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Stability and structural aspects of diketopyrrolopyrrole pigment and its *N*-alkyl derivatives

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ABSTRACT

An unsubstituted sample, three symmetrically *N*-substituted samples (methyl, butyl and heptyl) and two asymmetrically *N*-substituted samples (butyl and heptyl) of 3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP) were investigated using thermogravimetry and differential scanning calorimetry to reveal the influence on physical-chemical properties of different alkyl chains and symmetry of N-substitution. Stability tests revealed that in all cases the substitution brought significant destabilization of the structure in comparison with the unsubstituted DPP molecule. It was demonstrated that the length of the substituting alkyl chain is a crucial factor in the stability of *N*-alkyl derivatives; the shorter the alkyl chain was, the less stable was the derivative. Further, the symmetrical derivates were less stable than the asymmetrical ones. Unlike the unsubstituted DPP molecule, all the derivatives showed remarkable sensitivity to different cooling regimes which lead to the revealing of monotropical polymorphism in the symmetrical butyl and heptyl derivatives crystalline structure.

1. Introduction

Nowadays, a strong effort can be seen in seeking for high-performance and simultaneously photo- and oxidative-thermally stable materials used in organic electronics. Printing technology seems to be a leading technique for cheap large scale production of such devices. Using this technique, the layers of electronic devices are printed employing solutions containing the active materials. However, the increase in solubility can reversibly act on the stability of the materials. Derivatives of 3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione, commonly referred as DPPs, are potentially attractive materials for organic electronics. They belong to important industrial high-performance pigments [1] showing significantly high melting points with respect to other low molecular pigment standards. They also exhibit remarkable resistance against chemical, heat, light and climate influences. There is a wide range of possible applications which have been already investigated covering e.g. latent pigments [2], solid state dye lasers [3], gas detectors [4,5] or electroluminescent devices [6,7].

The DPPs are usually insoluble in common solvents [8]. One of the reason for their low solubility is the existence of hydrogen bondings between the H atom of the nitrogen functional group and oxygen. The unsubstituted DPP is perfectly planar, the π–π electrons stacking occurs in solid state and also contributes to their insolubility. In order to modify the solubility, it is necessary to carry out either the N-substitution and/or the breaking of the molecule planarity [8]. In our previous work [7], we discussed the influence of N-alkylation on optical properties, and the results were correlated with molecule geometry calculated by quantum chemical methods. It was found that while the parent DPP molecule (abbreviated as DPP in this work) is perfectly planar, the N-substitution causes rotation of the adjacent phenyl rings (see Fig. 1) and thus reducing the effective conjugation extent. This, in turn, causes hypsochromic shift of the absorption spectrum. Simultaneously, the fluorescence spectra move to the longer wavelength region increasing Stokes shifts. The effect is more pronounced for the double *N*-alkylated derivatives. Since the angle of distortion is not dependent on the length of the substituent, no differences between butyl substituted (DPP-B, DPP-BB) and heptyl substituted derivatives (DPP-H, DPP-HH) were found [7].

The stability and behavior of physical structure of photo-sensitive materials which were exposed to different thermal history is very important. In order to produce high quality devices in a controlled way, knowledge about the crystallinity, and polymorphism seems to be crucial. Since physical properties of polymorphs can significantly differ, polymorphism can cause

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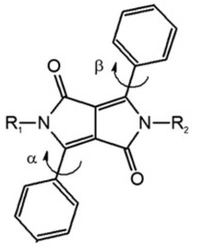

	R_1	R_2
DPP	H	H
DPP-MM	CH_3	CH_3
DPP-B	C_4H_9	H
DPP-BB	C_4H_9	C_4H_9
DPP-H	C_7H_{15}	H
DPP-HH	C_7H_{15}	C_7H_{15}

Fig. 1. The basic structure of 3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP), also known as DPP and the respective derivatives used in this study. The definition of calculated torsion angles α and β can be found in [7].

troubles in technological applications [15]. Essentially, the difference in crystal structure leads to different optical properties, structural stability, solubility, melting temperature, enthalpy etc. Since the crystallization of one specific polymorph is controlled by a combination of thermodynamic and kinetic factors [9], it is important to determine the relationship between such fraction and the others in the polymorphs mixture.

In this study, using thermogravimetrical analysis (TGA), our research was extended by the thermal and thermo-oxidative stability tests and by distinguishing between processes of evaporation or degradation. In fact, materials DPP and DPP-MM have already been investigated by TGA [10]; however, the large set of DPP materials and comparison of their properties can bring deeper insight into the physical chemistry of such interesting pigments. Furthermore, employing differential scanning calorimetry (DSC) we would like to shed light on the structural variability of investigated samples after different thermal history. The obtained results are discussed with respect to the chemical structure of the studied molecules.

2. Experimental

2.1. Materials

Samples of the studied derivatives were synthesized in VUOS, a.s. (Research Institute of Organic Syntheses, Inc., Rybitvi, Czech Republic) according to the procedures described in [7,8]. One unsubstituted sample (DPP), three symmetrically *N*-substituted samples (DPP-MM – methyl group substituted, DPP-BB – butyl group substituted and DPP-HH – heptyl group substituted) and two asymmetrically substituted samples (DPP-B with butyl group and DPP-H with heptyl group) were investigated in this study. Molecular structures of investigated samples are depicted in the Fig. 1.

Before all the experiments had been performed, the compounds were carefully milled in the agate mortar in order to maintain uniform heat flow to the whole dosing of sample in both thermal analysis methods.

2.2. Methods

2.2.1. Thermogravimetric analysis

Thermogravimetric studies were performed using TA Instruments TGA Q5000 (New Castle, DE, U.S.A.) device in 100 μL open platinum pans. The samples, typically 5 mg, were heated by using thermal ramp of 10 °C min^{-1} from 40 °C to 650 °C in either dynamic atmosphere of nitrogen (thermal stability) or air (thermo-oxidative stability). Flow rate of both gases was 25 mL min^{-1}.

2.2.2. Differential scanning calorimetry

Calorimetric analyses were carried out employing TA Instruments DSC Q200 equipped with an external cooler RCS90 allowing experimental temperature range from −90 to 400 °C. Experiments were conducted in open TA Tzero™ aluminum pans. The first heating run was conducted at 10 °C min^{-1} from 40 °C to the temperature 5 °C lower than the degradation temperature onset (T_{onset}) previously determined by using thermogravimetry under nitrogen. In order to simulate the moderate temperature decrease, cooling ramp of 0.5 °C min^{-1} was applied to reach −90 °C, followed by 1 min of isothermal stage. The first calorimetric measurement was performed using heating ramp of 10 °C min^{-1} from −90 °C to the temperature (T_{onset} − 5)°C. The second experiment was performed using the same heating ramp after the rapid equilibration of the sample down to −90 °C and 1 min of isothermal stage. It is necessary to point out that in this case, the averaged temperature of cooling exceeded 20 °C min^{-1}. All DSC experiments were made under 50 mL min^{-1} of nitrogen purge. The device was calibrated for temperature and enthalpy using indium, tin and zinc standards (Perkin Elmer). Additional measurement of sample DPP was carried out also by the TA Instruments Q600 (simultaneous DSC and TGA) under the same conditions as described above. All the records were assessed by TA Universal Analysis 2000 software version 4.4A.

3. Results

3.1. Stability tests – thermogravimetric analysis (TGA)

TGA measurements were conducted to test the temperatures of mass loss occurrence. These temperatures correspond either to the temperature of degradation (T_D), evaporation (T_{ev}) or sublimation (T_s). The character of two latter phenomenons was revealed by DSC. In principle, if the sample shows an endotherm on DSC record, the sample is melted and therefore, the temperature can be associated to evaporation. On the contrary, if DSC record does not show any melting, the sample is solid and the process can be attributed to the sublimation.

In order to distinguish between T_s and T_{ev} or T_s, the mass loss and its first (DTG) and second temperature derivative curves were used. The clarification of such an approach is explained further in the text. The typical TGA record and its DTG curve were obtained by using conditions described in Experimental part for sample DPP-MM and is reported in Fig. 2. In this work, the DTG is plotted in an inverse mode to improve the illustrative quality of Figures. Since the TGA record provides an integral piece of information regarding the mass loss, DTG or potential second derivation allows a closer look into the dynamics of the processes and frequently helps to distinguish the change in mass loss mechanism.

Sample DPP showed no event on the DSC curve when we used the temperature program reported in Experimental section. Therefore, in order to discover potential melting at temperatures above sublimation, the simultaneous DSC and TGA was carried out (Fig. 3). As it can be seen on the DSC curve, no overlapping of enthalpy processes occurred, and thus the sample cannot be melted under conditions used in this work. The respective 1st and 2nd derivative curves of TGA of DPP are reported in Fig. 4.

The results obtained from DTG records are summarized in Table 1. All of the samples in both atmospheres showed one or two degradation steps. If occurred, the second degradation step was only minor and was not taken for further assessment. The onset of a process in DTG is traditionally determined from the 1st derivative mass loss curve. However, it is clear that the determined temperature does not indicate whether the temperature corresponds to the degradation or to the evaporation. The determined onset only indicates the beginning of mass changes which can be attributed to both above-mentioned processes. Therefore, the 2nd derivative was carried out in order to enable the separation of possible overlapping processes. An example of such a separation for sample DPP is