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Report on Mr Parmeshwar SOLANKE thesis dissertation.

The Ph D dissertation presented by Mr Solanke concerns the design, the synthesis, as well as the photophysical and electrochemical characterizations of new chromophores based on indane-1,3-dione. These T-shaped dyes were designed for second order non linear optical (NLO) properties. The experimental results are completed by DFT calculations. Structure-property relationship where highlighted according to the experimental and computational data.

In a short introduction, Parmeshwar SOLANKE, gives some general points concerning indane-1,3-dione.

The first part of the dissertation is a bibliographic study concerning indane-1,3-dione derivatives. Firstly, the various strategies to obtain indane-1,3-dione building blocks are reviewed. Then the reactivity of the indane-1,3-dione moieties is highlighted: It concerns mainly the carbonyl and the C2 positions. The important point to be highlighted is that indane-1,3-dione derivatives substituted at the benzene moiety are really rare in the literature and justify the originality of the work presented here. Due to its strong electron withdrawing character, the indane-1,3-dione moiety appears as a really good attractor in push-pull systems. The second part of the bibliographic study concerns the use of such push-pull structures bearing indane-1,3-dione part as materials presenting NLO properties, solar cells, organic light emitting diodes and molecular glasses. It should be noted that some chromophores bearing indane-1,3-dione exhibit giant 2nd order NLO response. This bibliographic study is quite exhaustive and highlight well the interest indane-1,3-dione derivatives in the field of material exhibiting internal charge transfer for NLO. However, taking into account the applications of the molecules described in this thesis, I would have expected a chapter giving some generalities about NLO. This part is clearly missing in the dissertation.

The second part of the dissertation is the experimental part that details the synthetic protocols and the characterizations of all the molecules that are presented in the dissertation. The characterization (identification and purity) of all the compounds seems quite rigorous.

The last part of the manuscript is a description and discussion about the experimental and computational results. The first focus was the synthesis of tripodal structures with a 1,3-bis(dicyanomethylidene)indane central core that is substituted in positions 2, 5 and 6. Starting

from *o*-xylene, a four step synthetic route was envisaged but unfortunately, Mr Solanke failed in obtaining this series of chromophores due to problems of purification during the last step of the reaction sequence (functionalization of the 5 and 6 positions by palladium catalyzed cross-coupling reactions from dibromo derivative). Mr Solanke argues probable unstability of this series of compounds to justify the purification difficulties. This led to a new design based on tripodal structures with an indane-1,3-dione central core that is substituted in positions 2, 4 and 7. The 1,3-bis(dicyanomethylidene)indane moiety is replaced by indane-1,3-dione with a lower electron-withdrawing character to increase the stability of the chromophores. Target chromophores were obtained in four steps. The key step is a regioselective iodination of phthalanhydride in position 3 and 6 as proved by crystallographic analyses. Sixteen T-shaped molecules were obtained pure with reasonable yield. X-ray analyses were performed on two T-shaped chromophores. Cyclic voltametry and UV-visible analyses were performed on the sixteen chromophores. The absorption spectra are dominated by intensive charge transfer band. It appears that electrochemical behavior and absorption spectra are mainly influenced by the nature of the substituents in position 2 of the indane-1,3-dione core (nature of the electro-donating group and length of the π -conjugated core). Presence of an additional vinylene linkage and replacement of *N,N*-dimethylaniline by piperidinthiophen electron-donating groups lead to reduction of the electrochemical gap and bathochromic shift of the charge-transfer absorption band. The influence of lateral substituent is moderate. 2nd order NLO response have been evaluated by EFISH method (Coll. A. Barsella, Univ. Strasbourg) and $\mu\beta$ values up to $2100 \cdot 10^{-48}$ esu were obtained. The parameters leading to reduction of the electrochemical gap and bathochromic shift the absorption band also lead to increased $\mu\beta$ values. Thermal stability of all the chromophores was checked of DSC analysis and all target chromophores exhibit thermal decomposition in the 180–312°C range and thus can be considered as sufficiently thermally robust materials. DFT calculations were also performed to complete the experimental work.

When reading the dissertation, it appears that Mr Parmeshwar Solanke has to cope with complicated purification problem during the 1st part of his Ph D, which explains the limited number of characterized compounds. It appears however that an important experimental work either of synthesis and characterization (by electrochemistry, absorption spectroscopy and thermal analyses) has been performed. It should be highlighted that two articles in well recognized journal of organic synthesis (*Synthesis* and *Eur J. Org. Chem*) have been already published from this work.

To conclude, I consider that the Ph D of Mr Parmeshwar Solanke deserves to be defended to obtain the grade of doctor in Chemistry from the University of Pardubice.

Some questions:

- 1) How would you justify the T-shape design for 2nd order NLO chromophores? It seems that the lateral substituent are a moderate influence on linear and non linear optical properties. Could you compare the NLO response of your chromophores with similar linear chromophores (indane-1,3-dione derivatives that are not substituted at the benzene moiety)?

- 2) What is the influence of the position of substituents on the benzene part of the indane-1,3-dione core? Did you intend to obtain chromophores from dibromo indane-1,3-dione starting material **147**?
- 3) How do you explain the regioselectivity observed for the iodination of phthalanhydride?

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Referee's report of the Ph.D. thesis:

Solanke Parmeshwar: *Synthesis and properties of model push-pull systems based on indane-1,3-dione*

The presented Ph.D. thesis is devoted to the study of indane-1,3-dione and its derivatives, their synthesis, spectral and electrochemical studies and the utilization in modern applications as optoelectronics and photonics.

Very well processed theoretical part of Ph.D. thesis brings survey of present findings with accent on synthesis and reactivity of parent indanedione, historical overview of its participation in push-pull systems and its application in optoelectronics. In the next part applicant presents another structural fragments occurring in push-pull chromophores. Solar cells, organic light-emitting diodes and molecular glasses are presented as the most important fields of application of organic push-pull chromophores.

This part is made clearly and in an interesting way. Author compiled the informations from the latest literature.

Based on the literature-gained knowledge, novel indane-1,3-dione derivatives were designed. Unfortunately owing to instability and difficult purification author was not successful in preparation of derivatives with 1,3-bis(dicyanomethylidene)indane central unit. Even though 16 novel molecules which represent (D- π)²-A- π -D push-pull chromophores with potential NLO-responses, have been synthesised and studied. The prepared compounds contain the central indane-1,3-dione fragment bearing three conjugated substituents. All target chromophores present new extraordinary type of push-pull chromophores with T-shape arrangement.

The synthetic part is written clearly, the new compounds are fully characterized by the standard techniques. The structure of two target compounds as well as their ICT character were confirmed by X-ray analysis.

In the following the synthesised compounds have been studied by electrochemical, spectral, theoretical-DFT and NLO-EFISH methods. These methods offered valuable data that enabled to find interesting relation between structure and properties, the result is the best molecule 182. In this I see the notable strength of this thesis.

The thesis is nicely presented and well written, with only few misprints and small errors which do not diminish the excellent level of thesis.

p.5 – Dicyanovinyl;

p.5 – the abbreviations DMA and PIT are missing in list of abbreviations;

p.10 – the discussion about acidity of indandione could have been completed by the pK_a value;

p.12 , *Scheme 13* – the alkylation reagent is missing;

p.22 – (*Figure 15*) correct is (*Figure 17*)

p.24 – compound 75 in Table 6. is listed two times;

p.71 – *Figures 42* and *43* are not ORTEP plot.

Questions:

1. Could the substitution in the positions 4 and 5 of indandione fragment improve NLO-response?
2. How do you explain the regioselectivity of iodination of phthalanhydride?
3. Could you predict the structure with better NLO-response than compound 182 based on changing the peripheral donors or linkers?

Remark:

The prepared compounds could be active also in two photon absorption.

The scientific outcomes of this dissertation were already published in two articles in high-class journals.

Finally I can state that the subject of presented Ph.D. thesis is interesting and trendy and **Mr. Solanke Parmeshwar, M.Sc.** proved ability for scientific work with high scientific competence. His dissertation work entitled: *Synthesis and properties of model push-pull systems based on indane-1,3-dione* presents an interesting scientific document that obliged to all asking requirements and I recommend to accept it as a foundation towards conferment of the academic grade **Ph.D.**

Bratislava 8th September, 2015



Prof. RNDr. Pavol Zahradník, DrSc.