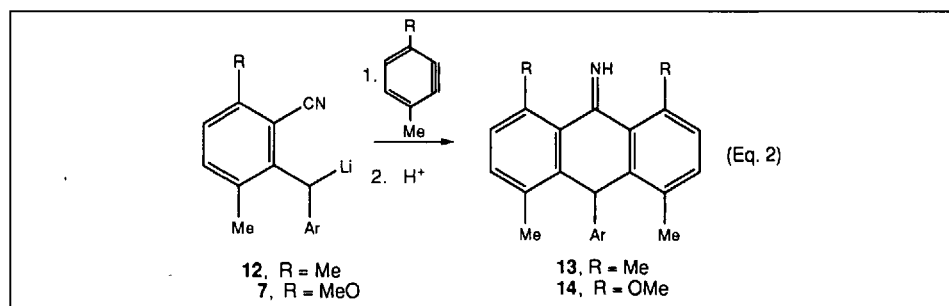
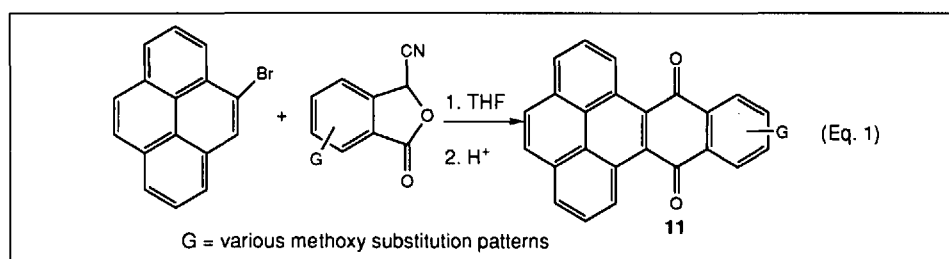


methodology by using 3-lithiated 3-cyanophthalides which not only greatly increased the reaction workup time (< 1 h compared to overnight in the case of Sammes lithiumphthalide-mediate reaction), but also because of readily availability using Swenton's elegant methodology [6], enables one to prepare a wide variety of anthraquinones, such as methyl ethers of anthraquinones, such as chrysophanol [7], helmintho-sporin [7], morindaparvin [8], and biologically active azaanthraquinones [9]. Recently, we have prepared hexacene quinones **11** by the reaction of 4-bromopyrene and cyanophthalides [10] (Scheme 3).

Other dipolar nucleophiles have been discovered that react with arynes to give polycyclics. *E.g.*, as shown in Scheme 4, the generation of another equiv. of aryne in the presence of α -lithiated rearranged nitriles **12** and **7** from the reaction of 2-bromo-1,4-dimethylbenzene and 2-bromo-4-methylanisole yields the respective 9-imino derivatives of 10-arylanthrones **13** [11] and **14** [12]. 10-Hydroxy-9-anthracenecarbonitriles [13] can be prepared similarly by generating arynes in the presence of α -lithiated *o*-(methoxycarbonyl)arylacetonitriles, with no apparent restriction on the nature of the aryne. 10-Amino-9-anthracenecarbonitriles can also be prepared by the reaction of α -lithiated α -cyano-*o*-tolunitrile with methoxy substituted arynes [14], 1-naphthalynes [15] and 1-pyrynes [12]. However, it yields rearranged dinitriles when treated with 3,6-dimethoxybenzynes, 9-phenanthryne [16] and 4-pyryne [12]. The 10-amino- and 10-aminoanthracenes are powerful fluores-



cent materials, whose excitation wavelengths occur from 320 to 360 nm and emission wavelengths range from 520 to 560 nm [12].

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Novel Perylene Derivatives as Highly Photostable Fluorescent Dyes

Heinz Langhals*

Abstract. Perylene-3,4-dicarboxylic imides are prepared by a new decarboxylizing condensation with moderately sterically hindered primary amines. Perylene-3,4-dicarboxylic anhydride is prepared *via* a saponification reaction of the dicarboximide and is a starting material for a number of new types of chromophores. A second route to novel perylene derivatives is a partial hydrolysis of perylene dyes and a condensation with diamines. The dyes thus obtained are orange to red fluorescing in solution.

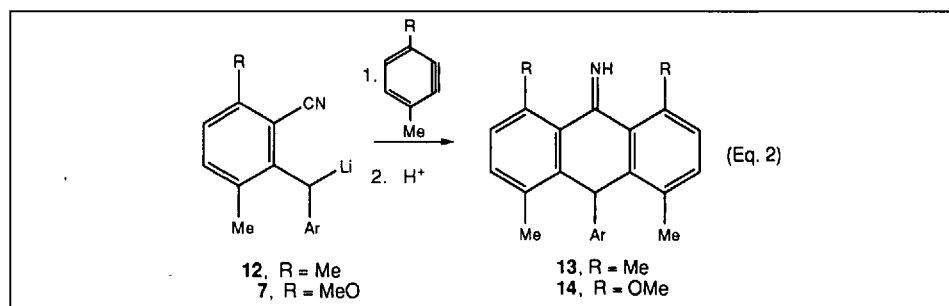
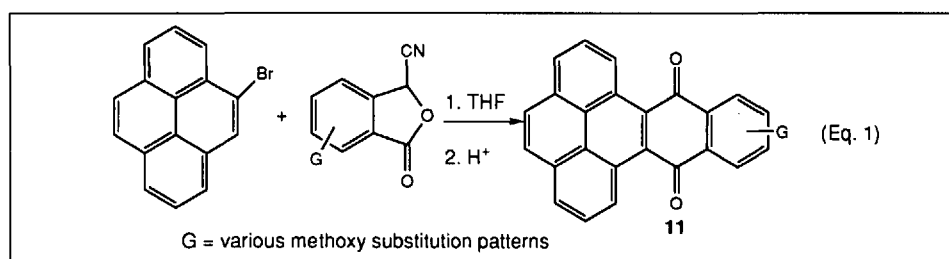
1. Introduction

Perylene-3,4:9,10-tetracarboxylic bis-anhydride (**1**, C.I. No. 71127) is prepared in an analytically pure state on technical scale and it is the starting material for the preparation of perylene dyes (perylene-3,4:9,10-tetracarboxylic bisimides, **2**) [1]. The perylenes **2** are well-known as highly photostable pigments and fluorescent dyes; for a review see [2]. An essential point for the lightfastness and inertness of **2** is the

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methodology by using 3-lithiated 3-cyanophthalides which not only greatly increased the reaction workup time (< 1 h compared to overnight in the case of Sammes lithiumphthalide-mediate reaction), but also because of readily availability using Swenton's elegant methodology [6], enables one to prepare a wide variety of anthraquinones, such as methyl ethers of anthraquinones, such as chrysophanol [7], helmintho-sporin [7], morindaparvin [8], and biologically active azaanthraquinones [9]. Recently, we have prepared hexacene quinones **11** by the reaction of 4-bromopyrene and cyanophthalides [10] (Scheme 3).

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Heinz Langhals*

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1. Introduction

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linkage of two units of the strongly resonance stabilized cyclic carboxylic bisimide structure element (3) to the perylene skeleton in *peri*-position.

The anhydride 1 is predominantly used for the preparation of 2, but it is also a

valuable starting material for other derivatives with a perylene structure element. This has been reported for the preparation of carboximides with five-membered rings [3], and will be demonstrated for a number novel fluorescent dyes.

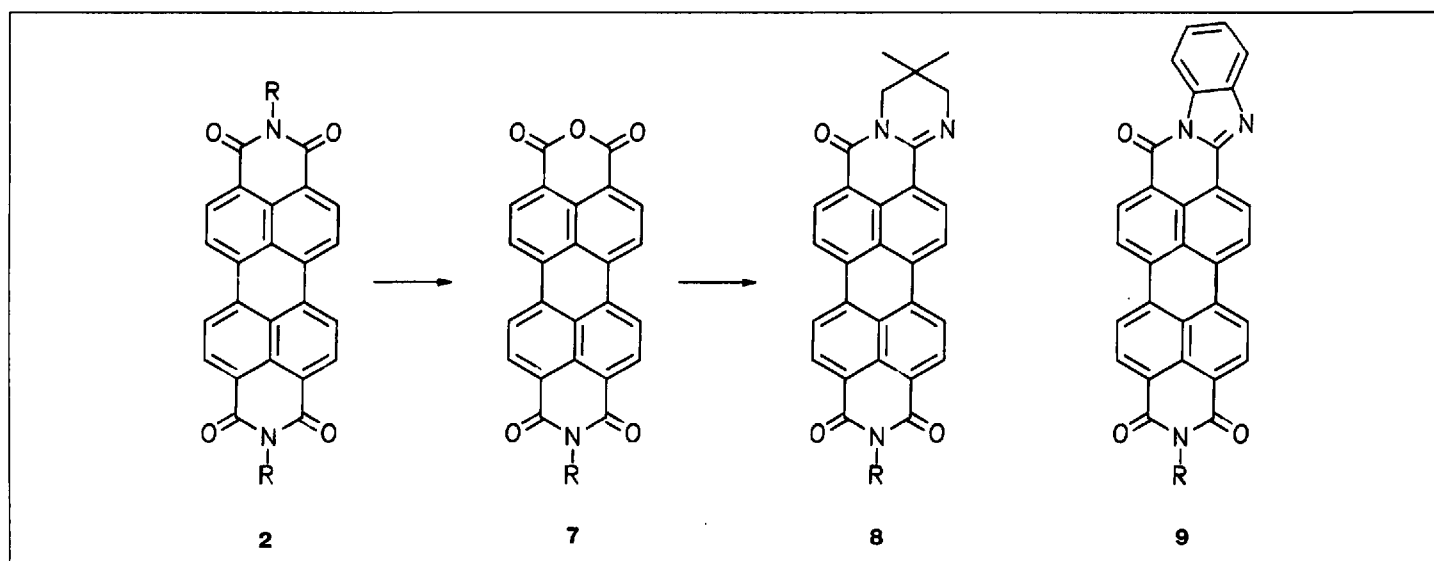
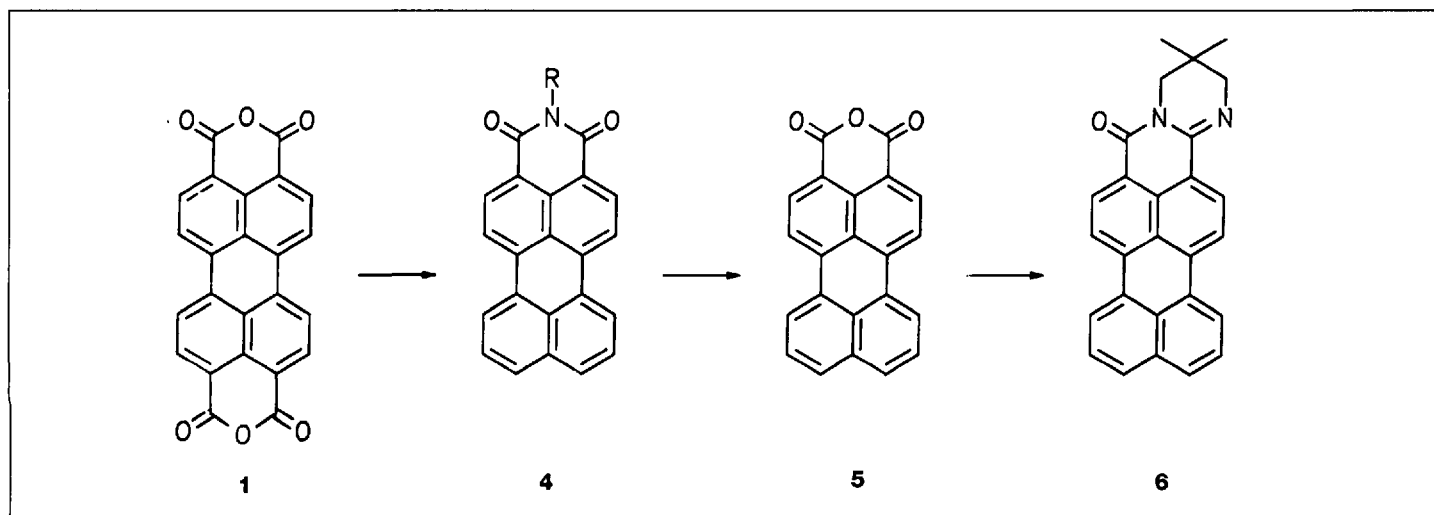
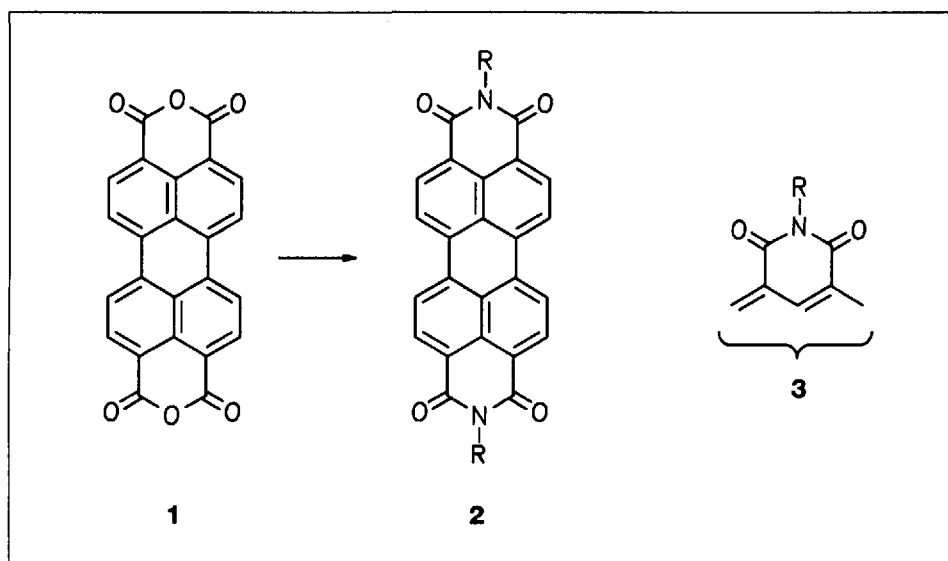
2. Results

2.1. Perylene-3,4-dicarboxylic Imides 4

Whereas 1 is a well established class of dyes there are only a few derivatives of the related 4, because there is no preparation procedure for 5. However, if moderately sterically hindered primary amines like 2,5-di(*tert*-butyl)aniline are condensed with 1 in presence of H₂O a decarboxylation proceeds with the condensation to the imide 4a in 50% yield.

The imides 4 are hydrolysed with KOH in *tert*-butyl alcohol to 5. The anhydride 5 is a general starting material for 4 and other perylene derivatives. The pure anhydride 5 is a red pigment with an intense solid-state fluorescence; the UV/VIS spectra are shown in the *Figure*.

The dyes 4 are extraordinarily photostable: in solution more even than a factor of 20 (!) compared to 2. This may be a consequence of the stabilizing structure element 3. The dyes are highly fluorescent. Some derivatives



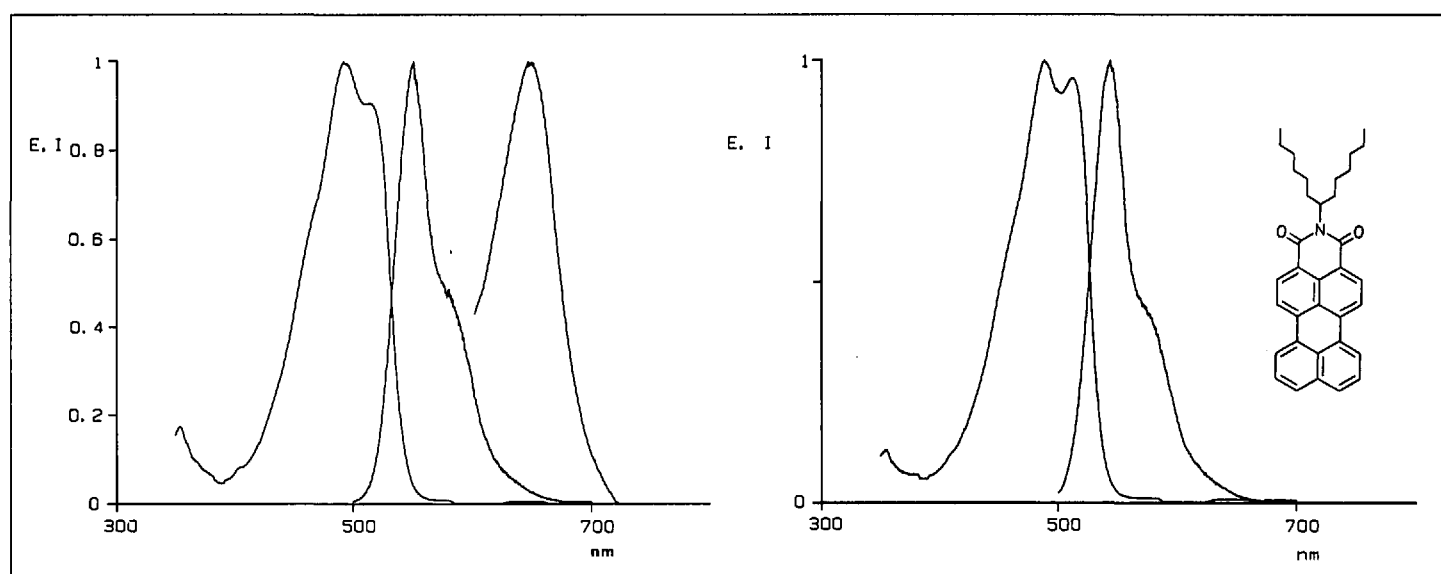


Figure. UV/VIS Spectra in CHCl_3 . Left: **5** (absorption, fluorescence and solid-state fluorescence); right **4b** (absorption and fluorescence).

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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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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