its initial value after the toluene gas is turned off, and this proves that the adsorption processes are reversible. The obtained response characteristics of the film of **6** can be explained as follows. The adsorption of a toluene molecule on the film surface leads to the creation of acceptor level. These states are located near the surface and extend into the bulk if diffusion takes place. These acceptor states, which lie below the Fermi level at the initial stage of adsorption, make the trapping of valence electrons easy. When the number of the trapped electrons reaches to a sufficient value Fermi level shifts toward the valence band. This shift in the Fermi level causes the reduction in the speed of trapping processes and the rate of increase in current slows down. When the sensor is then exposed to dry nitrogen it leads to desorption of adsorbed toluene molecules from the surface of the active sensing layer, decreasing the acceptor concentration and thus the current.

It was found that the sensitivities of the films to toluene greatly depended on the operating temperature. For the film of **6**, the highest sensitivities to toluene vapors were obtained at around 360 K. The sensitivity has been related to the surface area and the adsorption sites on the film surface. The present

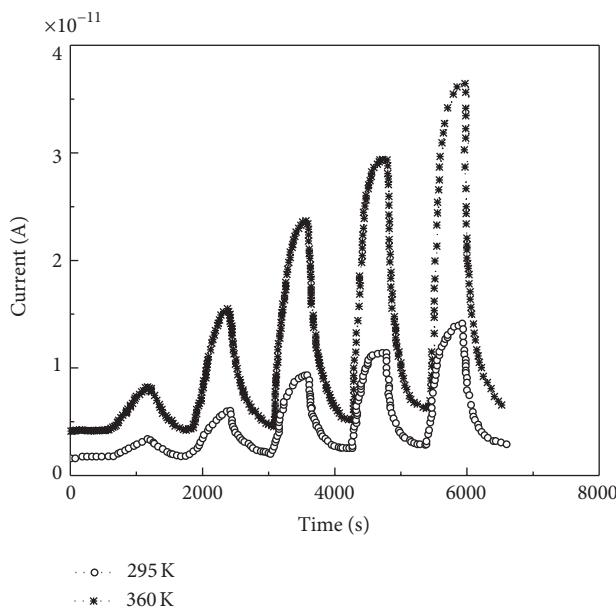


FIGURE 3: Response characteristics of **6** coated IDT on exposure to 5 different concentrations of toluene vapors.

result indicates that the increase of temperature gives rise to enhanced active adsorption sites of the film surface.

4. Conclusion

Elemental analyses results and IR, UV-Vis, ^1H NMR, ^{13}C NMR, and mass spectral data of the compounds confirm the proposed structures. The d.c. results showed that the order of electrical conductivities obtained is $7 > 3 > 8 > 4 > 6 > 2 > 1 > 5$ for all temperatures investigated. The response characteristics of the other film to VOC vapors were also investigated as a function of operating temperature. But we could not get any response to VOC vapors. In summary, all the observations demonstrate that the film of **6** would be a promising sensor element for the detection of toluene due to high sensitivity, selectivity, and quick response characteristics.

5. Experimental Section

5.1. Materials. 2-Methyl-, 4-methyl-, and 2,6-dimethylquinoline were obtained commercially and 2,4,6-trimethylquinoline was prepared according to a reported procedure [16]. Barbituric acid derivatives were purchased from commercial sources (Fluka and Acros) and were used without further purification. Solvents were distilled prior to reactions. All reported yields correspond to yields of purified products.

5.2. Equipments. Melting points were determined in a Galenkamp melting point apparatus. Absorption spectra were obtained on an Unicam UV-Vis spectrophotometer. IR spectra were recorded on a Shimadzu IR 9300 spectrophotometer (KBr pellets). ^1H NMR and ^{13}C NMR spectra were recorded on Varian 200 MHz Gemini and Varian 400 MHz Mercury

spectrophotometers and chemical shifts are given in ppm downfield from TMS as the internal standard. Mass spectra were acquired on a Shimadzu GC/MS QP 2000 A instrument. Elemental analyses were performed on a Thermoplast Flash EA 1112 CHNS elemental analyzer.

5.3. Synthesis. Quinolinecarboxaldehydes used in the reactions were prepared by the oxidation of 2-methylquinoline [17], 4-methylquinoline [18], 2,6-dimethylquinoline [17] and 2,4,6-trimethylquinoline [19] with selenium dioxide, which is a mild oxidant, in the medium of 1,4-dioxane.

5.3.1. General Procedure for **1–8** [14, 15]. Synthesis of the compounds **1–8** (Scheme 1) is presented as follows: A mixture of quinolinecarboxaldehyde (1.0 mmol) (**c–f**) and appropriate amount of barbituric acid derivative (1.0 mmol) (**a, b**) was heated by stirring in methanol (25 mL) at reflux temperature for 3 h. The progress of the reaction was monitored by TLC using n-hexane/ethyl acetate (1/1) as eluent. Upon completion of the reaction, the crude product which precipitated on cooling was collected by filtration. Further purification was accomplished by recrystallisation from methanol.

5.3.2. 1,3-Diethyl-5-(quinolin-2-ylmethylene)-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (1). Yellowish-orange brilliant needles. Yield 61% (0.21 g). M.p. 229°C. FTIR (KBr): $\bar{\nu} = 3066, 3031, 2977, 2931, 2904, 1613, 1542, 1488, 1438, 1384, 1269, 1107, 790, 775 \text{ cm}^{-1}$. UV (CHCl_3): $\lambda_{\text{max}} = 241, 297 \text{ nm}$. ^1H NMR (CDCl_3): $\delta = 1.14$ (t, 6 H, $2 \times \text{CH}_3$), 4.38 (m, 4 H, $2 \times \text{CH}_2$), 6.59 (s, 1 H, C=CH), 7.71 (d, $^3J_{3'4'} = 8.6 \text{ Hz}$, 1 H, $3'$ -H), 7.78 (t, $^3J_{5'6'} = ^3J_{6'7'} = 8.4 \text{ Hz}$, 1 H, $6'$ -H), 7.91 (t, $^3J_{7'8'} = 8.4 \text{ Hz}$, 1 H, $7'$ -H), 8.04 (d, 1 H, $5'$ -H), 8.20 (d, 1 H, $4'$ -H), 8.62 (d, 1 H, $8'$ -H) ppm. ^{13}C NMR (CDCl_3): $\delta = 12.4$ ($2 \times \text{CH}_3$), 44.2 ($2 \times \text{CH}_2$), 121.9–133.9 (C5, C3', C4', C5', C6', C7', C8' and C10'), 139.4 (C=CH), 144.1 (C9'), 160.0 (C2'), 162.4 (C4 and C6), 175.7 (C2) ppm. MS (EI) m/z : 341(M+2), 340 (M+1), 339 (M $^+$), 311, 310, 296, 278, 252, 251, 250, 239, 209, 195, 186, 181, 168, 153, 128, 115. Anal. calcd. for $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$; C, 63.70; H, 5.05; N, 12.38; S, 9.45. Found: C, 63.37; H, 4.78; N, 12.40; S, 9.72.

5.3.3. 1,3-Diethyl-5-(quinolin-4-ylmethylene)-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (2). Yellow rods. Yield 70% (0.23 g). M.p. 248–249°C. FTIR (KBr): $\bar{\nu} = 3085, 3055, 2974, 2927, 1616, 1542, 1434, 1384, 1269, 1110, 779, 744 \text{ cm}^{-1}$. UV (CHCl_3): $\lambda_{\text{max}} = 239, 271, 297 \text{ nm}$. ^1H NMR (DMSO-d_6): $\delta = 1.12$ (t, 6 H, $2 \times \text{CH}_3$), 4.41 (m, 4 H, $2 \times \text{CH}_2$), 7.00 (s, 1 H, C=CH), 7.83 (t, $^3J_{5'6'} = ^3J_{6'7'} = 8 \text{ Hz}$, 1 H, $6'$ -H), 7.85 (d, $^3J_{2'3'} = 5.5 \text{ Hz}$, 1 H, $3'$ -H), 8.03 (t, $^3J_{7'8'} = 8.2 \text{ Hz}$, 1 H, $7'$ -H), 8.16 (d, 1 H, $5'$ -H), 8.25 (d, 1 H, $8'$ -H), 9.08 (d, 1 H, $2'$ -H) ppm. ^{13}C NMR (DMSO-d_6): $\delta = 12.8$ ($2 \times \text{CH}_3$), 43.8 ($2 \times \text{CH}_2$), 95.8–129.9 (C5, C3', C5', C6', C7', C8' and C10'), 134.4 (C2'), 138.4 (C=CH), 144.8 (C9'), 161.9 (C4'), 162.4 (C4 and C6), 175.2 (C2) ppm. MS (EI) m/z : 341 (M+2), 340 (M+1), 339 (M $^+$), 311, 310, 306, 283, 254, 252, 210, 209, 199, 186, 182, 181, 169, 154, 153, 142, 128, 127, 116. Anal. calcd. for

$C_{18}H_{17}N_3O_2S$; C, 63.70; H, 5.05; N, 12.38; S, 9.45. Found: C, 63.82; H, 4.75; N, 12.38; S, 9.24.

5.3.4. 1,3-Diethyl-5-[(6-methylquinolin-2-yl)methylene]-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (3). Orange needles. Yield 61% (0.22 g). M.p. 223°C. FTIR (KBr): \bar{v} = 3109, 3035, 2977, 2931, 2904, 1616, 1542, 1496, 1438, 1384, 1269, 1107, 790, 775 cm⁻¹. UV (CHCl₃): λ_{\max} = 243, 296 nm. ¹H NMR (CDCl₃): δ = 1.13 (t, 6 H, 2 \times CH₃), 2.59 (s, 3 H, 6'-CH₃), 4.37 (m, 4 H, 2 \times CH₂), 6.62 (br.s, 1 H, C=CH), 7.66 (d, ³J_{3'4'} = 8.8 Hz, 1 H, 3'-H), 7.72 (d, ³J_{7'8'} = 8.6 Hz, 1 H, 7'-H), 7.80 (s, 1 H, 5'-H), 8.08 (d, 1 H, 4'-H), 8.53 (d, 1 H, 8'-H) ppm. ¹³C NMR (CDCl₃): δ = 12.4 (2 \times CH₃), 21.9 (6'-CH₃), 44.1 (2 \times CH₂), 121.4–137.9 (C5, C3', C4', C5', C6', C7', C8' and C10'), 139.8 (C=CH), 143.5 (C9'), 160.8 (C2'), 162.4 (C4 and C6), 175.6 (C2) ppm. MS (EI): *m/z*: 355 (M+2), 354 (M+1), 353 (M⁺), 325, 324, 296, 281, 266, 253, 224, 223, 210, 209, 195, 181, 167, 158, 157, 142, 116. *Anal.* calcd. for $C_{19}H_{19}N_3O_2S$; C, 64.57; H, 5.42; N, 11.89; S, 9.07. Found: C, 64.65; H, 5.76; N, 11.80; S, 9.28.

5.3.5. 1,3-Diethyl-5-[(4,6-dimethylquinolin-2-yl)methylene]-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (4). Orange plates. Yield 25% (0.07 g). M.p. 286°C. FTIR (KBr): \bar{v} = 3070, 3047, 2974, 2927, 2904, 1627, 1542, 1434, 1411, 1388, 1269, 1103, 783 cm⁻¹. UV (CHCl₃): λ_{\max} = 245, 303 nm. ¹H NMR (CDCl₃): δ = 1.35 (t, 6 H, 2 \times CH₃), 2.61 (s, 3 H, 6'-CH₃), 2.75 (s, 3 H, 4'-CH₃), 4.63 (m, 4 H, 2 \times CH₂), 6.00 (s, 1 H, C=CH), 7.50 (s, 1 H, 3'-H), 7.77 (d, ³J_{7'8'} = 8.6 Hz, 1 H, 7'-H), 7.82 (br.s, 1 H, 5'-H), 8.09 (d, 1 H, 8'-H) ppm. ¹³C NMR (CDCl₃): δ = 11.7 and 12.8 (2 \times CH₃), 19.5 (4'-CH₃), 21.9 (6'-CH₃), 42.8 and 43.1 (2 \times CH₂), 91.0–139.4 (C5, C3', C5', C6', C7', C8' and C10'), 139.3 (C=CH), 152.6 (C4'), 159.7 (C9'), 161.3 (C2'), 163.3 (C4 and C6), 175.8 (C2) ppm. MS (EI) *m/z*: 369 (M+2), 337, 336, 296, 282, 281, 267, 238, 237, 211, 210, 209, 183, 182, 181, 171, 170, 158, 157, 156, 128, 115. *Anal.* calcd. for $C_{20}H_{21}N_3O_2S$; C, 65.37; H, 5.76; N, 11.44; S, 8.73. Found: C, 65.43; H, 6.07; N, 11.56; S, 8.60.

5.3.6. 1,3-Dimethyl-5-(quinolin-2-ylmethylene)pyrimidine-2,4,6(1H,3H,5H)-trione (5). Yellowish-orange brilliant needles. Yield 33% (0.10 g). M.p. 248–249°C. FTIR (KBr): \bar{v} = 3066, 3030, 2954, 2931, 1681, 1608, 1515, 1454, 1384, 771, 740 cm⁻¹. UV (CHCl₃): λ_{\max} = 242, 320 nm. ¹H NMR (CDCl₃): δ = 2.92 (s, 3 H, 1-CH₃), 3.35 (s, 3 H, 3-CH₃), 6.03 (s, 1 H, C=CH), 7.69 (d, ³J_{3'4'} = 8.4 Hz, 1 H, 3'-H), 7.73 (t, ³J_{5'6'} = ³J_{6'7'} = 8 Hz, 1 H, 6'-H), 7.95 (t, ³J_{7'8'} = 8 Hz, 1 H, 7'-H), 7.97 (d, 1 H, 5'-H), 8.23 (d, 1 H, 4'-H), 8.38 (d, 1 H, 8'-H) ppm. ¹³C NMR (CDCl₃): δ = 27.3 (2 \times CH₃), 119.6–132.3 (C5, C3', C4', C5', C6', C7', C8' and C10'), 136.7 (C=CH), 146.6 (C9'), 149.9 (C2), 150.5 (C2'), 160.9 (C4 and C6) ppm. MS (EI) *m/z*: 297 (M+2), 296 (M+1), 282, 268, 239, 209, 183, 182, 181, 169, 167, 155, 154, 153, 143, 142, 129, 128, 115. *Anal.* calcd. for $C_{16}H_{13}N_3O_3$; C, 65.08; H, 4.44; N, 14.23. Found: C, 64.95; H, 4.65; N, 14.22.

5.3.7. 1,3-Dimethyl-5-[(6-methylquinolin-2-yl)methylene]pyrimidine-2,4,6(1H,3H,5H)-trione (6). Orange needles. Yield 45% (0.14 g). M.p. 252–253°C. FTIR (KBr): \bar{v} = 3047, 3101, 2954, 1681, 1612, 1508, 1454, 1384, 775 cm⁻¹. UV (CHCl₃): λ_{\max} = 244, 320 nm. ¹H NMR (CDCl₃): δ = 2.59 (s, 3 H, 6'-CH₃), 2.93 (s, 3 H, 1-CH₃), 3.33 (s, 3-CH₃, 3 H), 5.99 (s, 1 H, C=CH), 7.64 (d, ³J_{3'4'} = 8.4 Hz, 1 H, 3'-H), 7.70 (br.s, 1 H, 5'-H), 7.76 (d, ³J_{7'8'} = 8.8 Hz, 1 H, 7'-H), 8.11 (d, 1 H, 4'-H), 8.27 (d, 1 H, 8'-H) ppm. ¹³C NMR (CDCl₃): δ = 21.9 (6'-CH₃), 27.9 and 28.2 (2 \times CH₃), 122.4–137.2 (C5, C3', C4', C5', C6', C7', C8' and C10'), 139.4 (C=CH), 141.6 (C9'), 152.8 (C2), 162.1 (C2'), 163.6 and 164.7 (C4 and C6) ppm. MS (EI) *m/z*: 311 (M+2), 310 (M+1), 296, 282, 268, 253, 224, 223, 196, 195, 169, 168, 167, 157, 143, 142, 127, 115. *Anal.* Calcd. for $C_{17}H_{15}N_3O_3$; C, 66.01; H, 4.89; N, 13.58. Found: C, 65.97; H, 5.17; N, 13.61.

5.3.8. 1,3-Dimethyl-5-[(4,6-dimethylquinolin-2-yl)methylene]pyrimidine-2,4,6(1H,3H,5H)-trione (7). Orange ball crystals. Yield 18% (0.06 g). M.p. 249–250°C. FTIR (KBr): \bar{v} = 3055, 2981, 2943, 1674, 1608, 1558, 1512, 1446, 1369, 786, 775 cm⁻¹. UV (CHCl₃): λ_{\max} = 244, 313 nm. ¹H NMR (CDCl₃): δ = 2.60 (s, 3 H, 6'-CH₃), 2.74 (s, 3 H, 4'-CH₃), 3.02 (s, 3 H, 1-CH₃), 3.24 (s, 3 \times CH₃, 3 H), 6.02 (s, 1 H, C=CH), 7.54 (s, 1 H, 3'-H), 7.74 (d, ³J_{7'8'} = 8.6 Hz, 1 H, 7'-H), 7.80 (s, 1 H, 5'-H), 8.12 (d, 1 H, 8'-H) ppm. ¹³C NMR (CDCl₃): δ = 19.69 (4'-CH₃), 22.13 (6'-CH₃), 27.85 (1-CH₃), 29.91 (3-CH₃), 85.72–135.8 (C5, C3', C5', C6', C7', C8' and C10'), 139.2 (C=CH), 152.9 (C4'), 153.0 (C9'), 160.8 (C2), 164.0 (C2'), 164.7 (C4 and C6) ppm 19.69, 22.13, 27.9, 29.9, 85.7, 122.3, 123.7–153.3, 160.8, 164.7 ppm. MS (EI) *m/z*: 325 (M+2), 324 (M+1), 310, 296, 282, 267, 253, 238, 237, 210, 209, 183, 182, 181, 171, 157, 156, 142, 128, 115, 114. *Anal.* calcd. for $C_{18}H_{17}N_3O_3$; C, 66.86; H, 5.30; N, 13.00. Found: C, 66.68; H, 5.22; N, 12.74.

5.3.9. 1,3-Dimethyl-5-(quinolin-4-ylmethylene)pyrimidine-2,4,6(1H,3H,5H)-trione (8). Yellow ball crystals. Yield 29% (0.08 g). M.p. 218–219°C. FTIR (KBr): \bar{v} = 3116, 3035, 2954, 2889, 1681, 1604, 1562, 1504, 1442, 1427, 1380, 794, 756 cm⁻¹. UV (CHCl₃): λ_{\max} = 242, 262, 318 nm. ¹H NMR (DMSO-d₆): δ = 3.08 (s, 6 H, 2 \times CH₃), 6.95 (s, 1 H, C=CH), 7.83 (t, ³J_{5'6'} = ³J_{6'7'} = 8.2 Hz, 1 H, 6'-H), 7.90 (d, ³J_{2'3'} = 5.5 Hz, 1 H, 3'-H), 8.01 (t, ³J_{7'8'} = 8.4 Hz, 1 H, 7'-H), 8.13 (d, 1 H, 5'-H), 8.35 (d, 1 H, 8'-H), 9.06 (d, 1 H, 2'-H) ppm. ¹³C NMR (DMSO-d₆): δ = 28.46 (1-CH₃), 28.73 (3-CH₃), 90.21–129.8 (C5, C3', C5', C6', C7', C8' and C10'), 134.1–144.4 (C2', C=CH, C9' and C4'), 151.8 (C2), 163.4 (C4 and C6) ppm 28.46 (1-CH₃), 28.73 (3-CH₃), 90.21–129.8 (C5, C3', C5', C6', C7', C8' and C10'), 134.1–144.4 (C2', C=CH, C9' and C4'), 151.8 (C2), 163.4 (C4 and C6) ppm. MS (EI) *m/z*: 297 (M+2), 296 (M+1), 295 (M⁺), 280, 238, 237, 210, 209, 182, 181, 154, 153, 143, 142, 129, 128, 115. *Anal.* calcd. for $C_{16}H_{13}N_3O_3$; C, 65.08; H, 4.44; N, 14.23. Found: C, 65.17; H, 4.51; N, 14.30.

5.4. Electrical and Gas Sensing Measurements. The measurement electrodes used in the conductivity and gas sensing measurements consist of an interdigital array of metal electrodes photolithographically patterned on precleaned glass substrate. Glass substrates were thoroughly cleaned ultrasonically and then coated with 100 Å of chromium followed by 1200 Å of gold in an Edwards Auto 500 coater system. The film patterned photolithographically and etched to provide 10 finger pairs of electrodes having a width of 100 µm spaced 100 µm from the adjacent electrodes. A thin film of compounds was prepared by spin coating method on gold interdigital electrodes (IDT). For the spin coating, coating solutions were prepared by dissolving of the compounds in appropriate solvents at concentration of 1.10^{-3} M. Twenty microliters of such solutions were added with a glass pipette onto the IDT structure held onto spinner (Speciality Coatings Systems Inc., Model P6700 Series). The substrate spun at 2000 rpm for 30 s and the solvent had evaporated during this period, producing a homogeneous film of compounds. D.c. conductivity measurements were performed between 300 K and 440 K by using a Keithley 617 electrometer. A.c. conductivity measurements were carried out with a Keithley 3330 LCZ meter in the frequency range, 40– 10^5 Hz, and in the temperature range from 295 K to 440 K. All the measurements were performed under 10^{-3} mbar in the dark.

The effect of the VOC vapors on the conductivity of the films was measured in a homemade teflon chamber implemented in our laboratory where dry nitrogen was used as carrier gas. After each compound sensor in the chamber was stable, it was exposed to five different concentrations of the target gases. The test gas was mixed with dry nitrogen using computer driven mass flow controllers (MKS Inst.). A typical experiment consisted of exposure to test gases and subsequent purging with dry nitrogen. Both conductivity and gas sensing data were recorded using an IEEE 488 data acquisition system incorporated to a personal computer.

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