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Structures and photophysics of lophine and double lophine derivatives

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Abstract

Novel lophine (2,4,5-triphenylimidazole) derivatives, *ortho-*, *meta-* and *para*-substituted in the 2-phenyl ring and *p*-phenyl, *p*-tolyl, and *p*-anisyl rings in the 4- and 5-aryl rings and double lophine derivatives were synthesized and their physico-chemical properties were determined. We included arylimidazoles, derivatives substituted with electron-donating and electron attracting groups. MeO- and OH-groups release electrons and activate the ring. In contrast, COOH- and CN-groups withdraw electrons and deactivate the ring. Nitro derivatives of imidazole, phenol, 2-[4,5-bis(4-methoxyphenyl)-1*H*-imidazole-2-yl]-4-nitro **23** and phenol, 2-[4,5-bis(4-methyl-phenyl)-1*H*-imidazole-2-yl]-4-nitro **24** crystallize with guest molecules in various colors.

Double imidazole derivatives of lophine, 2,2′-(2,5-thiophenediyl)bis[4,5-diphenyl-1*H*-imidazole] **27** and 2,2′-(1,4-phenylene)bis[4,5-diphenyl-1*H*-imidazole] **29** show piezochromism, photochromism and thermochromism in the solid state and form inclusion compounds in various colors.

Four inclusion compounds in two different colors: yellow and green, depending on the solvent molecules were found for **27** and two different colors: light yellow and colorless were obtained for **29**. The fluorescence intensity for **27** substituted with MeO-group in the 4,5-phenyl rings is decreased and it is increased for **29** by changing phenyl rings to MeO-substituent in the 4,5-phenyl rings. Upon irradiation with UV light at room temperature, green solution of **29** turned into orange and colorless solution of **29** turned into light yellow. The photochemical properties of **27** and **29** and their derivatives were studied by irradiating basic and neutral degassed acetonitrile solutions with medium pressure xenon lamp and their photochemical quantum yields, ranging from 0.0011 to 0.0024, together with the corresponding fluorescence quantum yields, ranging from 0.52 to 0.90 and lifetimes, ranging from 1.03 to 1.42 ns were determined. These compounds are sensitive to different external stimulations, such as UV irradiation, heat, increasing pressure, and changing of the environmental pH, causing spectral changes. Our results suggest potential applications of these compounds in molecular photonics and sensing.

Keywords: Chromotropism; Imidazole; Lophine; Thiophene; Fluorescence

1. Introduction

Recently, heterocyclic imidazole derivatives have attracted considerable attention because of their unique optical properties [1–3]. These compounds play a very important role in chemistry as mediators for synthetic reactions, primarily as a means for preparing functionalized materials [4–8]. Imidazole nucleus forms the main structure of some well-known components of human organisms, i.e. the amino acid histidine, Vitamin B_{12}, a component of DNA base structure, purines, histamine and biotin. It is also present in structure of many natural or synthetic drug molecules, i.e. azomycin, cimetidine and metronidazole [9]. Lophine derivatives have significant analytical applications utilizing their fluorescene and chemiluminescence properties [10,11].

Some basic processes, such as excited state proton transfer (ESIPT) have been carried out for imidazole derivatives. Gostev et al. [12] have studied ESIPT in some (2,4,5-triphenylimidazole) lophine derivatives, utilizing steady state and femtosecond laser spectroscopy. Bu and co-workers [13] have shown how the fluorescence properties of lophine can be tuned utilizing thiophene and thiazole derivatives. The photochemistry of lophine was investigated in solutions by Testa and co-workers [14]. They found that the photochemistry of lophine **1** leads to 2-phenyl-9,10-phenanthroimidazole. In basic solutions the photochemical reaction is much faster and give a number of unidentified products at a higher quantum yield.

In the present paper we summarized a comprehensive study of the crystal structures, spectroscopy, photophysics and

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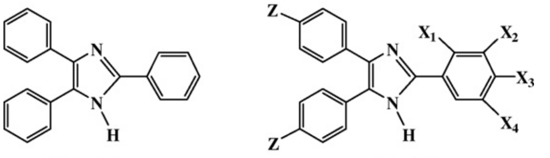


(1) Lophine

(2) - (26)

Fig. 1. Lophine derivatives. (**2**) $Z = H$, $X_3 = COOH$; (**3**) $Z = OMe$, $X_3 = COOH$; (**4**) $Z = H$, $X_3 = CN$; (**5**) $Z = Me$, $X_3 = CN$; (**6**) $Z = OMe$, $X_3 = CN$; (**7**) $Z = H$, $X_2 = CN$; (**8**) $Z = Me$, $X_2 = CN$; (**9**) $Z = OMe$, $X_2 = CN$; (**10**) $Z = H$, $X_1 = OMe$; (**11**) $Z = H$, $X_2 = OMe$; (**12**) $Z = H$, $X_3 = OMe$; (**13**) $Z = OMe$, $X_1 = OMe$; (**14**) $Z = OMe$, $X_2 = OMe$; (**15**) $Z = OMe$, $X_3 = OMe$; (**16**) $Z = OMe$, Ph = benzene; (**17**) $Z = H$, $X_1 = OH$; (**18**) $Z = H$, $X_2 = OH$; (**19**) $Z = H$, $X_3 = OH$; (**20**) $Z = OMe$, $X_1 = OH$; (**21**) $Z = OMe$, $X_2 = OH$; (**22**) $Z = Me$, $X_3 = OH$; (**23**) $Z = OMe$, $X_1 = OH$, $X_4 = NO_2$; (**24**) $Z = Me$, $X_1 = OH$, $X_4 = NO_2$; (**25**) $Z = H$ (Ph = thiophene); (**26**) $Z = H$ (Ph = (thiophene)$_2$).

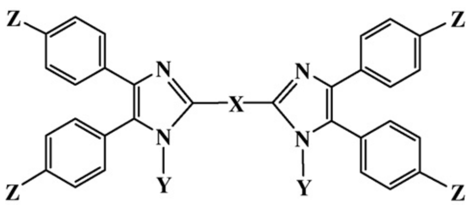
photochemistry of wide range of imidazole derivatives (shown in Figs. 1 and 2).

2. Experimental

Commercially available reagents were purchased from Aldrich and used without further purification. All synthesized imidazole derivatives were characterized by ^{1}H NMR. ^{1}H NMR spectra were recorded on a Bruker AC-400 or AC-500 spectrometer at 298 K.

We prepared a number of lophine (2,4,5-triphenylimidazole compounds **1**–**26**, see Fig. 1) and bislophine derivatives (compounds **27**–**32**, see Fig. 2) utilizing the slightly modified procedure of Davidson et al. [15]. Benzil or 4,4′-dimethoxybenzil or 4,4′-dimethylbenzil (0.5 mmol), suitable benzaldehyde (0.5 mmol), and ammonium acetate (0.8 g) were dissolved in boiling glacial acetic acid (8 ml) and refluxed for 3–5 h monitored by TLC. The reaction mixture was poured into ice-water and collected on a filter, washed with cold water, dried and recrystallized from the suitable solvent.

2,2′-(2,5-Thiophenediyl)bis[1-methyl-4,5-diphenyl-1*H*-imidazole] **28** and 2,2′-(1,4-phenylene)bis[1-methyl-4,5-diphenyl-1*H*-imidazole] **30** were synthesized, in 70% yield by *N*-methylation of **27** or **29**, respectively, according to the Tanino et al. method [16]. To a solution of **27** or **29** (0.2 mmol, 0.1 g) and dimethyl sulphate (0.72 mmol, 0.066 ml) in 10 ml of acetone was added powdered anhydrous potassium carbonate (0.72 mmol, 0.1 g) and the mixture was refluxed for 4.5 h. After cooling, the mixture was poured into water and the yellow crude was collected by filtration and dried in dessicator.



X = benzene, thiophene
Y = H, Me, Z = H, OMe

(27)-(32)

Fig. 2. Double lophine derivatives. (**27**) $Z = H$, $Y = H$, X = thiophene; (**28**) $Z = H$, $Y = Me$, X = thiophene; (**29**) $Z = H$, $Y = H$, X = benzene; (**30**) $Z = H$, $Y = Me$, X = benzene; (**31**) $Z = OMe$, $Y = H$, X = thiophene; (**32**) $Z = OMe$, $Y = H$, X = benzene.

The starting material for the synthesis of 2-[2,2′-bithiophene]-5-yl-(4,5-diphenyl)-1*H*-imidazole **26** was prepared from the bithiophene, that was treated with phosphorus oxychloride and DMF in dichloroethane [17] to afford the 2-bithiophene carboxyaldehyde in 62% yield. Then 2-bithiophene carboxyaldehyde and benzil were treated with ammonium acetate in glacial acetic acid for *ca.* 5 h according to the Davidson method [15].

Absorption spectra were recorded on a Cary 50 UV–vis spectrophotometer. Emission and excitation spectra were measured using a Perkin-Elmer LS 50-B spectrofluorimeter. For emission and excitation measurements, the sample concentration was maintained at $\sim 10^{-5}$ M. Spectroscopic grade solvents were used for spectral measurement, without further purification. Excitations at the 320–400 nm region were isolated from an Osram XBO 150 W medium-pressured xenon lamp by using a combination of corning 7-54 and 0-53 filters. Fluorescence lifetimes were determined by using time-correlated single photon counting (TCSPC) method. We have used the TCSPC experimental set-up in the laboratory of Professor Dan Huppert at Tel-Aviv University, as previously described [18]. Melting points for imidazole derivatives were carried out using a Thermal Analysis DSC Q10.

Data for X-ray crystallographic determination were collected on a Nonius Kappa-CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), operating at 50 kV and 20 mA. The crystal structures were solved by direct methods and refined by a full-matrix least-squares procedure using F^2. All non-hydrogen atoms were refined with anisotropic, hydrogen atoms with isotropic atomic displacement parameters. The software programs used for data collection and reduction were KappaCCD [19] and DENZO SMN [20] for structure solution and refinement SHELXS-97 and SHELXL-97 [21] and for graphic presentations Mercury 1.4.1 for Windows.

3. Results and discussion

3.1. Summary of crystallographic studies

Most of the lophine (2,4,5-triphenylimidazole) derivatives form inclusion compounds with various guest molecules. Lophine derivatives (**2**)–(**22**), *ortho*-, *meta*- and *para*-substituted with electron-donating (MeO- and OH-) groups and electron attracting (COOH- and CN-) groups in the 2-phenyl ring and *p*-phenyl, *p*-tolyl or *p*-anisyl rings in the 4- and 5-aryl rings. Nitro derivatives of imidazole, phenol, 2-[4,5-bis(4-methoxyphenyl)-1*H*-imidazole-2-yl]-4-nitro **23** and phenol, 2-[4,5-bis(4-methylphenyl)-1*H*-imidazole-2-yl]-4-nitro **24** crystallize with guest molecules in various colors. The crystal structure of these compounds showed that solvent of crystallization and intermolecular hydrogen bonds play an essential role in the chromotropic behavior and in the packing of molecules in the crystals. 2,2′-(2,5-Thiophenediyl)bis[4,5-diphenyl-1*H*-imidazole] **27** and 2,2′-(1,4-phenylene)bis[4,5-diphenyl-1*H*-imidazole] **29**