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A cyclic merocyanine UV-A absorber: mechanism of formation and crystal structure

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ABSTRACT

The product of the reaction of 3-(3-methoxypropylamino)cyclohex-2-en-1-one and diethylsulfate has been crystallized and its structure has been determined by X-ray crystallography. The study allowed insight into the formation mechanism of cyclic merocyanine UV absorbers. X-ray diffraction analysis of the merocyanine product made it possible to define the *E*/*Z*-stereoconfiguration.

Cyclic merocyanine structures of the general formula of **1** have recently gained interest as particularly efficient UV-AI absorbers. The UV-AI (360–400 nm) range is the longwave part of the UV-A (320–400 nm) radiation. Those compounds are industrially interesting as protectants for organic materials such as plastics, photographic materials,[1] organic photovoltaic materials,[2] dyes,[3,4] perfumes,[3,4] agrochemicals,[5] consumer products like liquid detergents[4] and for human skin and hair.[6] UV-AI absorbers complement UV absorbers which protect the UV-B (290–320 nm) or UV-AII (320–360 nm) range thus allowing complete UV protection of substrates.[7] The cyclic merocyanine compound **1a** exhibits an absorption maximum at 385 nm with an absorption coefficient ε of 63 052 (investigated in ethanol at 0.02 mM of **1a**) leading to a full coverage of the UV-AI region. We herein describe the synthesis and crystal structure of merocyanine **1a**. The X-ray diffraction analysis of an intermediate allowed insight into the mechanism of formation of cyclic merocyanines.

The synthesis of cyclic merocyanines of general formula **1** was first described by Oehlschlaeger et al.[1] The synthesis starts from 1-aminocyclohexan-3-one derivatives which are easily available through the condensation of 1,3-cyclohexandiones with amines under azeotropic removal of water. For the production of merocyanines the 1-aminocyclohexan-3-one derivatives are allowed to react with DMS (dimethylsulfate) at 100 °C for 40 min and subsequently with methylene active compounds like malonates in the presence of TEA (triethylamine) as a base at 110 °C for 40 min. On addition of water the product precipitates which can be recrystallized from a suitable solvent. We were particularly interested in the mode of action of the alkylating reagent DMS. Oehlschlaeger et al.[1] described a quaternarization without indicating the reaction site. Conventional wisdom implies quaternarization of the nitrogen atom resulting in the formation of a quaternary ammonium salt. However, this intermediate would not form the desired final merocyanine structure (Fig. 1).

We used an analogous synthesis protocol as described by Oehlschlaeger et al.[1] DES (diethylsulfate) was used as the alkylating reagent. The reaction sequence was performed in toluene as solvent. We were interested in the reaction mechanism of this synthesis and the nature of the intermediate formed by the reaction of enaminone **2** with the sulfate. The reaction product of the enaminone **2** with diethylsulfate was stored at 4 °C until

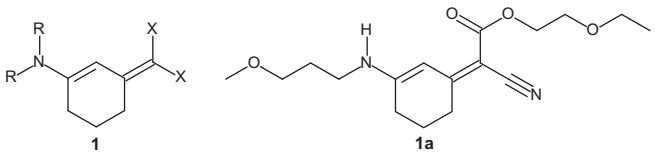

Figure 1. Chemical structure of cyclic merocyanine UV-AI absorbers.

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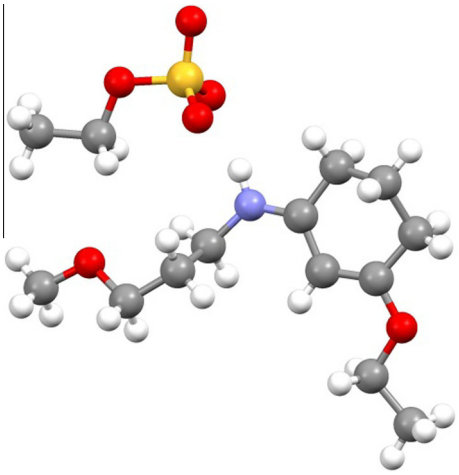


Figure 2. X-ray crystal structure of **3**.

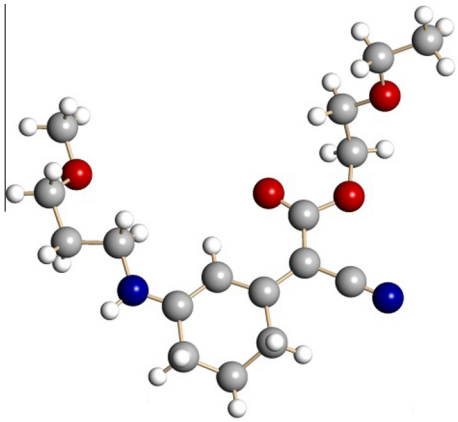
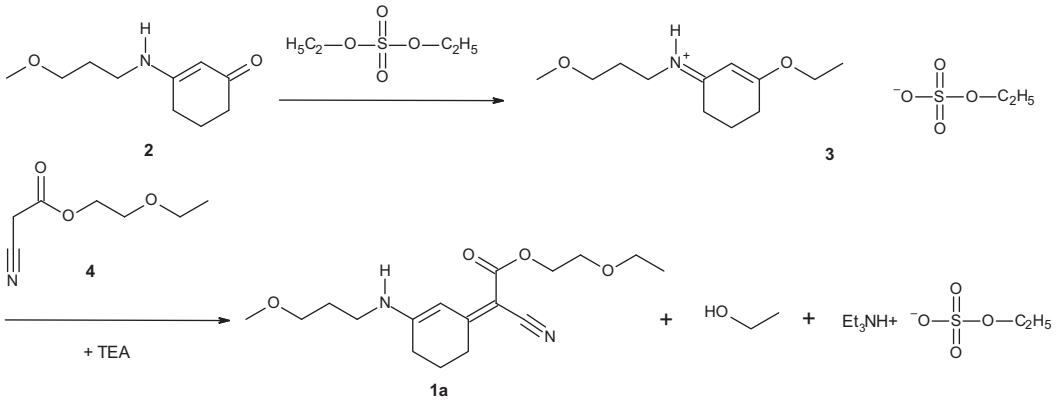


Figure 3. X-ray crystal structure of **1a**.

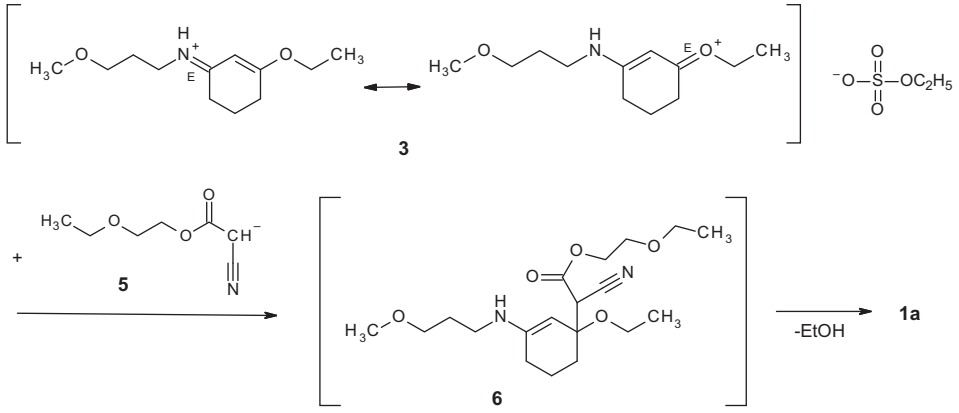
crystallization occurred. A yellow single-crystal with dimension $0.04 \times 0.15 \times 0.20\ mm^3$ was selected for data collection. As shown in Figure 2, single X-ray analysis unambiguously confirmed the formation of enolether **3** showing that alkylation occurs at the oxygen rather than at the nitrogen.

We propose that in the formation of merocyanine **1a** a nucleophilic attack of a cyanoacetate anion **5** toward the vinylogous iminium cation **3** is involved leading to adduct **6**. Anion **5** is formed from cyanoacetate **4** in the presence of the base TEA. The TEA assists the fast elimination of EtOH yielding subsequently merocyanine **1a** (Scheme 2).

Single crystals of merocyanine **1a** were produced by crystallization from heptane/ethyl acetate (2:1). A yellow single-crystal with dimension $0.02 \times 0.10 \times 0.16\ mm^3$ was selected for data collection. The X-ray analysis on those crystals showed the formation of only *Z*-isomers as depicted in Scheme 1 and presented in Figure 3.



Scheme 1. Conversion of 3-(3-methoxypropylamino)-cyclohex-2-en-1-one to the corresponding merocyanine **1a** by using DES.



Scheme 2. Proposed mechanism of merocyanine formation.

Supplementary material

Crystallographic data for the structures of **1a** and **3** have been deposited with the Cambridge Crystal Data Center as supplementary publication nos. (CCDC 973065 contains the supplementary crystallographic data for the compound **1a**. CCDC 973066 contains the supplementary crystallographic data for the compound **3**.) Copies of the data can be obtained, free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.Uk).

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