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Thermal and optical properties of benzofuran-2-yl 3-phenyl-3-methylcyclobutyl thiosemicarbazone

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Abstract

The thermal degradation of the benzofuran-2-yl 3-phenyl-3-methylcyclobutyl thiosemicarbazone (CBSC) was studied under air atmosphere using DSC and simultaneous TG/DTA at the temperature range 20–500 °C. Thermal melting activation energy which are 308.6 and 307.9 kJ/mol were evaluated using Kissinger method from DSC and DTA curves, respectively. The activation energy of thermal decomposition was calculated using the Ozawa method for two decomposition stages. The experimental results showed that the activation energy of decomposition for non-isothermal behavior are 123.8 and 135.2 kJ/mol for the first (at 5% weight loss) and second (at 20% weight loss) decomposition stages, respectively. By using hot probe method, electrical conduction mechanism of CBSC was found as p-type. The values of thermal activation energy of electrical conduction, E_1 and E_2 , as calculated from $\ln \sigma = f(1000/T)$ curves, were found to be 3.90 and 0.36 eV, respectively. Optical absorption studies in the wavelength range 190–900 nm showed that direct optical band gap of the benzofuran-2-yl 3-phenyl-3-methylcyclobutyl thiosemicarbazone is 2.80 eV.

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Keywords: Thermal activation energy; Optical band gap; Benzofuran; Cyclobutane

1. Introduction

In recent years, the investigations on the electrical conduction mechanism in organic compounds have been much intensified [1]. This is mainly due to attracting properties of organic semiconductors for the technology of solid state devices [1–4]. Electrically conducting and semi-conducting organic compounds have been a subject of extensive studies in view of both academic interest and potential technological applications [5]. Organic semiconductors can conduct charges due to partial delocalization or charge hopping through the molecules [6,7]. A number of organic-based PV cells, including organic/inorganic hybrid configurations, have been investigated [8–10]. Recently, the study on the thermal properties of heterocyclic compounds is attracting amount of researchers due to the compounds' compact and stable structure [11].

In this the paper, the thermal melting and thermal decomposition activation energies, electrical conductivity,

optical band gap of benzofuran-2-yl 3-phenyl-3-methylcyclobutyl thiosemicarbazone (CBSC) were investigated.

2. Experimental procedure

2.1. The synthesis of benzofuran-2-yl 3-phenyl-3-methylcyclobutyl thiosemicarbazone

In the light of the above observation, we have selected 1-aryl-1-methyl-3-(2-chloro-1-oxoethyl cyclobutane as the starting compound, which were synthesized according to the literature procedure published previously [12]; 10 mmol (2.225 g) of 1-phenyl-1-methyl-3-(2-chloro-1-oxoethyl) cyclobutane, 15 mmol (2.07 g) K_2CO_3 and 11 mmol (1.342 g) salicylic aldehyde were stirred in 100 ml of acetonitrile and were refluxed for 8 h. The mixture was cooled, filtrated and the solvent was evaporated. It was washed a few times. Then, it was crystallized in ethanol. And then, a mixture of ketone 1.933 g (6.7 mmol), 0.6075 g (6.7 mmol) thiosemicarbazide, 0.01 mg *p*-toluene sulfonic acid monohydrate in absolute ethanol (100 ml) was refluxed

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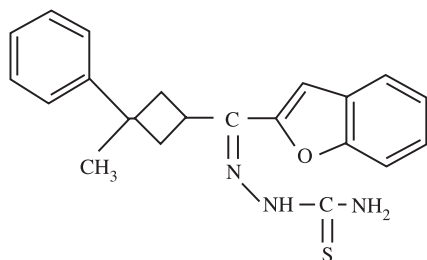


Fig. 1. The chemical structure of the CBSC compound.

for 12 h. It was left to cool, filtered, washed with water, dried and crystallized from ethanol to give pale yellow crystals (yield, 94%). The structure analysis of these was given in the literature [12]. The chemical structure of synthesized compound is given in Fig. 1 and it was shortly called as CBSC.

2.2. Physical measurements

IR analysis was performed using a Mattson 1000 FT-IR spectrometer. ^1H and ^{13}C -NMR spectra were recorded on a Gemmini Varian 200 MHz spectrometer.

The thermal behavior of the CBSC was investigated using a Perkin Elmer Sapphire DSC and Perkin Elmer Pyris Diamond TG/DTA. The instrument was calibrated using the melting point of high purity indium. All the DSC and TG/DTA experiments were performed with ~ 5 mg powder samples taken in crimped aluminum pans under air. The DSC curve was recorded in the temperature range of 20–300 °C for heating rates ranging from 5 to 20 °C/min. The TG/DTA curves were recorded in the temperature range of 20–500 °C for different heating rates ranging from 5 to 20 °C/min.

Electrical measurements were done using a Keithley 6514 System Electrometer and a Keithley 230 Programmable Voltage Source. Optical absorption spectra was recorded using a UV–VIS spectrophotometer (Perkin Elmer Lambda 2S Double Beam), in the wavelength range 190–1100 nm.

3. Results and discussion

3.1. Characterization studies

The CBSC sample was structurally characterized using FT-IR and ^1H and ^{13}C -NMR nuclear magnetic resonance [12].

3.2. Thermal properties

The DSC curves of the CBSC compound at heating rates ranging from 5 to 20 °C/min are shown in Fig. 2. The existence of the endothermic peaks in DSC curves is shown at temperature range 185–210 °C approximately. These endothermic peaks are relevant to melting peaks of CBSC compound.

The DTA curves were recorded in the temperature range of 20–500 °C for different heating rates ranging from 5 to 20 °C/min. Fig. 3a represents the DTA curves at 20–500 °C for 20 °C/min heating rate of CBSC compound. In the DTA plot in Fig. 3a, there is more than one peak. The first peak is related to melting, this peak's maximum is $T_m = 201.8$ °C, the other peaks correspond to the mass losses. The DTA curves for different heating rates ranging from 5 to 20 °C/min are shown in Fig. 3b.

Different methods are available in the literature for the calculation of the thermal activation energy values [13–17].

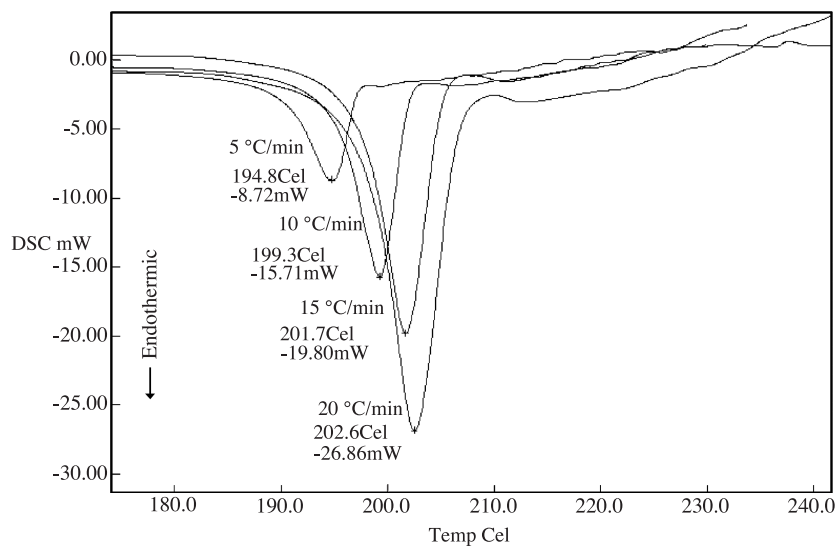


Fig. 2. DSC curves of the CBSC compound at heating rates ranging from 5 to 20 °C/min.

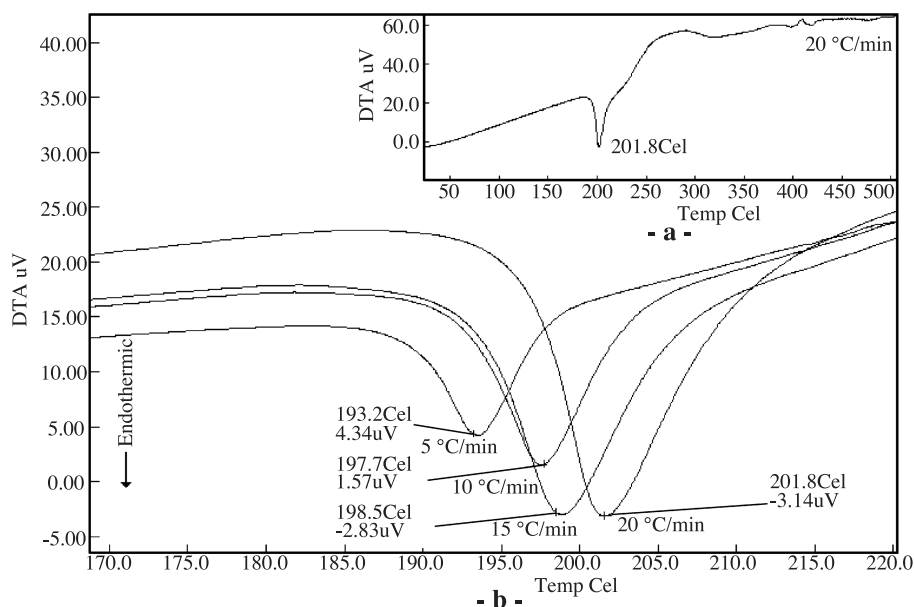


Fig. 3. (a) DTA curves of the CBSC compound at different heating rates ranging 5–20 °C/min under air flow, and (b) DTA curve of the CBSC at 20 °C/min heating rate at the 20–500 °C temperature range.

The melting activation energies, E_M , were obtained using the Kissinger method derived from dependence of the peak temperature, T_m , on the heating rate, Φ

$$d[\ln(\Phi/T_m^2)]/d(1/T) = -E_M/R \quad (1)$$

where E_M is the activation energy obtained from the Kissinger plot and R is the universal gas constant. Kissinger's plots, which were obtained from DSC and DTA curves of the CBSC compound, are presented in Fig. 4. The

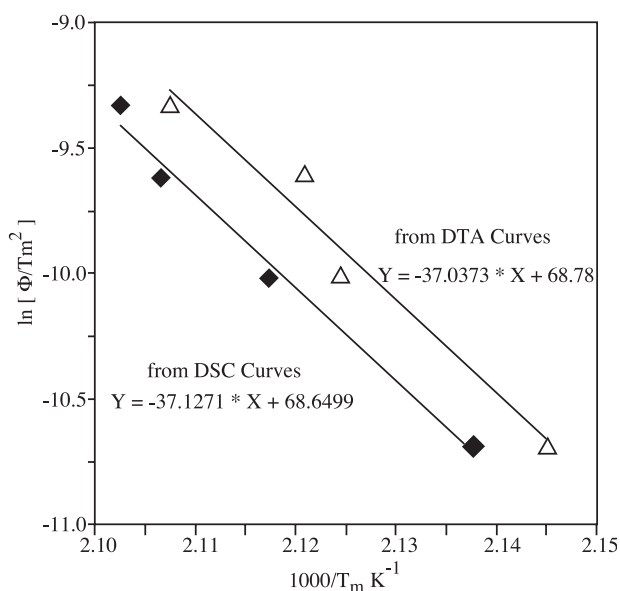


Fig. 4. Kissinger's plots of $\ln(\Phi/T_m^2)$ vs. $1/T_m$, for DSC curves and DTA curves of the CBSC compound.

calculated melting activation energy for DSC and DTA curves of the CBSC compound is 308.6 and 307.9 kJ/mol, respectively.

Thermal degradation curves of the CBSC sample obtained at different heating rates under air flow: 5, 10, 15, 20 °C/min are shown in Fig. 5. It can be seen that the weight loss is 40% at the temperature range of ~ 200–500 °C. The novel CBSC compound is thermal stable. As it can be seen from the TG curves of the CBSC sample in Fig. 5, the decomposition point appears at 199.9, 207.4, 211.5, 218.6 °C for 5, 10, 15 and 20 °C/min heating rates, respectively. The activation energy of thermal decomposition can be calculated by using the Ozawa method [15,16]. The decomposition activation energy, E_D , can be determined from the TG thermograms under various heating rates, such as in Fig. 6, and it is calculated from the following equation:

$$E_D = -\frac{R}{b} \left[\frac{d \log \beta}{d(1/T_d)} \right] \quad (2)$$

where b is a constant (0.4567) and T_d is absolute temperature (K). Ozawa's plot for the CBSC sample is presented in Fig. 6. The calculated thermal decomposition activation energy E_D for the CBSC is 123.8 and 135.2 kJ/mol for the first (at 5% weight loss) and second (at 20% weight loss) decomposition stages, respectively.

3.3. Electrical conductivity measurements

Hot probe method was used to find the type of charge carriers present in the film. When the film was heated with a

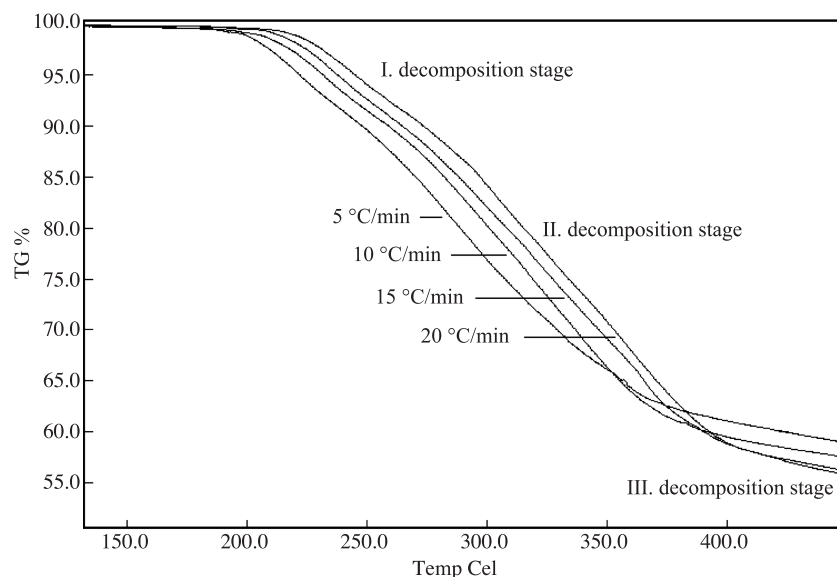


Fig. 5. TG curves of the CBSC compound at different heating rates ranging 5–20 °C/min under air flow at the 20–500 °C temperature range.

hot probe, charge carriers near the hot probe yielded higher velocities than those near the cold probe. This disturbs the equilibrium distribution of the charge carriers producing an electric field. The field will be positive with respect to the cold end if the charge carriers are electrons (n-type), and negative if the carriers are holes (p-type) [18–20]. By using this method, the charge carriers in the CBSC were found to be p-type.

Electrical conductivity studies were done to determine the thermal activation energy ΔE . According to thermal decomposition temperatures, electrical conductivity of the CBSC was measured at the range of 300–500 K temperature. It was found that the electrical conductivity values

increase with increasing temperature. The change in $\ln \sigma$ as a function of reciprocal temperature of CBSC is shown in Fig. 7. The activation energy of the CBSC is calculated from the slope of the Arrhenius plot of conductivity using the Arrhenius relation [18–20],

$$\sigma = \sigma_0 \exp(-\Delta E/kT) \quad (3)$$

where ΔE is the activation energy, σ_0 is a parameter depending on the semiconductor nature and k is the Boltzmann's constant. Activation energy is determined from Eq. (3) and $\Delta E = E_F - E_V$ for p-type semiconductor, where E_F and E_V are Fermi energy and valance band edge in the semicon-

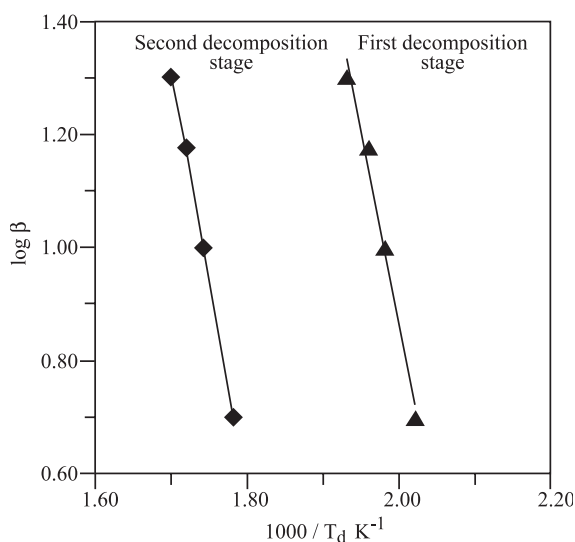


Fig. 6. Ozawa's plots of $\log(\beta)$ vs. $1000/T_d$ obtained from TG curves for the CBSC compound. The first (at 5% weight loss) and second (at 20% weight loss) decomposition stages are approximately the temperature range 200–290 and 290–370 °C, respectively.

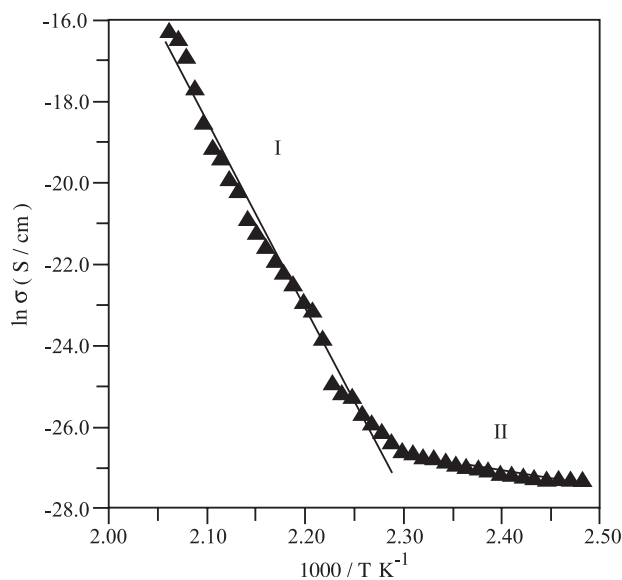


Fig. 7. The electrical conductivity of the CBSC compound in terms of Arrhenius theory.

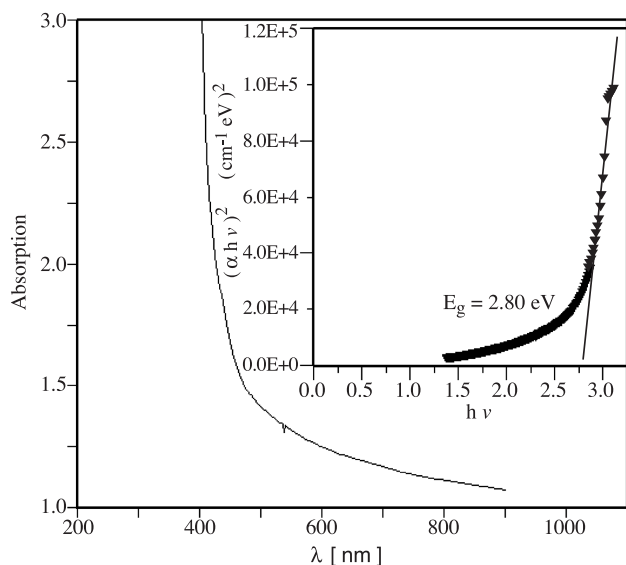


Fig. 8. The optical absorption spectra for the CBSC compound.

ductor, respectively. There are two linear regions for the plot in Fig. 7. We have reported two activation energies ΔE_1 and ΔE_2 above and below 435 K. The activation energies in the intrinsic region (ΔE_1) and impurity scattering region (ΔE_2) were found to be 3.90 and 0.36 eV, respectively.

3.4. Optical properties

The optical absorption spectrum of the CBSC sample was studied at UV–Visible range and it is shown in Fig. 8. The spectral variation is expressed by [20],

$$\alpha hv = A(hv - E_g)^n \quad (3)$$

where α is the linear absorption coefficient, ν is the frequency, h is Planck's constant and n depends on the kind of optical transition which it prevails. Specifically, n is 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. A is a parameter that depends on the transition probability and E_g is defined as the energy band gap between the valence band and the conduction band. We plotted $(\alpha hv)^2$ vs. (hv) photon energy using the data of absorption spectrum of these samples shown in Fig. 8. The optical energy band gaps of the direct transitions was evaluated from the intercept of the $(\alpha hv)^2$ vs. (hv) plots with the energy axis at $(\alpha hv)^2 = 0$ as shown in Fig. 8 and was found to be 2.80 eV. The magnitude of the activation energy obtained from conductivity data is different in comparison with optical band gap energy. This is due to the fact that their nature is different. While the activation energy corresponds to the energy required for conduction from one site to another, the optical band gap corresponds to interband transition [21].

4. Conclusions

The benzofuran-2-yl 3-phenyl-3-methylcyclobutyl thio-semicarbazone (CBSC) was synthesized and characterized. From the thermal analysis studies, it was found that CBSC sample has good thermal stability. The temperature dependence of the electrical conductivity was studied. The investigated CBSC sample has p-type semiconducting properties and it was found that it involves different conduction mechanism. In the high-temperature region, intrinsic conductivity by holes is found to contribute to the conduction process, whereas in the low-temperature range, impurity plays an active role. We concluded via the optical absorption measurement that the CBSC sample has direct optical band gap.

Acknowledgements

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References

- [1] L. Leontie, M. Roman, F. Brinza, C. Podaru, G.I. Rusu, *Synth. Met.* 138 (2003) 157.
- [2] L.S. Poman, M.R. Andersson, T. Johannes, O. Inganas, *Advanced Materials* 9 (1997) 1164.
- [3] G. Yu, J. Gao, J.C. Hummelen, F. Wudi, J. Heeger, *Science* 270 (1993) 1789.
- [4] P. Bertoncello, A. Notargiacomo, C. Nicolini, *Polymer* 45 (2004) 1659.
- [5] M. Ishihara, T. Noda, H. Kageyama, H. Nakano, Y. Shirato, *Synth. Metals* 120 (2001) 795.
- [6] H. Meier, *Organic Semiconductors: Dark and Photoconductivity of solids*, Verlag Chemie, Weinheim, 1974.
- [7] J.Y. Kim, A.J. Bard, *Chem. Phys. Lett.* 383 (2004) 11.
- [8] F.G. Gao, A.J. Bard, *Chem. Mater.* 14 (2002) 3465.
- [9] L. Schmidt-Mende, A. Fechtenkötter, K. Mullen, E. Moons, R.H. Friend, J.D. MacKenzie, *Science* 293 (2001) 1119.
- [10] W.U. Huynh, J.J. Dittmer, A.P. Alivisatos, *Science* 295 (2002) 2425.
- [11] J. Zhang, W. Liu, Q. Xue, *Wear* 231 (1999) 279.
- [12] M. Koca, *Synthesis of Ketone and Ketoxime Derivatives Containing Cyclobutane and Benzofuran Rings*, PhD Thesis, 2003, in Turkish.
- [13] J.A. Augis, J.E. Bennett, *Adv. Mater.* 13 (1978) 283.
- [14] H.E. Kissinger, *J. Res. Natl. Bur. Stand.* 57 (1956) 217.
- [15] T.J. Ozawa, *Therm. Anal.* 2 (1970) 301.
- [16] J.H. Flynn, L.A. Wall, *Polym. Lett.* 4 (1989) 323.
- [17] H.H. Horowitz, G. Metzger, *Anal. Chem.* 35 (1963) 1464.
- [18] G. Baburaya Kamath, C.M. Joseph, C.S. Menon, *Mater. Lett.* 57 (2002) 730.
- [19] N.F. Mott, E.A. Davis, *Electronic Processes in Non-Crystalline Materials*, Clarendon Press, Oxford, 1979.
- [20] F. Gutmann, *Organic Semiconductors*, Wiley, New York, 1967.
- [21] C. Uma Devi, A.K. Sharma, V.V.R.N. Rao, *Mater. Lett.* 56 (2002) 167.