Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Aggregation - An Interesting Phenomenon in Polymethine Dyes

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Version of record first published: 24 Sep 2006.

To cite this article: U. Schedler , B. Ziemer , J. Bendig & T. Harder (1994): Aggregation - An Interesting Phenomenon in Polymethine Dyes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 248:1, 13-19

To link to this article: http://dx.doi.org/10.1080/10587259408027158

*Mol. Cryst. Liq. Cryst.* 1994, Vol. 248, pp. 13–19
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Printed in the United States of America



# AGGREGATION - AN INTERESTING PHENOMENON IN POLYMETHINE DYES

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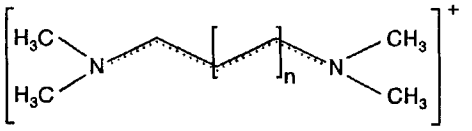
**Abstract**

Bisdimethylamino-tri- (BDT), -penta- (BDP), -hepta- (BDH), and nonamethines (BDN) on surfaces were investigated with regard to detect absorption bands caused by aggregation. The experiments prove that the aggregation tendency increases with prolonging the chain length. A new method preparing non-aggregated and aggregated layers of heptamethines on surfaces of glass was used. X-ray results and RHEED measurements were compared. We think that a "thin layer modification" is formed.

## INTRODUCTION

Aggregation of polymethine dyes has an immense importance for sensitization of photographical materials and semiconductors [1]. Furthermore there are references that polymethine aggregates show nonlinear optical properties with high efficiency [2]. In order to clarify common structure-property relations we investigated open-chained polymethines which are easy to survey and they have only small organic substituents which influence should be neglected.

Polymethines with the following formula were investigated (1):

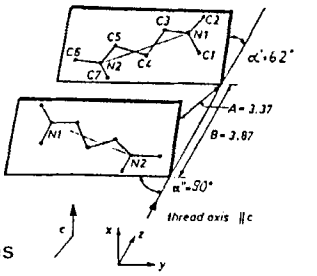



X = Cl, Br, I, $N_3$, $ClO_4$, $BF_4$

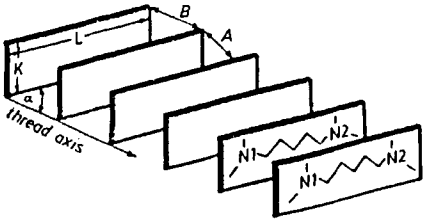
n = 1, 2, 3, 4

A lot of different types of aggregates are formed [3]:

- *no aggregation* in the case of trimethines

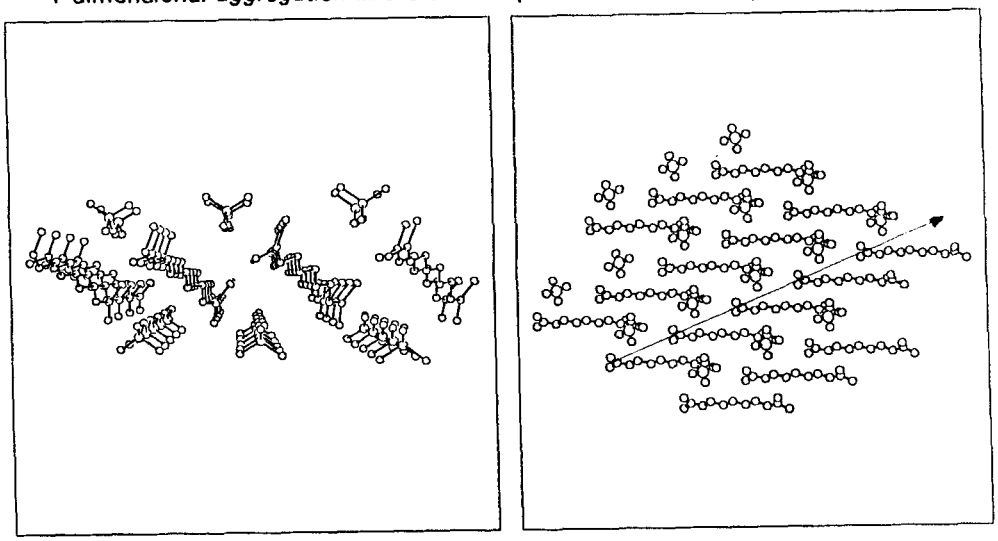



- *1-dimensional aggregation* in the case of pentamethines

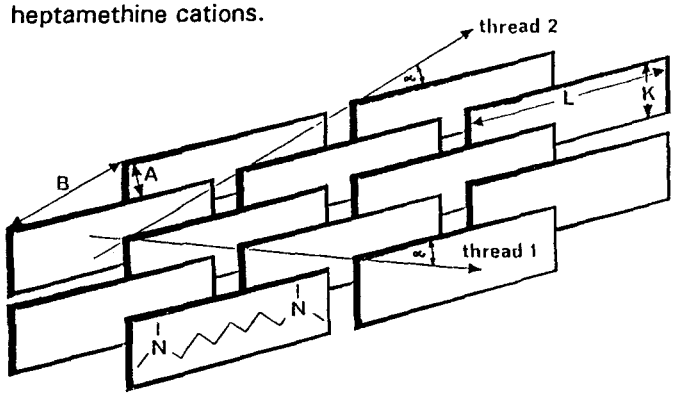


In dependence of the kind of anion, bisdimethylheptamethines (BDH) exist in different aggregate structures, e.g.:

- *1-dimensional aggregation* in the case of perchlorate ($BDHClO_4$ , Fig. 2) [4] and



- *2-dimensional aggregate structure* consisting of layers parallel (001) in the case of the bromide salt (BDHBr, Fig. 3) [5]. There are brick work like connected heptamethine cations.




Because of the well known fact, that the aggregation tendency of open-chained polymethines increases with prolonging chain length, the unknown aggregates of heptamethines and nonamethines were investigated.

Experiments show that aggregation takes place on different surfaces of glass, paper and silver halides and also in polymer matrices. A novel method to prepare and investigate polymethine aggregates in thin layers on surfaces of glass was used.

In order to determine the kind of aggregates diffuse reflection spectroscopy, UV/VIS transmission spectroscopy and electron diffraction (RHEED) were applied.

**Aggregation of Polymethines (heptamethine and nonamethine) on Surfaces**

***Paper***

Bisdimethylamino-tri- (BDT), -penta- (BDP), -hepta- (BDH), and nonamethines (BDN) on surfaces were investigated with regard to detcet absorption bands caused by aggregation. In the case of **tri- and pentamethine absorption of aggregates could not be detected**. The aggregation of heptamethines and nonamethines was studied on surfaces of glass and paper. In the case of **heptamethine** absorption bands at **580 nm** and **630 nm**, in the case of **nonamethine** at **740 nm** and **830 nm** were detected. These absorption spectra, polymethines on surfaces of paper, are presented in the following Figures (4a - d):

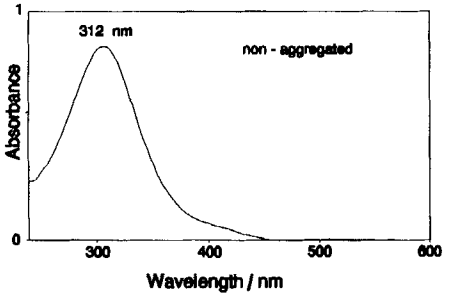



Fig. 4a: $BDTClO_4$ monomere non-aggregated

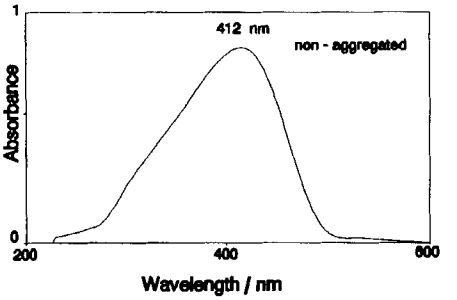



Fig. 4b: $BDPClO_4$ monomere non-aggregated

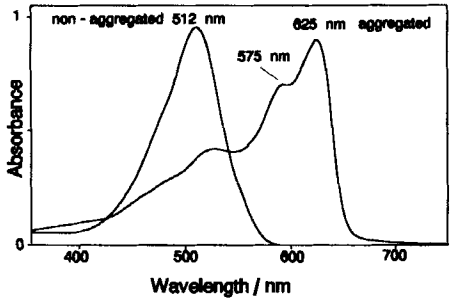



Fig. 4c: $BDHClO_4$ non-aggregated and aggregated

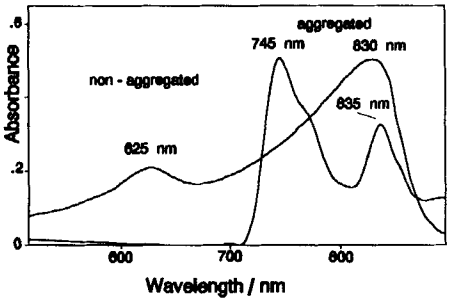



Fig. 4d: $BDNClO_4$ non-aggregated and aggregated

We investigated different kind of paper with differences in surface roughness. It was found that the absorptive capacity is very important.

Filter paper with a very great absorptive capacity causes fast evaporation of the solvent, that means no aggregation takes place.
A very fast evaporation of the solvent is the precondition to prepare non-aggregated polymethine layers on surfaces.
But a leveled, smoothed surface of paper with a small absorptive capacity shows good aggregation.

### *Glass*

Knowing the results of experiments with paper (evaporation of solvent) it is possible using a new method to prepare non-aggregated and aggregated layers on surfaces of glass.
Aggregates of heptamethines were prepared on surfaces in thin layers to minimize the influence of the kind of the surface. The UV/VIS spectra obtained as transmission spectra are shown in Figure 5a and 5b:

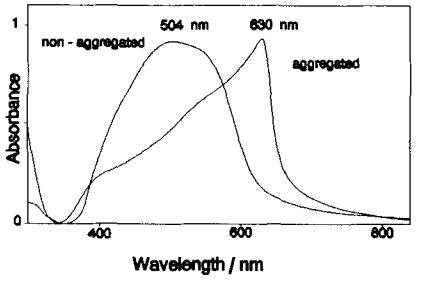



Fig. 5a: BDHClO$_4$non-aggregated and aggregated

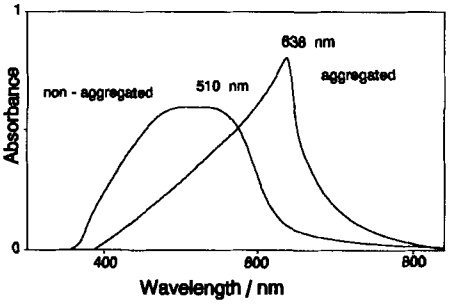



Fig. 5b: BDHBr non-aggregated and aggregated

## Electron Diffraction (RHEED) of BDHBr on a Surface of Glass

In order to determine the *aggregation stucture* of **BDHBr** on glass the compound already investigated by UV/VIS spectroscopy (Fig. 5b) was investigated by RHEED, too.

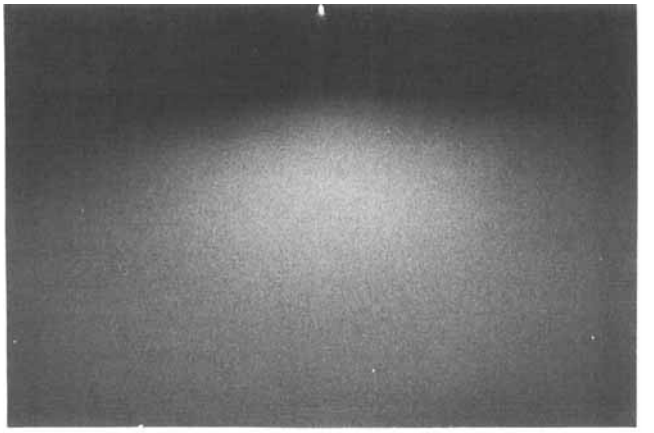


Fig. 6a:
BDHBr aggregated on a surface of glass investigated by RHEED (typical)

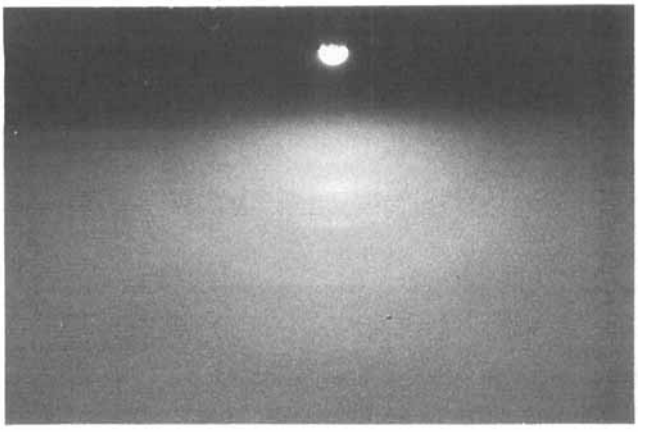


Fig. 6b:
BDHBr aggregated on a surface of glass investigated by RHEED (selected site)

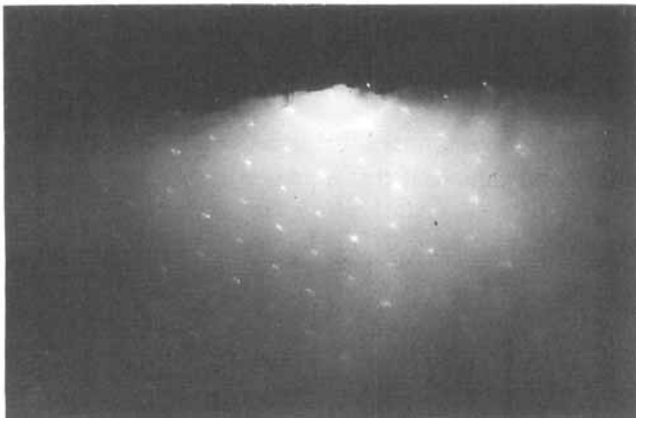


Fig. 6c:
BDHBr aggregated on a surface of glass investigated by RHEED (exception)

**d-values / Å and estimated intensities**

| Figure 6a (typical) | Figure 6b (selected site) | | Figure 6c (exception) | | | |
|---|---|---|---|---|---|---|
| | | | powder | | single crystal | |
| *no sharp Debye rings detectable* | 4.641 | *b* | 2.422 | *vst* | 4.263 | *n.o.* |
| | 3.670 | *b* | 1.883 | *st* | 4.072 | *n.o.* |
| | 2.936 | *st* | 1.581 | *vw* | 3.756 | *st* |
| | 2.180 | *st* | 1.416 | *m* | 2.321 | *n.o.* |
| | 1.868 | *vw* | 1.278 | *w* | 2.485 | *n.o.* |
| | | | | | 2.131 | *st* |
| | | | | | 2.036 | *n.o.* |
| | | | | | 1.878 | *m* |
| | | | | | 1.635 | *st* |
| | | | | | 1.599 | *st* |
| | | | | | 1.564 | *st* |
| | | | | | 1.499 | *st* |
| | | | | | 1.421 | *vst* |
| | | | | | 1.411 | *w* |
| | | | | | 1.357 | *st* |
| | | | | | 1.242 | *vst* |
| | | | | | 1.160 | *vst* |

*vst* very strong
*st* strong
*m* medium
*w* weak
*vw* very weak
*b* diffus
*n.o.* not observed

The Debye rings of the RHEED patterns could not be matched with the X-ray Debye rings. The electron diffraction patterns of the single crystal shows two mirror planes (orthorhombic or higher symmetry ! ), what is not in accordance with monoclinic symmetry of phases former investigated by X-ray analysis.

That's why we think this "thin layer modification" represents a metastable intermediate phase of BDHBr.

But in both cases (X-ray and RHEED) a hexagonal substructure is recognizable in the corresponding diffraction patterns, showing that common structures should exist.

## CONCLUSIONS

The experiments prove that the aggregation tendency increases with prolonging the chain length. In the case of BDHBr two types of aggregates on surfaces are formed in contrast to single crystal structure results: a metastable one (only observed on surfaces) at 580 nm and a stable one (more similar to those in crystal structures) at 630 nm. The nonamethine has the greatest number of absorption bands caused by aggregates but it has a lower stability than the other investigated polymethines. Heptamethines and even more nonamethines should show very significant differences of non-linear optical effects between monomeres and aggregates due to their very good aggregation behaviour.
Further surface analytical methods, e.g. atomic force microscopy should be applied to study the aggregate structures on thin layers.



## ACKNOWLEDGEMENT

We thank the DFG for financial support of this project.
The autors also thank Dr. L. Däweritz for the RHEED measurements.

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