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Photochemical activity of crystalline dihydropyridine derivatives studied by differential scanning calorimetry

Outline and aim of the communication

Outline

1. Photochromic phenomenon
2. Experimental
3. Total heating technique
4. Fractional heating technique and activation energy
5. Conclusions

Aim

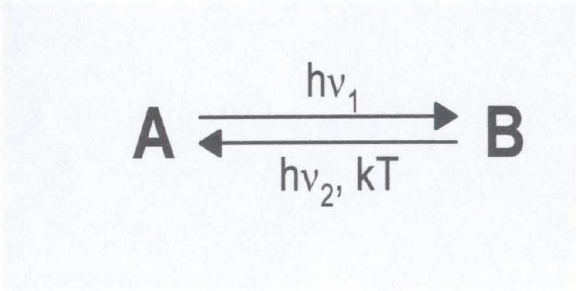
to demonstrate the applicability of the DSC method in kinetic and energetic studies of thermally driven reactions in the solid state

Introduction

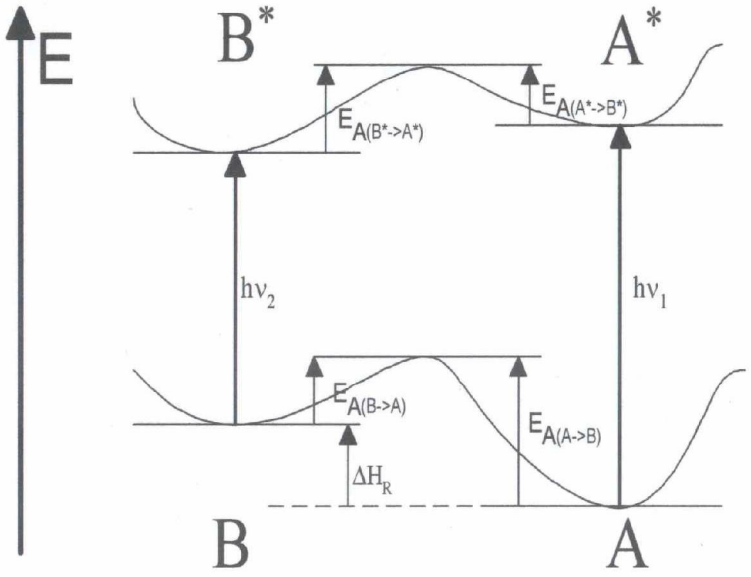
Photochromic materials have recently been extensively studied due to their potential use in modern technologies such as information recording, nonlinear optics etc. Parameters characterising the kinetics of photochromic process are often determined from isothermal measurements, usually employing spectroscopic methods. The use of methods working in non-isothermal regime such as Differential Scanning Calorimetry (DSC) allows us to gain the same kinetic information in a shorter time. Moreover, the calorimetric technique provides information about the enthalpy of reactions occurring in materials under study.

Photochromism

A photochromic process can be schematically presented as a photochemical reversible reaction:

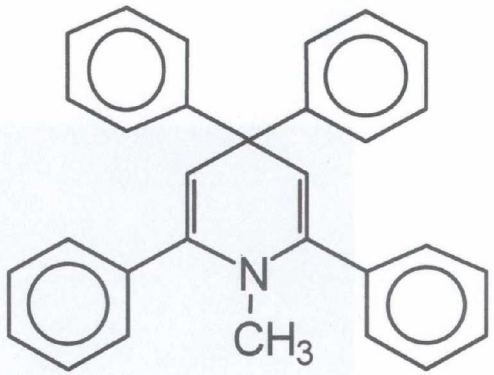


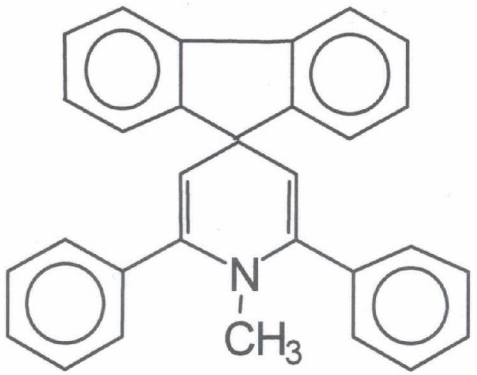
B is thermodynamically less stable and can revert to the original form A via a thermal excitation or by light.



Potential energy diagram for two forms of a photochromic system

Chemical formulae of materials under study

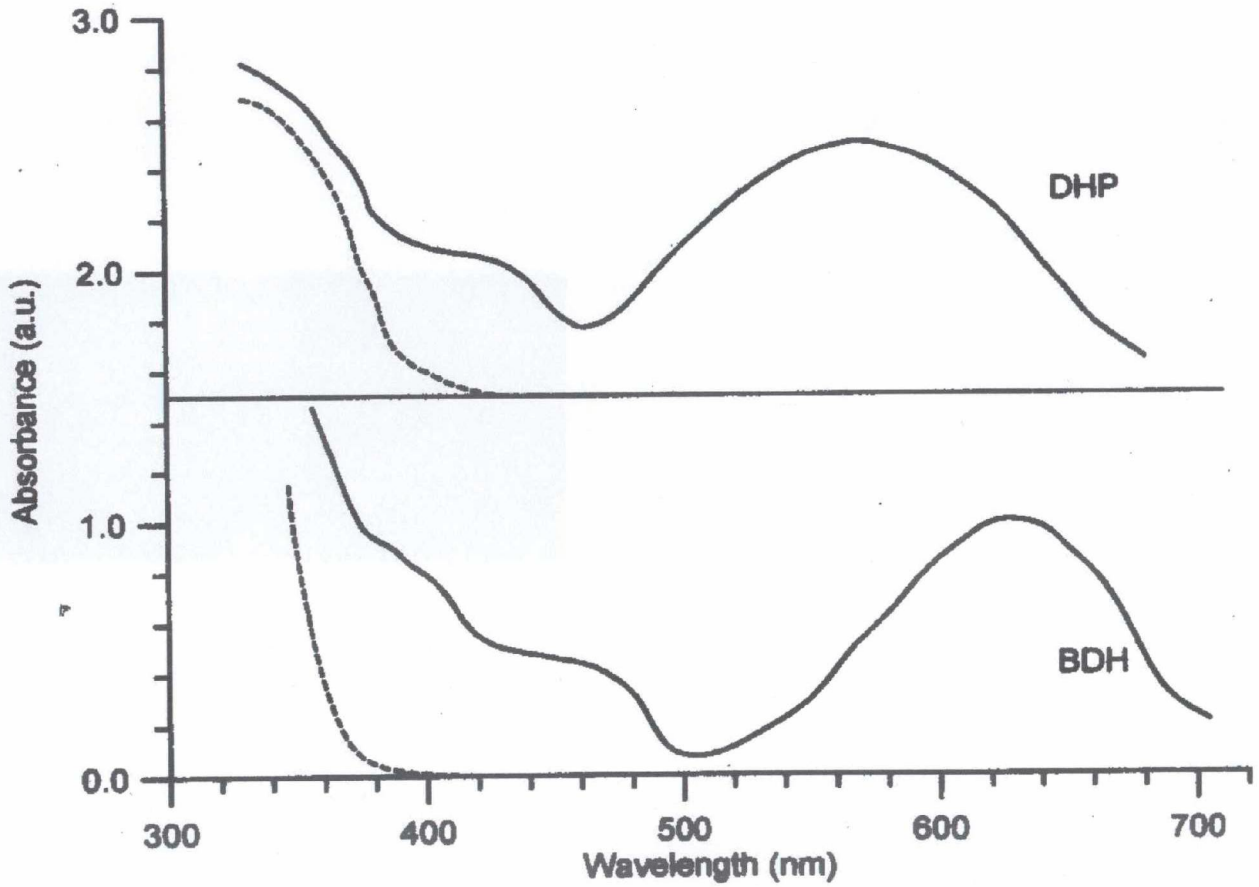




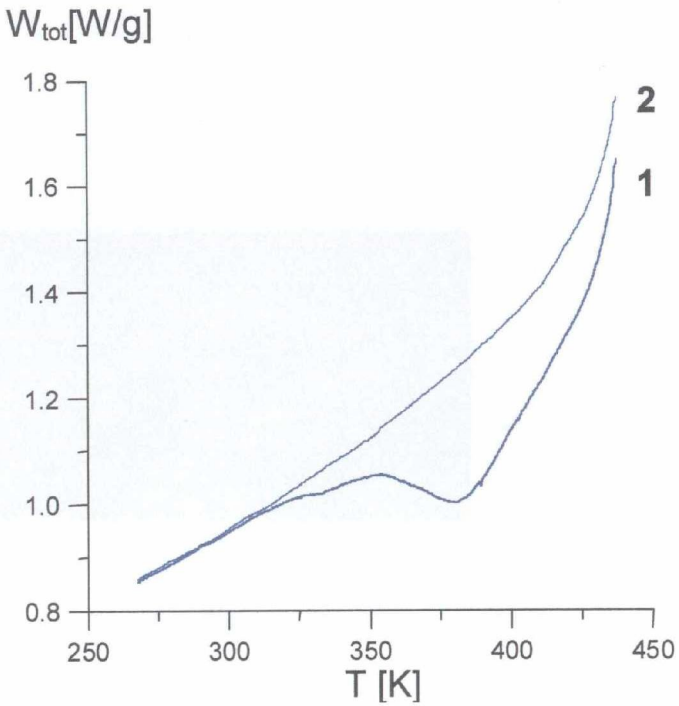
DHP (left): 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine

BDH (right): 4,4-(diphenyl-2,2'-diyl)-2,6-diphenyl-1-methyl-1,4-dihydropyridine

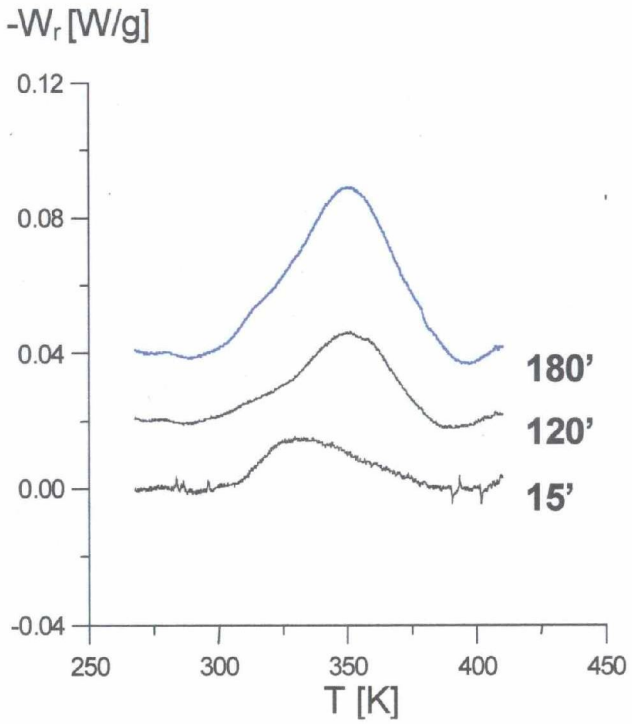
Absorption spectra of DHP and BDH



Measurements of the heat flow on a DHP sample

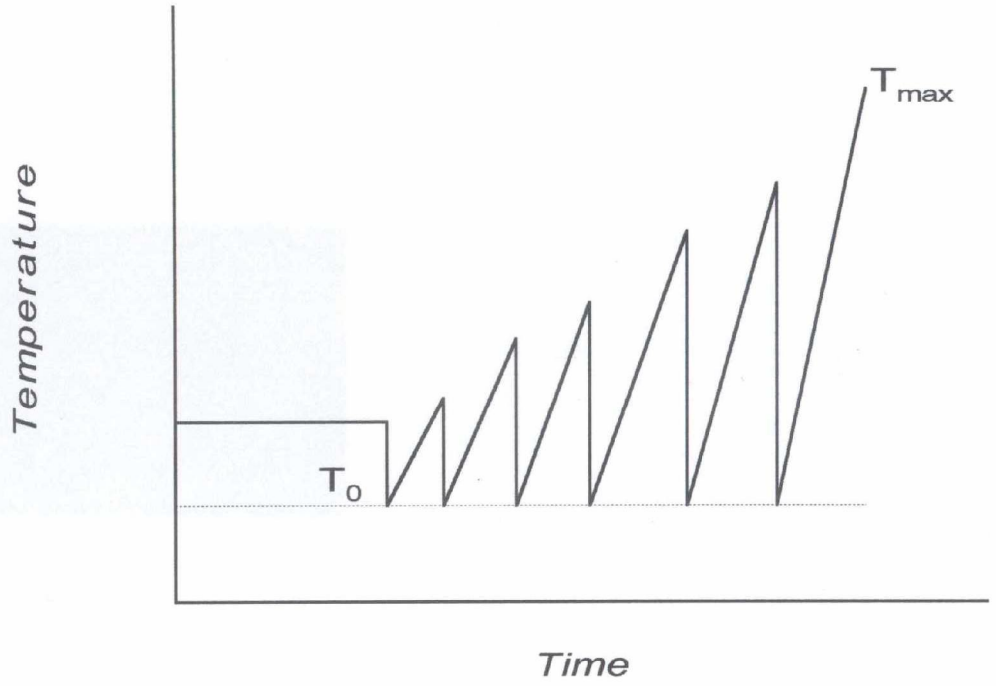


Curve 1: the sample immediately after irradiation.
Curve 2: the second run of the sample just after the first run



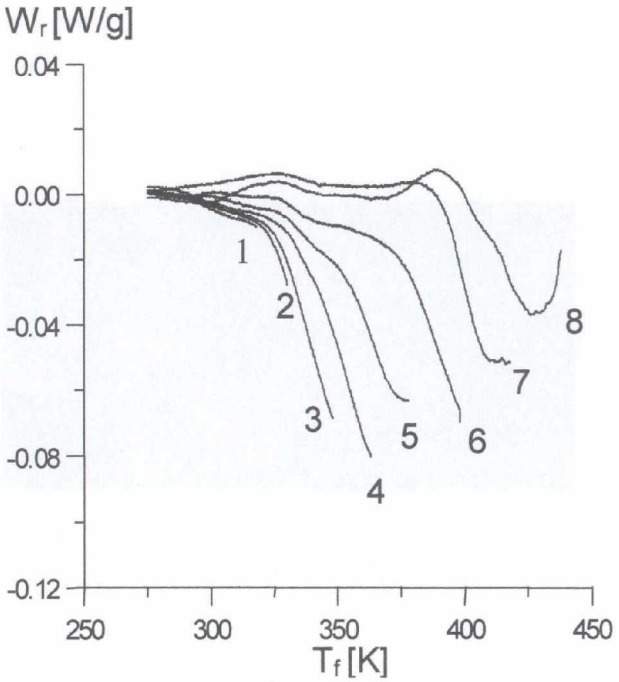
Dependence of the shape of the excess heat flow peak on the irradiation time. The parameter is the irradiation time

Fractional heating DSC experiment

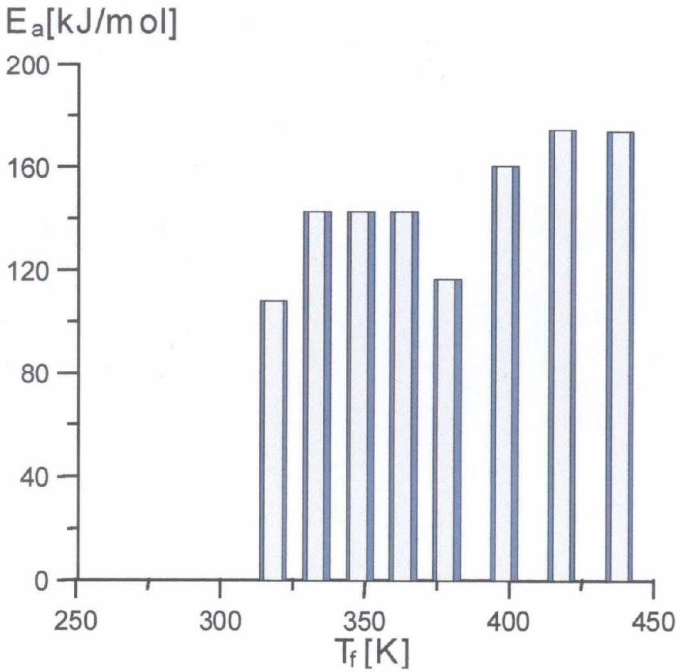


A scheme illustrating the principle of the experiment

Fractional heating DSC experiment in BDH system

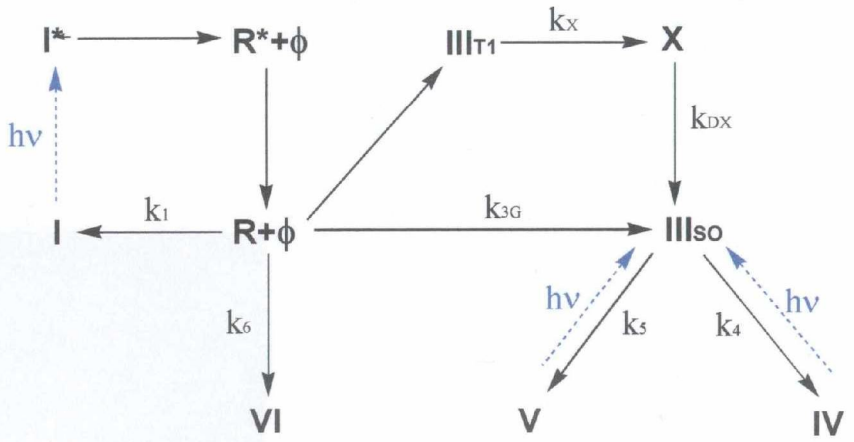


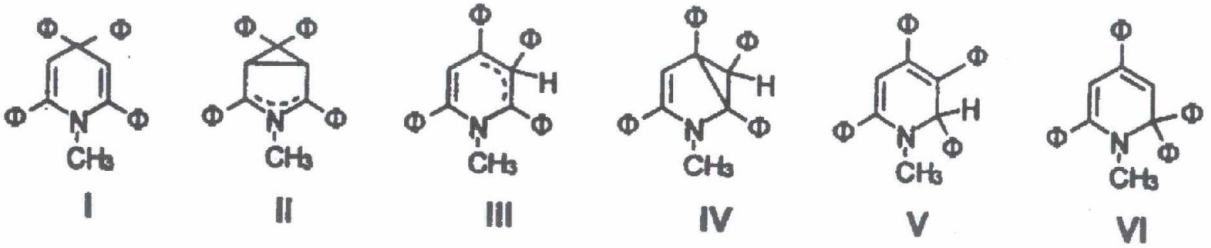
A series of the heating runs measured after irradiation of the BDH sample at 298 K



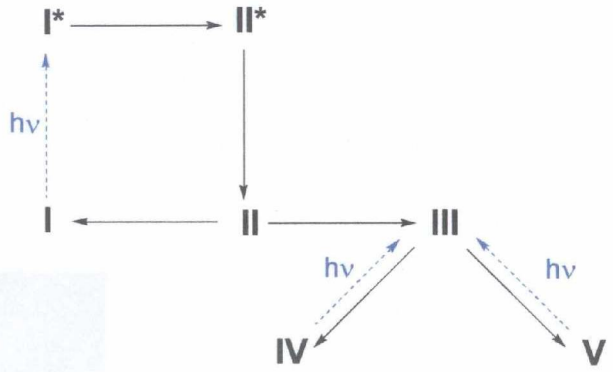
Dependence of the activation energy on the final temperature of runs

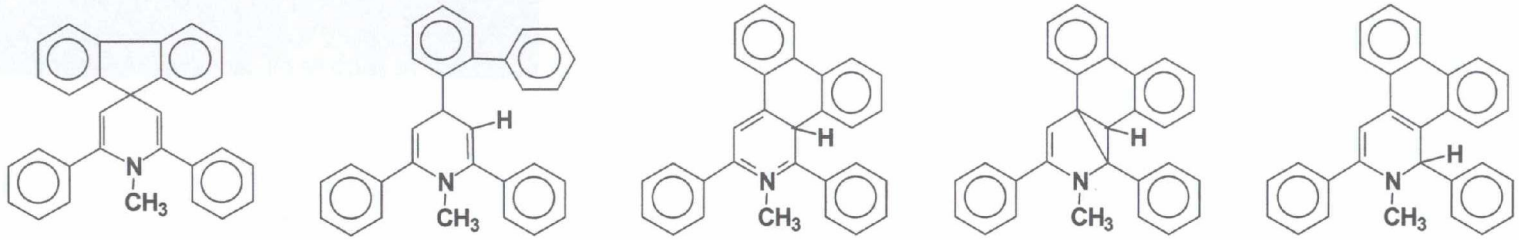
Postulated reaction scheme in DHP system





Possible reaction scheme in BDH system





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Conclusions

- In all irradiated samples we observed broad exothermic anomalies on their heat flow curves, attributed to thermally driven reverse reactions from the metastable to the stable form of DHP and BDH (bleaching reaction). The difference between the first and the subsequent runs (excess heat flow W_r) provides information about the enthalpy of the bleaching process.

- Analysis of the dependence of the shape of the excess heat flow on the irradiation time seems to point out to the existence of two bleaching processes.

- Fractional heating DSC were performed enabling us to get information about distributions of activation energies.

- The results obtained are burdened with substantial errors due, among other factors, to phase transitions occuring in BDH system.

- A comparison of the results of calorimetric measurements with those obtained from spectroscopy and with the quantum-chemical calculations allowed us to propose a mechanism of the photochemical behaviour of DHP and BDH.

- The DSC method can be successfully used to analyse kinetics and energetics of reactions following UV illumination of photoactive materials.

References

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