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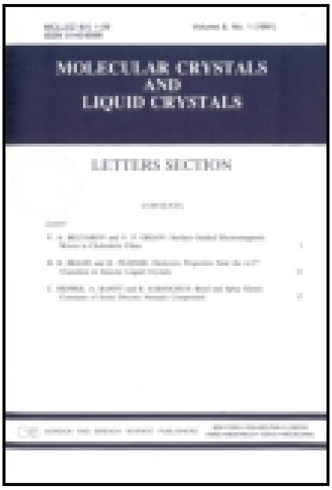

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Synthesis and Properties of the Derivatives of 2,4,6-Tris(Phenoxy)-1,3,5-Triazine

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Synthesis and Properties of the Derivatives of 2,4,6-Tris(Phenoxy)-1,3,5-Triazine

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Five derivatives of 2,4,6-tris(phenoxy)-1,3,5-triazine were synthesized and characterized by ^1H NMR, IR and mass spectrometries. The optical and electrochemical properties of the synthesized compounds were studied. Dilute solutions of 1,3,5-triazines compounds in acetonitrile absorb electromagnetic radiation in the region of 200-400 nm with the band gaps of 3.96–4.58 eV. Cyclic voltammetry studies revealed that the electron affinities of the synthesized compound range from −3.24 eV to −3.58 eV, and solid state ionization potentials range from 7.20 eV to 8.16 eV.

Keywords substituted 1,3,5-triazine; cyclic voltammetry; band gap; spectrometry.

1. Introduction

Tri-substituted 1,3,5-triazines are known as one of the oldest classes of organic compounds. These compounds have been used as subunits in the formation of supramolecular structures, since they possess interesting optical, electronic, and electrochemical properties [1]. They are able to form multiple hydrogen bonds [2] and exhibit good thermal stability [3]. Some of the derivatives of triazine are desirable for various optoelectronic and electronic applications including light-emitting diodes (OLEDs), solar cells, and organic field-effect transistors (OTFTs) [4]. Each chlorine atom of cyanuric chloride can be substituted by various nucleophiles in the presence of a base. The process can be controlled by temperature to run in a stepwise manner [5]. An empirical rule, based upon observation, is that the mono-substitution of chlorine occurs below or at 0°C, di-substitution at room temperature, and tri-substitution above 60°C. Development of valuable methods for the preparation of many new substituted compounds is still a challenge. Here, we report on the synthesis, characterization, and properties of the derivatives of 2,4,6-tris(phenoxy)-1,3,5-triazine.

2. Experimental

2.1. Materials

2,4,6-Trichloro-1,3,5-triazine, phenol, 4-nitrophenol, 4-cyanophenol, 4-methoxyphenol, 4-*tert*-amylphenol, sodium hydride were purchased from “Aldrich” and used as received.

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2.2. General Procedure for the Preparation of 2,4,6-Tris(Phenoxy)-1,3,5-triazine Derivatives (1-5)

Sodium hydride (50 mmol, 55 % suspension in mineral oil) was added to dry THF (40 ml) in a round bottom flask. The corresponding phenol (35 mmol) was added at 0°C and stirred for 1-3 h until the effervescence was damped. Then a solution of 2,4,6-trichloro-1,3,5-triazine (10 mmol) dissolved in dry 20 ml THF was added at 0–5°C, and the reaction was monitored by TLC. After completing the reaction, the solvent was evaporated under vacuum, and water (100 ml) was carefully added. The crude product was extracted, concentrated, and dried. The product was purified by column chromatography using an eluent mixture of hexane and ethyl acetate in a volume ratio of 2:1, followed by recrystallization to obtain the target product in 45-64 % yield. The spectral characterization data are given below for each compound.

2,4,6-Tris(phenoxy)-1,3,5-triazine (1). Yield: 0.44 g (64 %) of white crystals (m.p.: 225–226°C, FW = 354 g/mol). ^{1}H NMR spectrum yielded the following chemical shifts (300 MHz, $CDCl_3$, δ, ppm): 7.51–7.36 (m, 6H, Ar), 7.34–7.31 (m, 2H, Ar), 7.29–7.26 (m, 1H, Ar), 7.25–7.09 (m, 6H, Ar). IR (KBr), cm^{-1}: 3061, 3012, 2946, 2923, 2867, 1562, 1511, 1452, 1369, 812. MS (APCI$^+$, 20 V), m/z: 355 ([M+H]$^+$).

2,4,6-Tris(4-nitrophenoxy)-1,3,5-triazine (2). Yield: 0.35 g (49 %) of white crystals (m.p.: 203–204°C, FW = 489 g/mol). ^{1}H NMR spectrum yielded the following chemical shifts (300 MHz, DMSO, δ, ppm): 8.37–8.26 (m, 6H, Ar), 7.62–7.48 (m, 6H, Ar). IR (KBr), cm^{-1}: 3059, 3013, 2937, 2922, 2866, 1562, 1510, 1369, 810. MS (APCI$^+$, 20 V), m/z: 490 ([M+H]$^+$).

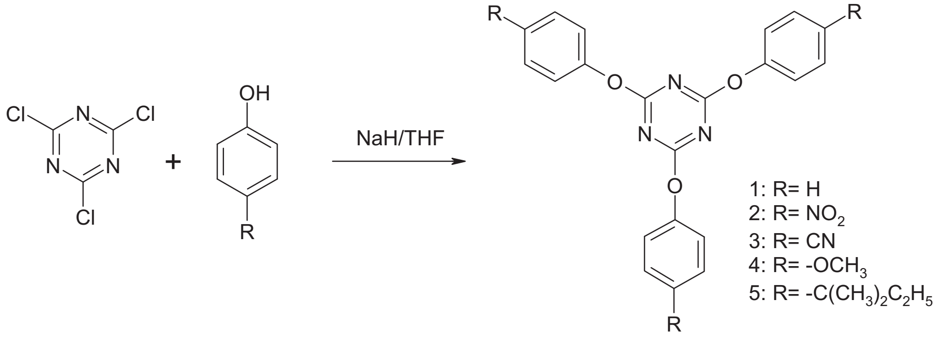
2,4,6-Tris(4-cyanophenoxy)-1,3,5-triazine (3). Yield: 0.38 g (52 %) of white crystals (m.p.: 277–278°C, FW = 429 g/mol). ^{1}H NMR spectrum yielded the following chemical shifts (300 MHz, DMSO, δ, ppm): 8.02–7.91 (m, 6H, Ar), 7.53–7.42 (m, 6H, Ar). IR (KBr), cm^{-1}: 3064, 2946, 2925, 2865, 1561, 1511, 1450, 1364, 812. MS (APCI$^+$, 20 V), m/z: 430 ([M+H]$^+$).

2,4,6-Tris(4-methoxyphenoxy)-1,3,5-triazine (4). Yield: 0.31 g (61 %) of white crystals (m.p.: 181–182°C, FW = 444 g/mol). ^{1}H NMR spectrum yielded the following chemical shifts (300 MHz, $CDCl_3$, δ, ppm): 7.13–7.04 (m, 6H, Ar), 6.93-6.85 (m, 6H, Ar), 3.83 (s, 9H, $-OCH_3$). IR (KBr), cm^{-1}: 3061, 3014, 2946, 2923, 2867, 1562, 1508, 1369, 818. MS (APCI$^+$, 20 V), m/z: 445 ([M+H]$^+$).

2,4,6-Tris(4-*tert*-amylphenoxy)-1,3,5-triazine (5). Yield: 0.26 g (45 %) of white crystals (m.p.: 151–152°C, FW = 564 g/mol). ^{1}H NMR spectrum yielded the following chemical shifts (300 MHz, $CDCl_3$, δ, ppm): 7.39–7.31 (m, 6H, Ar), 7.16–7.06 (m, 6H, Ar), 1.68 (m, 6H, $-C(CH_3)_2C\underline{H_2}CH_3$), (s, 18H, $-C(C\underline{H_3})_2CH_2CH_3$), 0.73 (t, 9H, $-C(CH_3)_2CH_2C\underline{H_3}$). IR (KBr), cm^{-1}: 3068, 3016, 2942, 2929, 2864, 1562, 1452, 1372, 814. MS (APCI$^+$, 20 V), m/z: 565 ([M+H]$^+$).

2.3. Methods

^{1}H NMR spectra were recordered by Varrian Unity Inova (300 MHz (1H)) apparatus. Infrared (IR) spectra were recorded using a Perkin Elmer Spectrum GX spectrometer. The spectra of solid compounds were recorded using KBr pellets. Mass spectra were recorded using a Waters ZQ (Waters, Milford, MA) mass spectrometer. Ultraviolet (UV) absorption spectra were recorded with Hitachi U-3000 and Spectronic Unicam Genesys 8 spectrometers (resolution of 1 nm). Melting points of the materials were measured using an Electrothermal Mel-Temp apparatus. The cyclic voltammetry (CV) measurements were



Scheme 1. Synthesis of 2,4,6-tris(phenoxy)-1,3,5-triazines (1–5)

carried out by a three-electrode assembly cell from Bio-Logic SAS and a micro-AUTOLAB Type III potentiostat-galvanostat. The electrochemical cell used for the estimation of electrochemical properties of the synthesized compounds was composed of three electrodes. The working electrode was a glassy carbon with 0.12-cm^2 surface. The reference electrode and the counter electrode were Ag/Ag$^+$ 0.01 M and Pt wire, respectively. Argon-purged dichloromethane with tetrabutylammoniumhexafluorophosphate (TBAHFP$_6$) 0.1 M were used as an electrolyte. Differential scanning calorimetry (DSC) measurements were carried out with a Perkin Elmer DSC 8500. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA 4000.

3. Results and Discussion

The molecules consisting of a central acceptor triazine ring with different groups symmetrically attached to 1,3,5 positions were obtained as shown in Scheme 1 from 2,4,6-trichloro-1,3,5-triazine and *p*-substituted phenols, containing nitro, cyano, methoxy, and *tert*-amyl groups in good yields in a one-pot procedure. For the comparison, compound **1** having no substituents at the *p*-position of phenoxy groups was synthesized. All the target products (**1–5**) were purified by column chromatography. The synthesized compounds were found to be soluble in common organic solvents such as chloroform, dichlormethane, DMF, and DMSO. The chemical structures of the synthesized compounds were confirmed by ^{1}H NMR, mass spectrometry, and IR spectrometries.

The thermal transitions of compounds **1-5** under heating were studied by DSC and TGA in the nitrogen atmosphere. The values of melting points (T_m), crystallization temperature (T_{cr}), and the temperatures, at which the initial loss of mass was observed (T_{ID}), are summarized in Table 1. All the derivatives demonstrate a high thermal stability. The mass loss occurs at the temperatures higher than 307°C, as confirmed by TGA with a heating rate of 10°C/min (Fig. 1). The derivatives were obtained as crystalline materials after the purification by column chromatography. Their transition into the glassy state appeared to be impossible. For the illustration of this statement, the DSC thermograms of **1** are shown in Fig. 2. When the crystalline sample was heated, the endothermic peak due to melting was observed at 236°C. When the melt sample was cooled down, the liquid crystallized at 214°C. When the sample was heated again, an endothermic peak was observed at 236°C.

UV absorption spectra of dilute acetonitrile solutions of the synthesized compounds and of starting compound 2,4,6-trichloro-1,3,5-triazine (**TR**) are shown in Fig. 3. The wavelengths of absorption maxima (λ_{max}) for respective molecules are shown in Table 2.

Table 1. Thermal characteristics of **1–5**

Compound	T_m, (°C)	T_{cr}, (°C)	T_{ID}, (°C)
1	236	214	307
2	210	161	374
3	244	166	388
4	202	169	366
5	172	139	381

The absorption edge of compound **2** having 4-nitrophenoxy substituents was found to be considerably red-shifted (by ca. 100 nm) with respect to those of the other compounds. The absorption intensities of compounds **1**,**4**,**5** having no accepting species at the phenoxy group are relatively weak. Such weak absorption intensity is a typical characteristic of compounds with a break in conjugation [6]. The substitution at the central triazine ring with phenoxy moieties having electron-rich methoxy or *tert*-amyl groups seems to have a little effect on the optical properties of the compounds. The spectra of compounds **1**,**4**,**5** are similar to that of **TR**. The optical band gaps of the derivatives **1–5** estimated from the onsets of absorption bands of the solutions were found to be in the range of 3.96-4.58 eV. We did not observe fluorescence of **1-5** from dilute acetonitrile, DCM, and THF solutions.

The cyclic voltammograms of **1–5** are shown in Fig. 4. The electrochemical characteristics of compounds **1–5** are presented in Table 3. Compounds **1-5** exhibit quasi-reversible

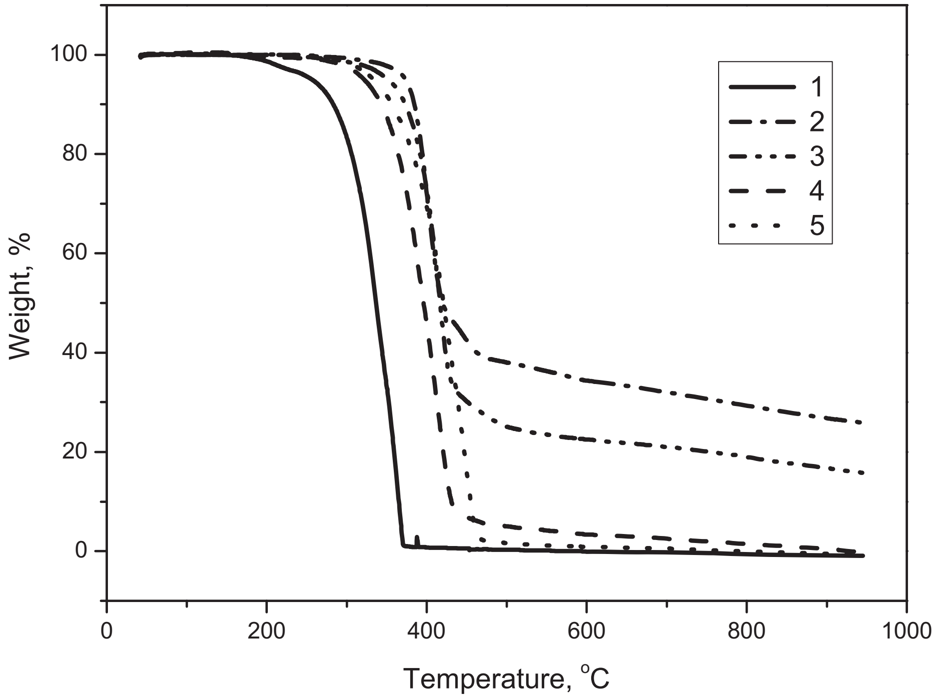


Figure 1. TGA curves of **1–5**, heating rate 10°C/min, N_2 atmosphere.

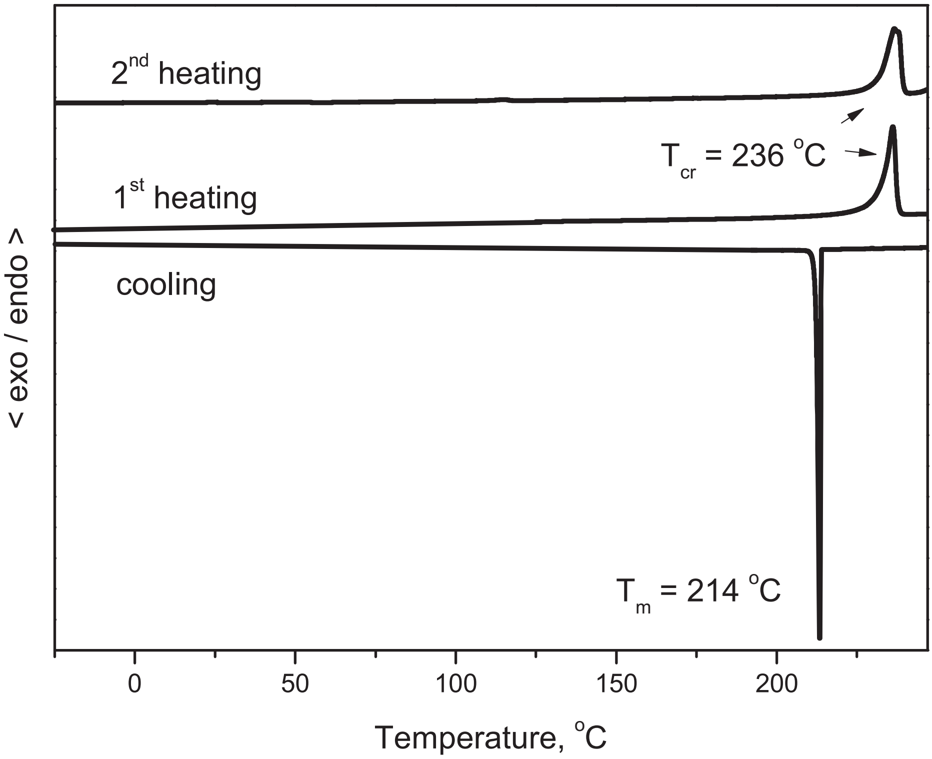


Figure 2. DSC curves of material **1**, heating rate 10°C/min, N_2 atmosphere.

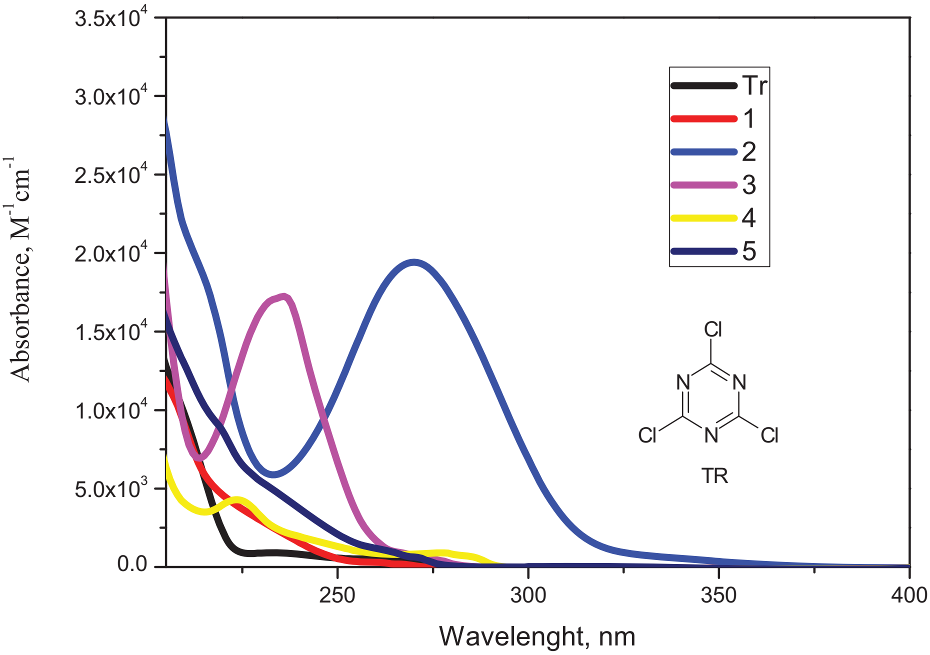


Figure 3. UV-vis absorbtion spectra of dilute (10^{-5} M) acetonitrile solutions of **TR** and **1–5**.

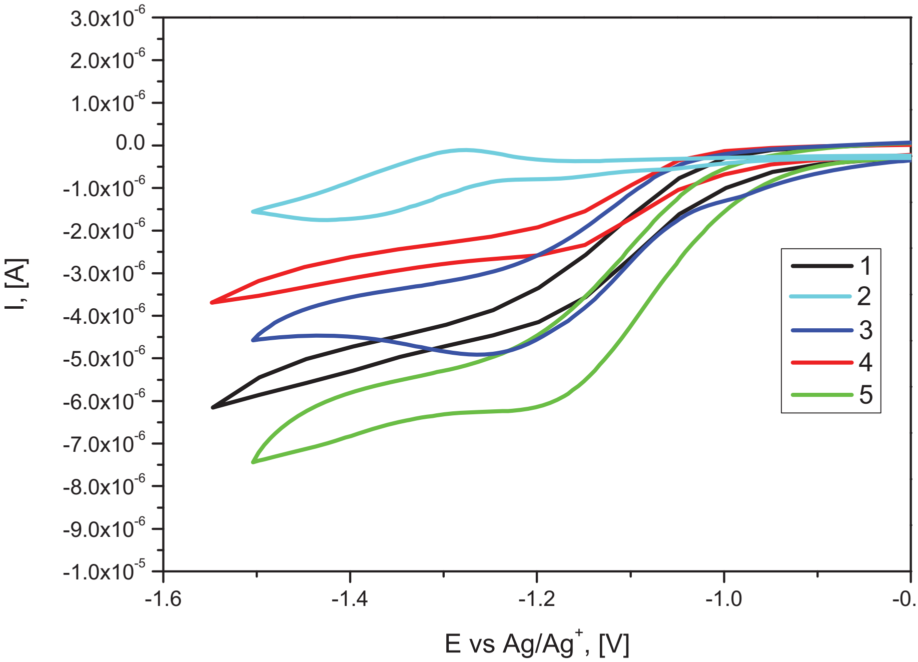


Figure 4. Cyclic voltammograms of **1-5** (10^{-5} M solutions, scan rate of 100 mV·s^{-1} vs Ag/Ag^{+}) in 0.1 M solution of TBAHFP$_6$ CH$_2$Cl$_2$.

reduction and oxidation peaks in the negative potential range. This observation indicates the stable radical anion formation. The reduction potentials were calculated as the average of the anodic and cathodic peak potentials. The electron affinities (EA) were established from the reduction potentials. They were found to be in the range of −3.58 eV–−3.24 eV. The solid state ionization potentials (IP$_{\text{echem}}$) were calculated using the values of optical band gaps. They range from 8.16 eV for compound **5** to 7.20 for **2**. These values are similar to those of other triazine derivatives [7,8,9].

In conclusion, we have synthesized and characterized five derivatives of 2,4,6-tris(phenoxy)-1,3,5-triazine. The optical and electrochemical properties of the synthesized

Table 2. Optical characteristics of compounds **1–5**

Compound	λ_{abs} [nm] [a)]	E_g^{opt} /eV [b)]
TR	262	4.41
1	268	4.51
2	270	3.96
3	277	4.48
4	279	4.25
5	271	4.58

[a)] The wavelengths of the lowest energy absorption maxima.

[b)] $E_g^{opt} = 1240/\lambda_{edge}$, where λ_{edge} is the onset value of absorption spectrum in the long-wave direction.

Table 3. Electrochemical characteristics of compounds **1–5**

Compound	E_{onset}^{red} vs Fc/V [a)]	IP_{echem} /eV [b)]	EA /eV [c)]
1	−1.23	8.08	−3.57
2	−1.56	7.20	−3.24
3	−1.26	8.02	−3.54
4	−1.25	7.80	−3.55
5	−1.22	8.16	−3.58

[a)] E_{onset}^{red} was measured vs. ferrocene/ferrocenium.

[b)] $IP_{echem} = EA - E_g^{opt}$.

[c)] $EA = -(E_{onset}^{red}+4.8)$ [eV] (where, E_{onset}^{red} is the onset reduction potential versus Fc/Fc^+).

compounds were studied. Methoxy and *tert*-amyl substituents at the C-4 positions of phenoxy groups have little effect on the absorption maxima, while the introduction of nitro and cyano ones results in a considerable bathochromic shift of the absorption edge. Cyclic voltammetry studies revealed that the electron affinities of the synthesized molecules range from −3.58 eV to −3.24 eV, and solid state ionization potentials are in the range of 7.20–8.16 eV.

Acknowledgments

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