

Figure. UV/VIS Spectra in CHCl_3 . Left: **5** (absorption, fluorescence and solid-state fluorescence); right **4b** (absorption and fluorescence).

of **4** exhibit an intense solid-state fluorescence.

2.2. Peryleneamidineimides **8** or **9**

Many properties of **2** can be controlled by the substituents R, but not the UV/VIS spectra in solution [4] because of nodes in the orbitals HOMO and LUMO at the N-atoms [5]. On the other hand, little is achieved by altering the basic chromophore of **2**. A possibility of shifting the UV/VIS spectra is an exchange of carbonyl groups of the imide structure **3** by the related imino

group. This has been done in a preceding work [6] for one carbonyl group of each imino ring. A bathochromic shift was obtained, but the fluorescence quantum yields went down to 60% or even lower.

A more moderate altering of the chromophore of **2** is the exchange of one single carbonyl group to an imino group [7]. This can be attained by a partial alkaline saponification of **2** to **7** and a condensation of **7** with diamines to amidineimides like **8** or **9**. These are intensely orange to red fluorescing photostable dyes.

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- [5] H. Langhals, S. Demmig, H. Huber, *Spectrochim. Acta, Part A* **1988**, *44*, 1189.
- [6] I. Lukac, H. Langhals, *Chem. Ber.* **1983**, *116*, 3524.
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Malononitrile, a Synthetic Tool for New Chromophoric Systems

Jean-Marie Adam*, Peter Sutter, and Tammo Winkler

Abstract. New near-IR-absorbing dyes were synthesized by condensation of the dicyanovinyl derivative of 1-acetyl-3-oxo-2,3-dihydroindole with nitroso compounds. The resulting products were found to be mixtures (ca. 9:1) of the (*E*)- and (*Z*)-isomers. The more bathochromic (*E*)-form could be converted into the (*Z*)-form by heating in methanol. At higher temperature new cyclization products were obtained. A mechanism of the isomerisation and cyclization is proposed.

1. Introduction

At the present time, there is current interest in the development of near-IR absorbing dyes for use e.g. in diode-laser optical storage systems. Several investigations have been reported on the synthesis and properties of IR dyes suitable for electro-optical applications [1]. Methine dyes are widely applied in this area because their absorption bands can be easily shifted into the longwave region by the suitable choice of dye end-groups or by extending the methine chain. In this re-

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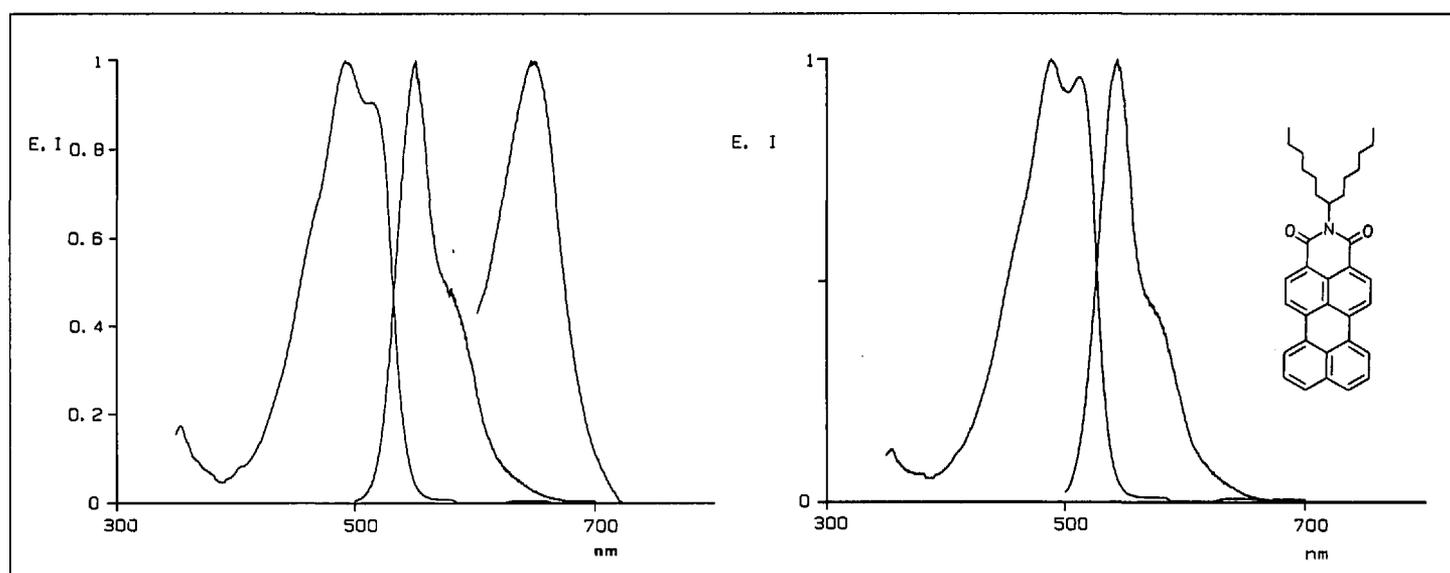


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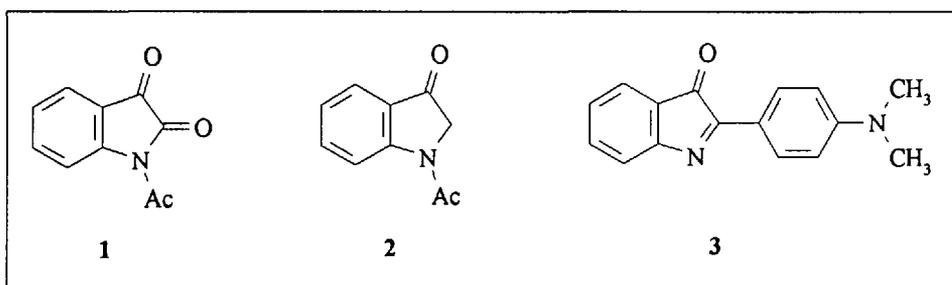
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Abstract. New near-IR-absorbing dyes were synthesized by condensation of the dicyanovinyl derivative of 1-acetyl-3-oxo-2,3-dihydroindole with nitroso compounds. The resulting products were found to be mixtures (ca. 9:1) of the (*E*)- and (*Z*)-isomers. The more bathochromic (*E*)-form could be converted into the (*Z*)-form by heating in methanol. At higher temperature new cyclization products were obtained. A mechanism of the isomerisation and cyclization is proposed.

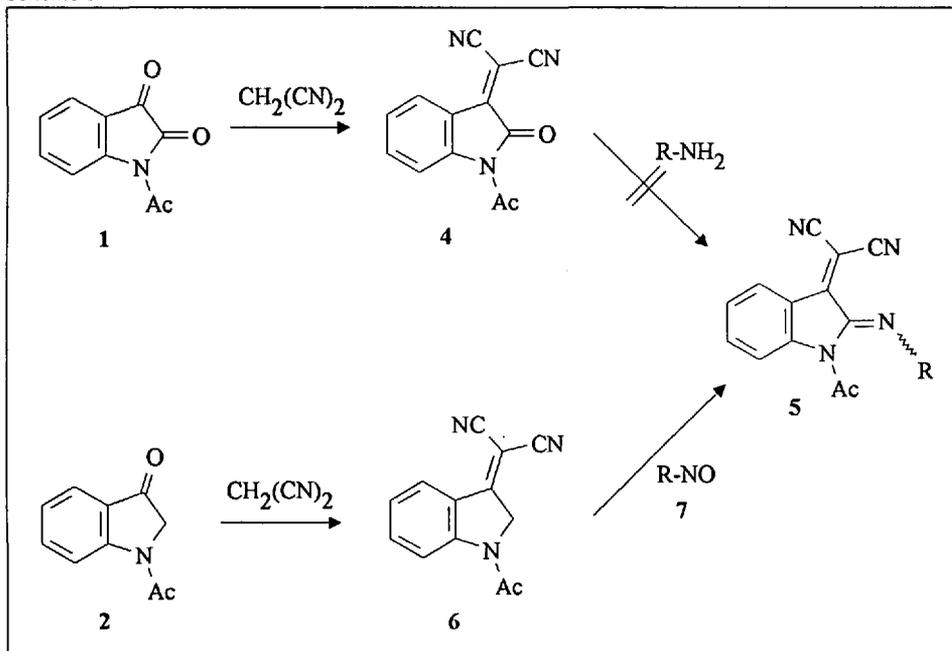
1. Introduction

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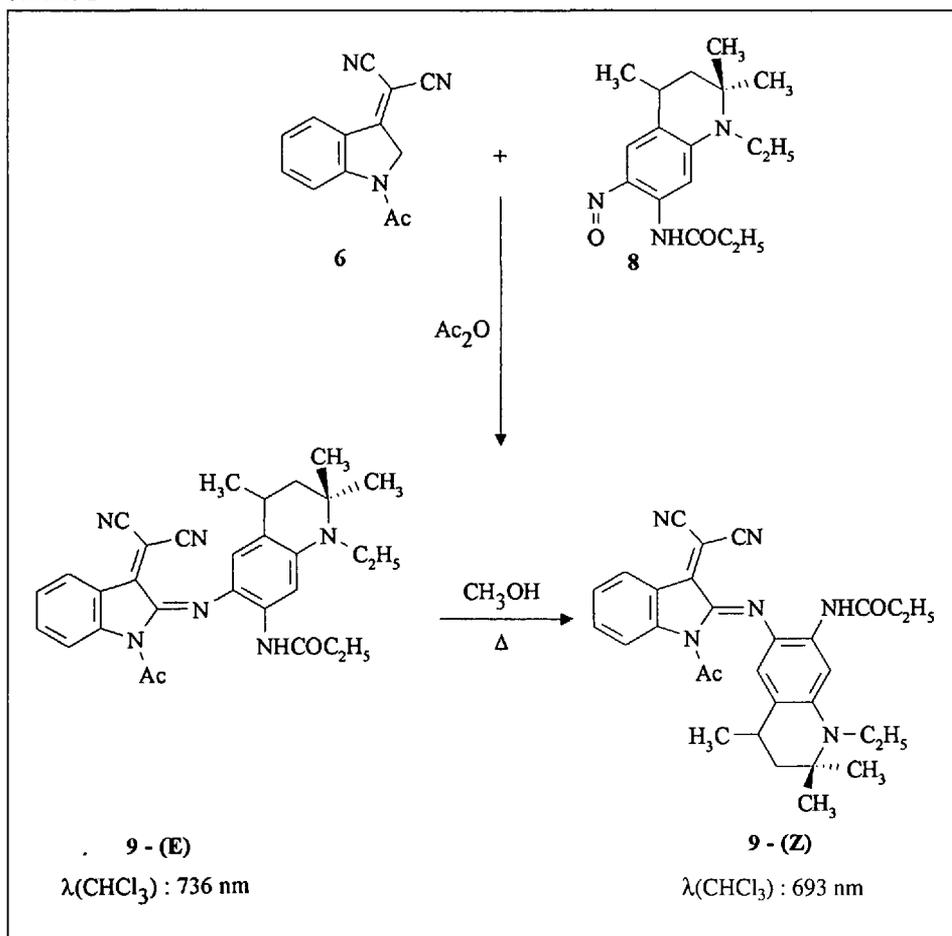
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Scheme 1



Scheme 2



regard the dicyanomethylene group is of particular interest, because its strong electron-acceptor property confers chromophoric and highly efficient auxo-chromic character and can be easily introduced as dye end-group by a *Knoevenagel* reaction of a carbonyl function with malononitrile. Although some dicyanomethylene derivatives of methine dyes based on indan-1,3-dione have already been synthesized [2], less attention has been given to other analogues such as *N*-acetylindatin (1) and 1-acetyl-3-oxo-2,3-dihydroindole (2) and nothing has been published about the chemical behaviour of these dicyanomethylene derivatives.

The purpose of this paper is to describe the synthesis and reactivity of these new near-IR absorbing compounds as well as their visible absorption properties, as an extension of our previous studies on the functionalization of 2-arylindolenin-3-ones (3) with malononitrile [3].

2. Experimental Results

Reaction of *N*-acetylindatin (1) with malononitrile gives 1-acetyl-3-(dicyanomethylene)-1,3-dihydro-2*H*-indol-2-one (4) (Scheme 1), which is known to react with aromatic amines *via* ring expansion or cyanide exchange, depending upon the reaction conditions [4]. In any case, no reaction with the carbonyl group leading to 5 could be observed. We decided to investigate the more promising starting material 1-acetyl-3-oxo-2,3-dihydroindole (2), readily synthesized from anthranilic acid by known methods [5][6].

Our first aims were to prepare 1-acetyl-3-dicyanomethylene-2,3-dihydroindole (6) and to attempt the reaction of this intermediate with various aromatic nitroso derivatives 7 to give condensation adducts 5. A full description of these dyes is given in [7]. Reaction of 2 with a large excess of malononitrile and piperidine as a catalyst gave quantitatively the dicyanomethylene derivative 6. The condensation of 6 with the nitroso derivative 8 was achieved smoothly in acetic anhydride and afforded 9 as a mixture (*ca.* 9:1) of the (*E*)- and (*Z*)-isomers (Scheme 2), which could be separated by chromatography. By heating in methanol, (*E*)-9 could be readily converted into (*Z*)-9, the mechanism of this isomerisation is discussed in Scheme 5. The somewhat longer wavelength absorption of (*E*)-9, ($\lambda_{\text{max}}(\text{CHCl}_3) = 736 \text{ nm}$), relative to (*Z*)-9, ($\lambda_{\text{max}}(\text{CHCl}_3) = 693 \text{ nm}$), reflects the larger steric crowding in the former structure, inducing a torsion of the central C=N unit.

Although analogues of **9**, based on 3-dicyanovinylindan-1-one and 3-dicyanovinyl-1,1-dioxobenzo[*b*]thiophene have already been synthesized [2], the formation of isomers have not been reported by the authors. These products have a λ_{\max} below 700 nm, which is significantly less bathochromic than (*E*)-**9**.

The NMR spectra did not enable one to clearly distinguish between the (*E*)- and (*Z*)-isomers; nevertheless, their structures could be established indirectly by chemical methods. Surprisingly, we found that, on heating both isomers in DMF, one of

them cyclized quickly [8], giving a mixture of two new compounds **10** (main product) and **11** (trace) the structures of which were proven by analytical and physical means (Scheme 3). It is obvious that only the (*E*)-isomer has the right geometry to be the precursor of the cyclization products.

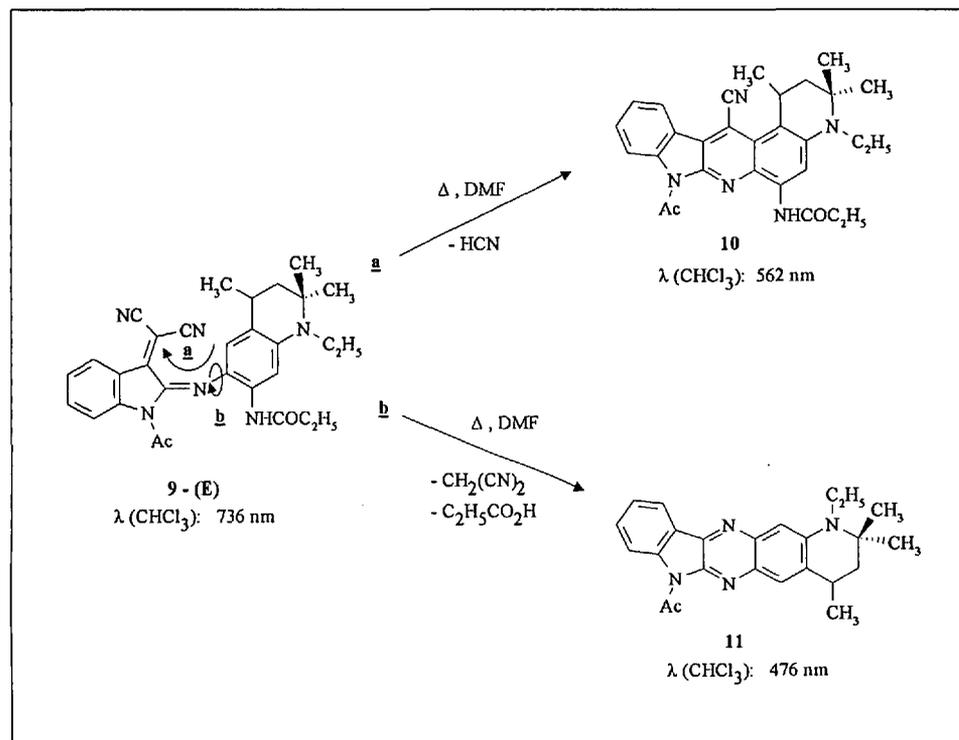
3. Discussion

The cyclization giving **11** (way **b**) can be rationalized as a concerted mechanism

involving a *retro-Knoevenagel* reaction with elimination of malononitrile affording the corresponding ketone, which reacts with the amine resulting from the hydrolysis of the propionylamino group. The dramatic red shift of **11**, ($\lambda_{\max}(\text{CHCl}_3) = 476 \text{ nm}$), relative to **9**, reflects the loss of the powerful electron acceptor, leading to a system with a very low chromophoric character.

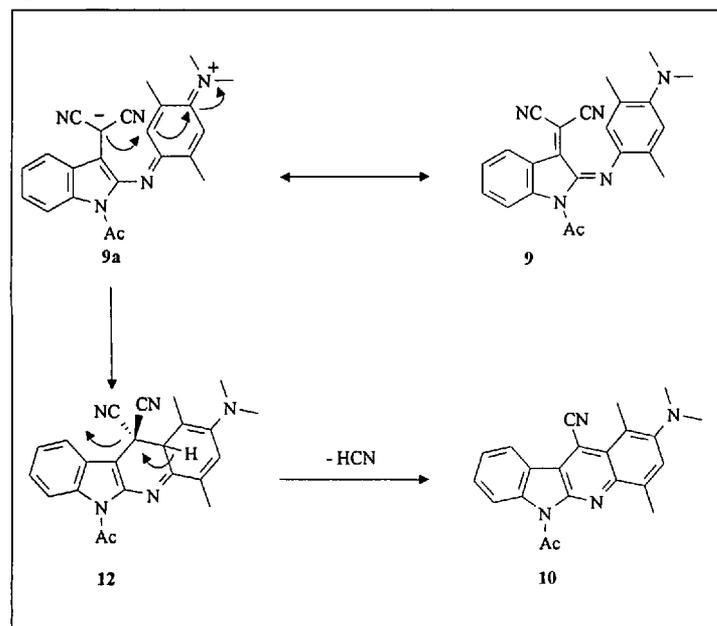
To explain the cyclisation leading to the main product **10** (way **a**), we believe that the reactive intermediate is probably the tautomeric structure **9a** (Scheme 4), which cyclizes spontaneously into **12**. The aromatization occurs through elimination of cyanhydric acid. The visible absorption band of **10** in CHCl_3 exhibits a maximum at 562 nm. This proposed mechanism could explain the conversion of (*E*)-**9** into (*Z*)-**9** in methanol (Scheme 5). Solvents with high dielectric constant such as methanol stabilize the separation of the electronic charges in **9a**, facilitating a rotation about the central C–N bond leading to **9b**.

Scheme 3



- [1] Z. Yoshida, T. Kitao, in 'Chemistry of Functional Dyes', Eds. Z. Yoshida and T. Kitao, Mita Press, Tokyo, 1989.
- [2] K.A. Bello, L. Cheng, J. Griffiths, *J. Chem. Soc., Perkin Trans. 2* **1987**, 815.
- [3] J.M. Adam, T. Winkler, *Helv. Chim. Acta* **1984**, 67, 2186.
- [4] M.I. Younes, *Liebigs Ann. Chem.* **1990**, 703.
- [5] S.J. Holt, A.E. Kellie, D.G. O'Sullivan, P.W. Sadler, *J. Chem. Soc.* **1958**, 1217.
- [6] S.J. Holt, P.W. Sadler, *Proc. R. Soc. London [Ser.] B* **1958**, 148, 481.
- [7] *Ciba-Geigy*, Eur. Pat. 462928 (19.6.1990).
- [8] *Ciba-Geigy*, German Pat. 4215654 (16.5.1991); *Ciba-Geigy*, German Pat. 4215718 (16.5.1991).

Scheme 4



Scheme 5

