

**CYCLIC CARBOXYLIC IMIDE STRUCTURES AS STRUCTURE
ELEMENTS OF HIGH STABILITY.
NOVEL DEVELOPMENTS IN PERYLENE DYE CHEMISTRY**

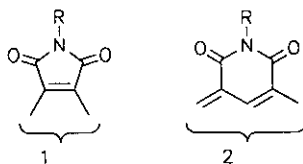
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Abstract - Cyclic carboxylic imides are structure elements in aromatic heterocycles with high persistency. Their attachment to perylene leads to the perylene dyes; the synthesis and unique properties of the dyes are reported and discussed. An extension of the principle to other aromatics is made.

INTRODUCTION

Carboxylic imides¹ are stabilized by their very high resonance energy which exceeds even that of carboxylic amides. A further stabilization is achieved by their incorporation into five (1) or six membered (2) heterocyclic rings.

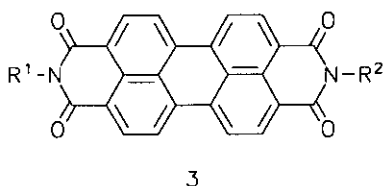


1 and 2 are therefore especially useful as structural parts of substances with a high persistency: for example, the wellknown² polyimide high temperature polymers. The ring closure of the imide structure element to give a heterocycle is essential for thermal stability. The rupture of one bond in these cycles will not lead to a thermal degradation of the polymer because of the fast recombination of the reactive fragments which are linked together. The simultaneous rupture of two bonds, which is less probable, would however be a degra-

dation process (compare ladder polymers). The inertness towards aggressive reagents is very high so that some derivatives of **2** withstand molten alkali and can be saponificated only by hot concentrated sulfuric acid!

An interesting field for the application of the structures (**1**) and (**2**) is the development of highly photostable fluorescent dyes.³ Not only are the excitation energies 160 to 300 kJ/mol (38 to 71 kcal/mol) for the visible region but electronic transitions with such high energies have to be tolerated for more than one million times⁴ in these dyes.

The attachment of structure element (**2**) to the peri position of perylene leads to perylene-3,4:9,10-tetracarboxylic bisimides, the so called perylene dyes (**3**).



3a: $R^1 = R^2 = H$

3b: $R^1 = R^2 = CH_3$

3c: $R^1 = R^2 = 2,5-(CH_3)_2C_6H_3$

3d: $R^1 = R^2 = CH(C_6H_{13})_2$

3e: $R^1 = R^2 = CH(C_4H_9)_2$

3f: $R^1 = R^2 = CH(C_9H_{19})_2$

3g: $R^1 = R^2 = C_6H_5$

3h: $R^1 = R^2 = CH(C_8H_{17})_2$

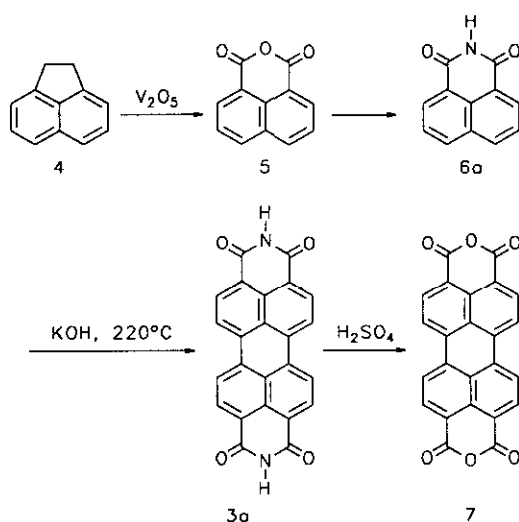
PERYLENE DYES

Perylene dyes (**3**), discovered in 1913 by *Kardos*, are wellknown as very lightfast vat dyes.⁵⁻⁷ They have also been used and still are used as technical pigments. Because of their low solubility however it was not before 1959 that their high fluorescent potential was discovered.⁸ Novel applications arise from the strong fluorescence of the dyes in combination with other unique properties.

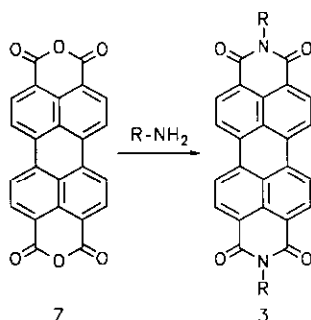
SYNTHESIS OF SYMMETRICALLY SUBSTITUTED PERYLENE DYES

The synthesis of symmetrically substituted perylene dyes (**3**, $R^1 = R^2$) from the corresponding anhydride (**7**) is straightforward. In the technical process acenaphthene (**4**) is oxidized⁹ to naphthalene-1,8-dicarboxyanhydride (**5**). This anhydride cannot be dimerized directly to the perylene derivative. Therefore, it is converted to the imide (**6a**) with ammonia and subsequently dimerized with molten alkali to **3a** (C.I. Nr. 71129). Saponification with hot concentrated sulfuric acid gives the perylene tetracarboxylic bisanhydride (**7**;

C.I. Nr. 71127) which itself is a pigment. Finally the anhydride is condensed with primary amines to the dyes (3).



The bisanhydride (7) is also a very good starting material for the preparation of other perylene derivatives because it can be easily obtained analytically pure, even on a technical scale. As an example, highly pure perylene itself can be prepared by a simple decarboxylation reaction of 7 with aqueous alkali.^{10,11}



The condensation of 7 with reactive primary aliphatic amines can be carried out without any problems, for example in media like water¹² or benzene.¹³ For less reactive aliphatic amines the solvents quinoline^{14,15} or molten imidazole^{16,17} are useful.

For the condensation of less reactive aromatic amines the use of quinoline or molten imidazole as a solvent is necessary. Zinc salts like zinc acetate or zinc chloride are essential catalysts for the reaction. Other metal

salts, for example iron or lead or copper salts, can be also used, but are less effective. Additionally, the separation of these metal salts from the reaction products can be difficult. The role of the zinc salts is not clear - they are denoted as dehydrating reagents. A more plausible interpretation is that the zinc salts might be solutizers on the basis of complexation of the anhydride (7). The bisanhydride (7) or the bisimide (3a) are insoluble in any organic solvent used for synthesis; no coloration or fluorescence! However their solubility is strongly increased by the addition of zinc salts, so that, for example, uv/vis-spectra can be reported. This is shown for the first time in Figure 1 for 7.

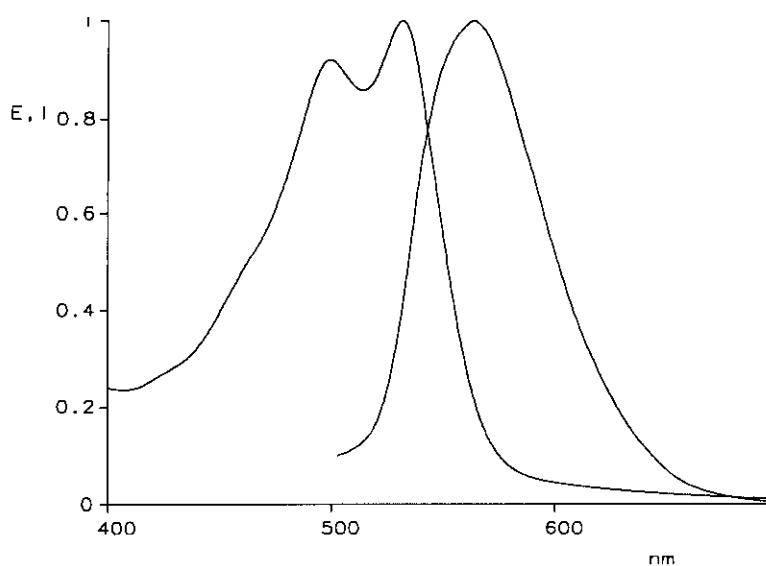
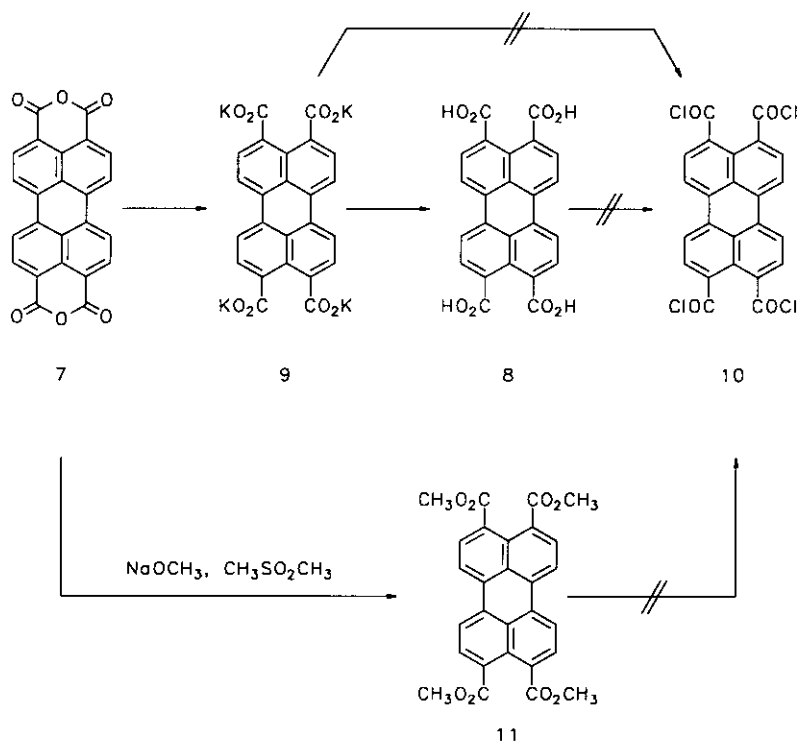


Figure 1: Uv/vis-absorption and fluorescence spectra of 8 in quinoline with addition of zinc acetate.

The more reactive acid chloride (10) of perylene-3,4,9,10-tetracarboxylic acid (8) cannot be used for the preparation of 3, because it is unknown. Neither the anhydride (7) nor the tetramethylester (11) nor the tetrapotassium salt (9) can be converted into the acid chloride, not even with phosphorus pentachloride in boiling POCl_3 !

In contrast to the analog naphthalene tetracarboxylic acid the free acid (8) cannot be prepared in the usual manner. One obtains 7 directly when solutions of salts of 8 are acidified. The kinetics of the cyclization in solution has been measured by Ford.¹⁸ When an aqueous, alkaline solution of the tetrapotassium salt of 8 is acidified with CO_2 below 5°C a yellow, thermally instable precipitate of the yellow perylenetetracarboxylic

monopotassium salt dihydrate is formed ($\text{pH} \approx 6$). The structure of this salt is established by ir spectroscopy,¹⁹ elemental analysis²⁰ and the fact that it can be thermally transformed to the tetracarboxylic mono

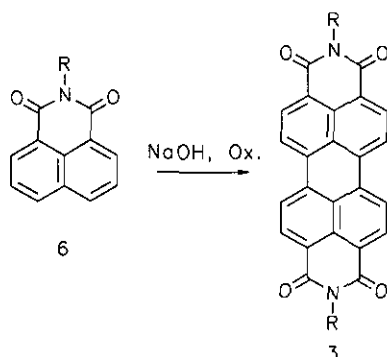


anhydrid monopotassium salt (comparison of the ir spectra). When a solution in methanol/water of the tetrapotassium salt monohydrate of **8**, prepared by a precipitation with ethanol and recrystallisation from ethanol/water,^{21,22} is acidified with a cooled solution of acetic acid in water and methanol at -40°C a yellow orange crystalline powder precipitated. It is washed with ethanol and dried.²³ This yellow orange powder has the empirical formula of $\mathbf{8}\cdot\text{H}_2\text{O}$ ($\text{C}_{26}\text{H}_{12}\text{O}_9$) based on elemental analysis.²⁴ It is soluble in chloroform to give a yellow solution with a green fluorescence. The crystal powder turns slowly to the red color of the bisanhydride (**7**) at room temperature; this ring closure reaction might be controlled by entropy and proceeds rapidly at higher temperatures. The yellow orange color of **8** is a strong evidence that both heterocyclic rings are cleaved, because even one ring closure turns the color to red or even deeper. Further evidence for the structure is given by the absence of anhydride absorptions at $1800\text{-}1720\text{ cm}^{-1}$ in the infrared spectrum and absorptions at $3600\text{-}2400$ (broad) and 1699 cm^{-1} which are typical for carboxylic acids. Finally the anhydride (**7**) is obtained by heating the hydrate of **8**. It has correct values of elemental analysis and the ir

spectrum is identical with the spectrum of an authentic sample. The free acid (**8**) is not a good starting material for the preparation of **3** because of its instability.

The conversion of the hydrate of **8** to the acid chloride (**10**) has been tried with SOCl_2 or $\text{PCl}_5/\text{POCl}_3$ at low temperatures.²³ Yellow solutions with a moderately intense green fluorescence have been obtained, but a conversion could not be done on a preparative scale. On the other hand, at higher temperatures a complete cyclization to **7** takes place.

The salts of **8** are a less favorable starting materials for the preparation of the imides (**3**) than the anhydride (**7**) in terms of energy. However, they are better starting materials in terms of entropy because of the unfavorable ring opening of the anhydride. In this way ammonium and alkaline earth salts of **8** have been converted to **3** by high temperature baking processes. These methods are very useful for the preparation of technical pigments, but less applicable for laboratory synthesis.



Nucleophilic displacement reactions can be carried out with dye (**3a**) after deprotonation because the N-H groups are acid. However the yields are low for most substituents because of the low solubility of **3a** and its deprotonated form in solvents.

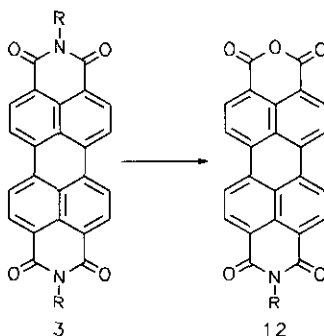
Finally, an alternative route for the preparation of bisimides is the dimerization of substituted naphthalene imides. However this method has only been reported for short-chain aliphatic substituents R, for example **3b** with $\text{R} = \text{CH}_3$ in the technical synthesis of indanthrene red GG (C.I. Nr. 71130).^{25,26}

The dimerization of naphthalene units can also be carried out stepwise - see for example ref.^{27,28} - but this is important only for special cases because of the more complicated synthesis. It has been used for textile printing with the development of perylene dyes directly on the textiles.^{29,30}

Perylene bisimides can be chlorinated up to four times at the aromatic nuclei in the presence of iodine. The main product is the 1,6,7,12-tetrachloro derivative, but other chlorinated products are formed, which are difficult to remove. The tetrachloro derivative has an appreciably high steric strain. This is the driving force for nucleophilic displacement reactions. Displacement with phenoxy groups e.g. leads to a tetra phenoxy derivative which is a photostable, red fluorescing dye.^{31,32}

SYNTHESIS OF NON SYMMETRICALLY SUBSTITUTED PERYLENE DYES

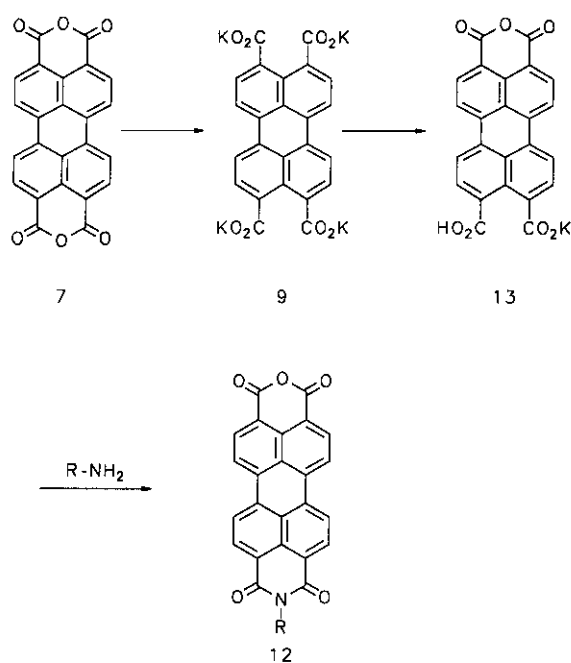
It is not possible to prepare non symmetrically substituted **3** ($R^1 \neq R^2$) by a stepwise condensation of the technical **7** with primary amines. A reaction of the anhydride (**7**) with a primary amine as a minor component will not produce **12** as might be expected, rather the amines are completely converted to **3** ($R^1 = R^2$) and the excess of **7** remains unreacted (compare ref.³³). In some special cases a simultaneous condensation of **7** with a mixture of primary amines has been carried out, but the reactivity of the two amines must be similar and the reaction mixtures so obtained are difficult to separated.



Nagao, Misono and coworkers have found a synthetic route to **12** by a partial acid saponification of **3**. However the rather rough reaction conditions - conc. sulfuric acid at 180-200°C³⁴ - limit this interesting method to special substituents R. Simple aliphatic substituents R = methyl, ethyl, propyl and butyl have been used. Problems occur with aromatic substituents which can be sulfonated.

An elegant synthesis has been found by *Tröster*.³⁵ The insoluble **7** is converted to the tetra potassium salt (**9**) which is readily soluble in water. The monoanhydride monopotassium salt (**13**) is precipitated by a moderate acidification with orthophosphoric acid. This procedure can be further optimized by the application of acetic acid,³⁶ because traces of the latter can be more easily removed. The driving force for the formation of **13** is its extraordinarily high lattice energy - the substance is absolutely insoluble in any solvent, even at high

temperatures - which removes it from the protonation equilibria. **13** can be condensed to **12** with primary amines in water. With this synthetic method the unsymmetrically substituted perylene dyes can be prepared in large scale amounts. The necessity of an aqueous medium, however, limits the scope of the reaction from **13** to **12**. The yields of **3** are excellent to good with short-chain readily water soluble amines, moderate to low with less water soluble amines and very low with highly hydrophobic amines. However the condensation of the latter is important for the preparation of perylene dyes with a high solubility in organic solvents (see below).



A general way for the preparation of **12** is the partial alkaline saponification of the symmetrically substituted dyes (**3**). Although these are very resistant towards alkali - some bisimides are prepared in molten alkali - they are readily hydrolyzed by a concentrated solution of KOH in *tert*-butyl alcohol or *tert*-amyl alcohol.³⁶ A separation of **12** from the starting material (**3**) and the product of complete saponification (**7**) can be easily carried out because only **7** is soluble in concentrated alkali (as tetraanion of **8**), whereas **3** is insoluble and also the dianion derived from **12** because of the high isoionic concentration. **12** can be obtained by a treatment of the residue with hot distilled water and acidification.

The anhydride-imides (**12**) can be condensed with primary amines to unsymmetrically substituted perylene dyes in the same way as described before for the symmetrical dyes (see ref.^{36,37}).

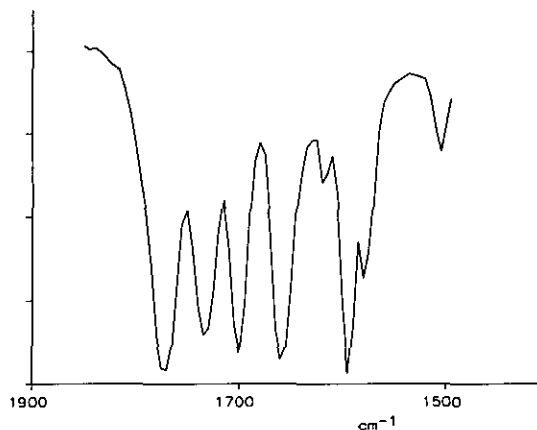


Figure 2. Ir spectrum of **12d** in KBr. Absorptions at 1510, 1580, 1595, 1660, 1701, 1733 and 1772 cm^{-1} .

The saponification and condensation reactions can be easily followed by means of ir spectroscopy as shown in Figure 2. The pattern of absorption at 1510, 1580 and 1595 cm^{-1} is typical for the perylene skeleton. The absorption bands at 1660 and 1701 cm^{-1} indicate the imide group and the absorption at 1733 and 1772 cm^{-1} the anhydride group. The position and shape of imide and anhydride absorptions remains nearly unaffected by substituents.

OPTICAL PROPERTIES OF PERYLENE DYES

A central factor for the applications of perylene dyes is their extraordinarily high lightfastness which exceeds that of any fluorescent dye in solution known to date (compare also ref.³⁸). The heterocyclic rings are, as mentioned before, the essential stabilizing factor. The only weak point is the single bond to the terminal groups R, but this is of less importance concerning fluorescence, because the chromophore has nodes in the orbitals HOMO and LUMO (and LUMO+1 as well as HOMO-1) at the nitrogen atoms.³⁹ This will cause a decoupling of the chromophore from these single bonds.

Together with the photostability the dyes are also very stable thermally; some derivatives can be sublimed at temperatures up to 550°C!⁴⁰ Furthermore, they are very resistant towards ionizing radiation⁴¹ and aggressive reagents.⁴² For example, they can be dissolved in concentrated sulfuric acid and reobtained by dilution

without decomposition (compare ref.⁴³). Concentrated hypochlorite solution does not give any bleaching effect.

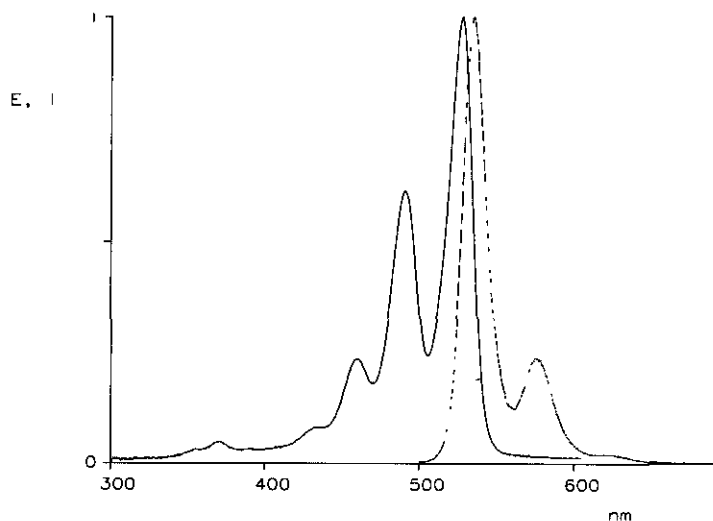


Figure 3: Absorption and fluorescence spectrum of perylene dye (3c) in chloroform.

Perylene dyes (3) form red purple solutions in organic solvents with an intense yellow fluorescence. A typical uv/vis spectrum for dye (3c) is given in Figure 3. The spectra depend only weakly on the substituents R because of the nodes in LUMO and HOMO at the nitrogen atoms as mentioned above. Besides that, the perylene dyes are only weakly solvatochromic.⁴⁴ Absorption maxima have been found for dye(3c) at 526.0, 490.2, 459.0, 432.6 and 369.5 nm in chloroform solution. Fluorescence maxima are at 537, 579 and 628 nm. The molar coefficient for the extinction maximum at long wavelength is $95000 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ for aromatic substituents R like 3c and 88000 for aliphatic substituents like 3d. The bulk spectrum is a little hypsochromically shifted for the latter, for example to 526.3, 489.6, 458.5, 432.7 and 369.3 nm for 3d. The spectra depend only slightly on the other properties of R. The dyes have some tendency of aggregation in solution at high concentration forming dimers⁴⁵ and H-aggregates with a substantial line broadening, a hypsochromic shift of absorption and quenching of fluorescence.

Nearly all perylene dyes are soluble in conc. sulfuric acid via protonation. This causes a bathochromic shift of the absorption of 80 nm. However neither the structure of the spectrum as given in Figure 4 nor the coefficient of extinction is noticeably altered. Therefore the uv/vis spectra in sulfuric acid are an excellent tool for the quantitative determination of perylene pigments which otherwise would be insoluble in solvents.

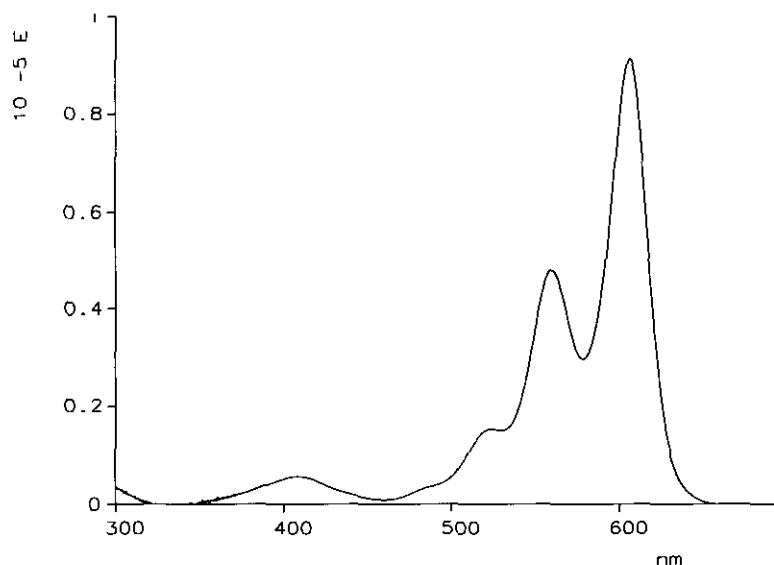
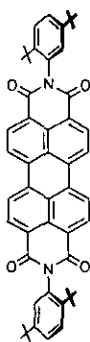
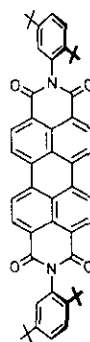


Figure 4: Uv/vis absorption spectrum of perylene dye (3c) in H_2SO_4 (λ_{max} (ϵ) = 606.2 (91280), 560.3 (48140), 523.8 (15370)).

The free rotation around the R-N bond can be hindered if R has an appropriate structure.³⁹ An example is a phenyl group with bulky *tert*-butyl groups in *o*-position as in dye(3c). It has been possible to prepare both atropic isomers(3c1 (*trans*))and(3c2 (*cis*))⁶ so that their spectra could be studied. Surprisingly, their uv/vis spectra are completely identical.⁴⁶ Even the ir spectra are nearly identical. This fact can be used for the study of dye-matrix interactions.⁴⁶ On the other hand, this result is important because it is not necessary to prepare pure atropic isomers for dye applications.



3c1



3c2

Most of solid perylene dyes are red. Besides that orange, maroon, bluish black and black derivatives are known. Some of them exhibit an intense bronze like metallic surface lustre.⁴⁷ Many of the red dyes have a red solid-state fluorescence which is very pronounced for **3e**.⁴⁸ The orange colored derivatives are generally fluorescent.

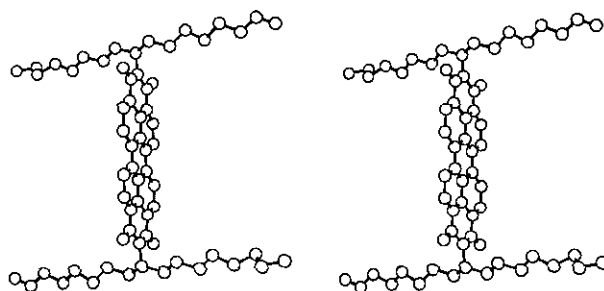


Figure 5: Stereo plot of the crystal structure of **3f**.

Relations between crystal structure and solid-state color of perylene dyes have been sought.⁴⁹⁻⁵³ Some rules were found, but a final solution of the problem is still lacking. Force field calculations have been made to predict the packing of perylene chromophores in pigments.⁵⁴ Crystal structures are known for perylene dyes with small substituents R. With larger substituents the structure analysis becomes more and more difficult. Structure analysis⁵⁵ could be hardly done for dye (**3f**).^{48,56} The chromophores can be located in this structure with acceptable precision, but problems arise with the flexible side-chains which are disordered (for a more detailed discussion see ref.⁴⁸); **3f** is the only known perylene dye where a structure analysis of dyes with long-chain secondary alkyl groups was successful. The structure of **3f** is given in Figure 5 and the atomic coordinates in Table 1. A further general problem for crystal structure analysis is the low tendency of perylene dyes to scatter X-rays. This experimental problem is partially overcome by the high persistency of the dyes against ionizing radiation⁴¹ which allows measuring times of a week or even longer.

Perylene dyes have a high tendency to form allotropic modifications which may differ in solid-state color because of the different interactions in the solid state. In some cases the energies of transformation have been measured.⁴⁸

Table 1: Atomic coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) of perylene dye (3f)

Atom	x	y	z	U(eq)	Atom	x	y	z	U(eq)
C(1)	4249(14)	723(12)	88(19)	92(7)	C(15)	355(28)	3812(26)	-369(45)	233(19)
N(2A)	3380(13)	668(12)	184(15)	110(6)	C(16)	801(29)	4380(27)	622(42)	248(20)
C(3)	3049(17)	38(15)	418(19)	105(8)	C(17)	508(46)	3987(42)	1376(70)	384(38)
O(3)	3483(11)	-427(9)	496(13)	130(6)	C(18)	1151(39)	4560(34)	2471(63)	307(29)
C(4)	2175(17)	-119(14)	304(18)	99(8)	C(19)	1074(53)	4538(47)	3446(91)	419(47)
C(5)	1794(14)	-836(12)	318(17)	96(7)	C(20)	1488(57)	4871(46)	4581(88)	423(43)
C(6)	952(14)	-1024(11)	277(16)	89(6)	C(21)	1453(60)	4851(48)	5697(81)	552(51)
C(7)	509(13)	-569(12)	73(15)	78(6)	C(22)	2514(66)	5399(52)	6191(84)	578(58)
C(8)	832(16)	178(14)	110(17)	100(7)	C(23)	-79(24)	3565(21)	-2585(37)	211(15)
C(9)	320(15)	702(13)	-72(17)	100(7)	C(24)	87(27)	3299(22)	-3472(39)	241(17)
C(10)	704(14)	1385(12)	-192(17)	94(7)	C(25)	-748(28)	2955(23)	-4684(40)	252(18)
C(11)	1603(16)	1550(14)	-117(19)	117(8)	C(26)	-532(42)	2797(33)	-5539(59)	349(32)
C(12)	2079(14)	1020(12)	-27(16)	91(6)	C(27)	-1423(40)	2627(30)	-6755(55)	350(26)
C(13)	2985(21)	1143(19)	76(23)	149(11)	C(28)	-1254(53)	2824(41)	-7678(72)	509(41)
O(13)	3184(12)	1767(11)	-50(15)	159(7)	C(29)	-2356(51)	2379(37)	-8870(58)	446(34)
C(14)	1693(17)	327(14)	177(19)	108(8)	C(30)	-2765(92)	2303(75)	-8291(119)	944(107)
C(15)	4104(22)	649(20)	-1026(31)	175(13)	C(1)	6715(22)	-2925(19)	3076(25)	164(12)
C(16)	3483(22)	19(20)	-1915(32)	183(13)	N(2C)	6274(16)	-2378(14)	3514(22)	154(9)
C(17)	3353(28)	-146(23)	-3097(38)	218(17)	C(3)	6490(22)	-1901(20)	4583(31)	176(12)
C(18)	2641(28)	-615(23)	-3890(39)	217(17)	O(3)	7064(14)	-2163(12)	5280(18)	191(9)
C(19)	2648(29)	-778(24)	-4946(43)	243(18)	C(4)	6218(19)	-1403(18)	5062(27)	135(10)
C(20)	1910(54)	-1149(46)	-6110(71)	417(46)	C(5)	6594(17)	-941(16)	6209(24)	129(9)
C(21)	2289(33)	-1670(28)	-6491(46)	359(23)	C(6)	6328(17)	-392(15)	6603(22)	126(9)
C(22)	1746(34)	-1682(28)	-7590(46)	308(24)	C(7)	5664(14)	-173(13)	5792(20)	97(7)
C(23)	4822(21)	1455(19)	1084(30)	184(13)	C(8)	5250(14)	-616(12)	4592(19)	90(6)
C(24)	4935(20)	1618(16)	2245(27)	152(11)	C(9)	4671(13)	-446(12)	3882(18)	80(6)
C(25)	5750(31)	2142(26)	3232(43)	273(21)	C(10)	4338(14)	-796(13)	2734(20)	107(7)
C(26)	5631(26)	2226(23)	4229(36)	239(17)	C(11)	4615(15)	-1400(13)	2370(19)	102(7)
C(27)	6367(28)	3022(24)	5250(40)	240(18)	C(12)	5224(15)	-1566(14)	3116(21)	99(7)
C(28)	6344(33)	3068(27)	6303(47)	262(22)	C(13)	5546(21)	-2151(19)	2724(30)	158(12)
C(29)	7100(69)	3447(58)	7188(92)	529(69)	O(13)	5309(14)	-2556(12)	1721(20)	187(9)
C(30)	7120(41)	3582(34)	8146(55)	372(34)	C(14)	5545(14)	-1184(13)	4241(20)	91(7)
C(1)	382(27)	3884(21)	-1336(39)	218(15)	C(15)	6383(23)	-3656(19)	3270(26)	184(13)
N(2B)	1419(16)	4075(14)	-1082(17)	140(8)	C(16)	5560(22)	-3941(19)	3139(26)	179(12)
C(3)	1852(21)	3594(18)	-870(22)	131(10)	C(17)	5553(24)	-4731(21)	3266(28)	202(14)
O(3)	1562(11)	3004(11)	-806(14)	141(7)	C(18)	4588(32)	-5063(28)	3029(36)	282(20)
C(4)	2792(21)	3790(17)	-451(22)	143(10)	C(19)	4435(36)	-5887(31)	3201(41)	289(24)
C(5)	3343(20)	3393(16)	-155(22)	138(10)	C(20)	3393(37)	-6164(31)	2952(41)	301(24)
C(6)	4204(18)	3548(15)	-22(20)	127(9)	C(21)	3378(39)	-6902(33)	2919(44)	324(26)
C(7)	4556(16)	4288(14)	-1(18)	102(8)	C(22)	2446(37)	-7014(30)	2676(43)	341(26)
C(8)	4091(6)	4802(5)	-300(7)	0(2)	C(23)	7649(22)	-2494(20)	3396(26)	177(12)
C(9)	4523(16)	5463(13)	-354(18)	103(7)	C(24)	7788(22)	-1789(19)	3218(26)	177(13)
C(10)	4053(19)	5939(15)	-412(21)	131(9)	C(25)	8716(24)	-1534(21)	3271(28)	189(14)
C(11)	3134(21)	5804(18)	-706(25)	169(12)	C(26)	8790(23)	-787(21)	3325(28)	193(14)
C(12)	2766(18)	5004(16)	-727(20)	126(9)	C(27)	9755(29)	-415(26)	3253(35)	256(20)
C(13)	1762(21)	4844(20)	-989(24)	150(11)	C(28)	9870(23)	326(21)	3118(28)	198(14)
O(13)	1356(15)	5285(13)	-1160(18)	186(9)	C(29)	10777(25)	706(22)	3124(30)	235(16)
C(14)	3212(16)	4501(15)	-565(19)	110(8)	C(30)	10599(28)	1522(26)	3053(36)	290(20)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Besides the traditional applications of **3** as vat dyes or pigments there are several new developments. There are numerous publications concerning applications of **3** in electrophotography - see for example ref.^{42,57} - and for photovoltaic devices - see for example ref.⁵⁸ Perylene dyes have been used in camouflage painting^{59,60} because of their strong ir reflecting properties. This might be a consequence of their high dielectric constants.^{61,62} However special care must be taken to avoid any fluorescence of the dyes because it is very pronounced and characteristic. Many other novel applications use the strong fluorescence of the dyes.

FLUORESCENCE - NOVEL DEVELOPMENTS

The fluorescence of perylene dyes in solution was firstly described by *Geissler and Remy*⁸ in 1959. However the high fluorescence potential of the dyes could not be realized and applied because of the low solubility of these substances. Two approaches have been made to obtain readily soluble perylene dyes:

1. *Substitution with tert-butyl groups.*^{4,63}

When *tert*-butyl groups are attached to aromatic systems the solubility of the substances in organic solvents is enormously increased so that deeply colored solutions of dyes can be prepared. Additionally the rate of dissolving is considerably increased. For example, the insoluble perylene dye (**3g**) with phenyl substituents becomes readily soluble in organic solvents by the attachment of four *tert*-butyl groups as in **3c**. *Tert*-butyl groups are much more useful than primary or secondary alkyl groups as solubility increasing substituents in dyes. Additionally the *tert*-butyl groups have no hydrogen atoms in the benzylic position which make dyes instable against a radical attack (compare the *Hock* process).

2. *Substitution with long-chain secondary alkyl groups (swallow-tail substituents).*^{48,64,65}

In contrast to primary alkyl groups long-chain secondary alkyl groups give a pronounced increase in solubility when attached to the nitrogen atoms of the perylene dyes. For example, the solubility of **3d** is much higher even than the solubility of dye (**3c**).

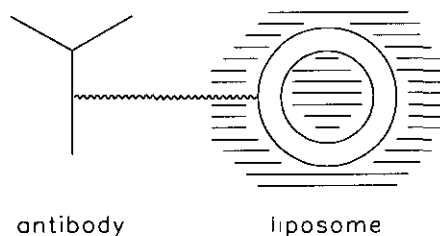
Perylene dyes (**3**) exhibit an intense, yellow fluorescence in solution. The quantum yield is about unity for the majority of derivatives; for a systematic study see ref.^{15,66} The photostability depends strongly on the substituents R¹ and R². Other uv/vis spectroscopic properties have also been studied.^{18,67-69}

Perylene dyes are interesting for dye laser applications.^{38,70,71} The photostability of perylene dyes is even higher than that of rhodamin 6G, one of the most stable laser dyes known to date. The laser-light efficiency

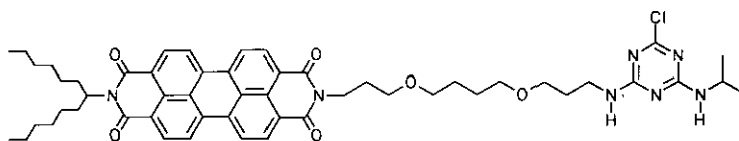
is a little lower than for the latter. This might be due to a small amount of $S_1 - S_n$ absorption. Spectral hole burning effects have been studied with these dyes.⁷²

Perylene fluorescent dyes may be applied in light concentrating systems^{4,73} for the concentration of diffuse solar radiation as well as for scintillators. They can also be used as light emitting species in oxalate chemiluminescent devices⁷⁴⁻⁷⁷ because of their chemical persistency.

The high photostability and fluorescent quantum yield of **3** make the perylene dyes ideal tools for highly sensitive fluorescent analysis methods. A quantitative determination of **3** is possible in a concentration of 10^{-13} mol/l and for an absolute amount of 10^{-18} mol with an accuracy of 5%.^{78,79} **3** has been even used in optical fluorescent sensors where the long-term stability is a critical point.⁸⁰



A further amplification of the analytical signal is achieved if the dyes are incorporated in the double layer of liposomes.⁸¹ Best results are obtained with dye (**3h**) with two C_{17} -swallow-tail substituents from which up to 500 dye molecules can be dissolved in the double layer of one single liposome (90 nm diameter) without destabilization or fluorescence quenching. These fluorescent liposomes can be attached to antibodies⁸² as a general selectively binding system and thus a universal analysis system can be established. Because of the high lightfastness of the dyes even single fluorescent immunoantibodies can be visually observed and their binding site located under a fluorescence microscope.



3i

A second possibility for a quantitative determination of a substrate by means of fluorescent liposomes is to link the fluorescent liposome to a hapten as a second substrate and then to measure the competitive binding of the two. This has been demonstrated for atrazin as a hapten with dye (3i). The long-chain secondary hydrocarbon substituent with the chromophore can be incorporated into the liposome and the atrazin unit which is bound via the polar spacer remains free for binding to antibodies.

ELECTRON TRANSFER PROCESSES

Perylene dyes can be electrochemically reduced and oxidized. The redox potentials have been reported.⁸³ Up to six electrons can be taken up by the chromophore and the spectra of radical ions have been measured.⁸³⁻⁸⁷

The high degree of reversibility of the reduction make the dyes useful for the storage of electrical energy. Piles have been developed by *Domschke* and others with lithium metal as counter electrode.⁸⁸⁻⁹⁰ The piles have not only a large number of charging cycles, but also their voltage decreases stepwise because of the stepwise electron transfer concerning the chromophore. By this way information about the charge state of the pile can be simply obtained by a voltage measurement.

FIVE MEMBERED HETEROCYCLIC RINGS

Five membered heterocyclic rings (1) can be easily prepared by the *Diels-Alder* reaction of maleic anhydride with appropriate polycyclic aromatic systems⁹¹ followed by an rearomatization reaction which proceeds with oxygen directly after the reaction. A condensation of the resulting anhydride can be carried out as described for the perylene dyes.⁹²

For example, 7 is decarboxylated with aqueous alkali to perylene (14) which is converted to the anhydride of benzperylene dicarboxylic acid (15). This can be condensed, as described above, to the imide (16).¹⁰ A decarboxylation of 15 yields benzperylene (17). The anhydride of coronenedicarboxylic acid (18) is obtained by a further *Diels-Alder* reaction and the imide (19) by a further condensation.

16 and 19 are very photostable fluorescent dyes just as the six membered ring derivatives. However their molar coefficient of extinction is more than a factor of 10 smaller than that of 3 and their fluorescence quantum yield Φ is only about 40% (Figures 5,6). The thermal stability of the imides with five membered rings is also high, but it seems that dyes of the type (1) are more readily hydrolyzed by alkali than those of type (2).

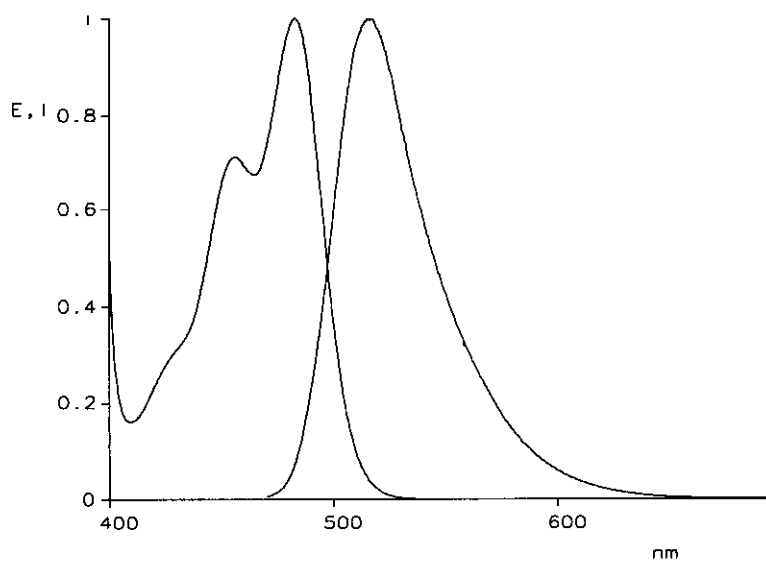
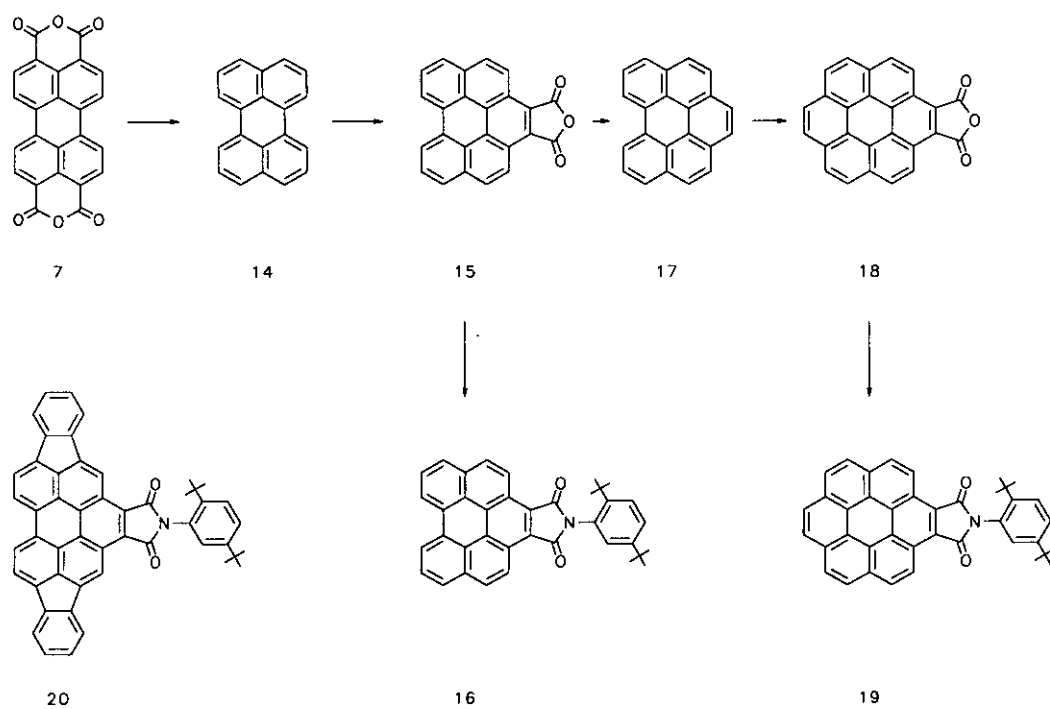


Figure 6: Uv/vis absorption and fluorescence spectrum of the benzperyleneimide (**16**) (λ_{\max} (ϵ) = 482.7 (6750), Φ = 0.42).

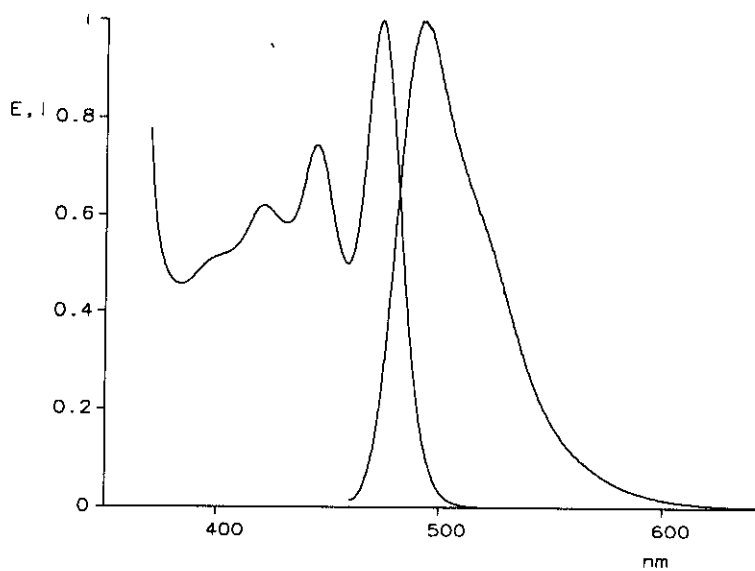


Figure 7: Uv/vis absorption and fluorescence spectrum of the coroneneimide (**19**) ($\lambda_{\text{max}}(\epsilon) = 473.8 (9340)$, $\Phi = 0.41$).

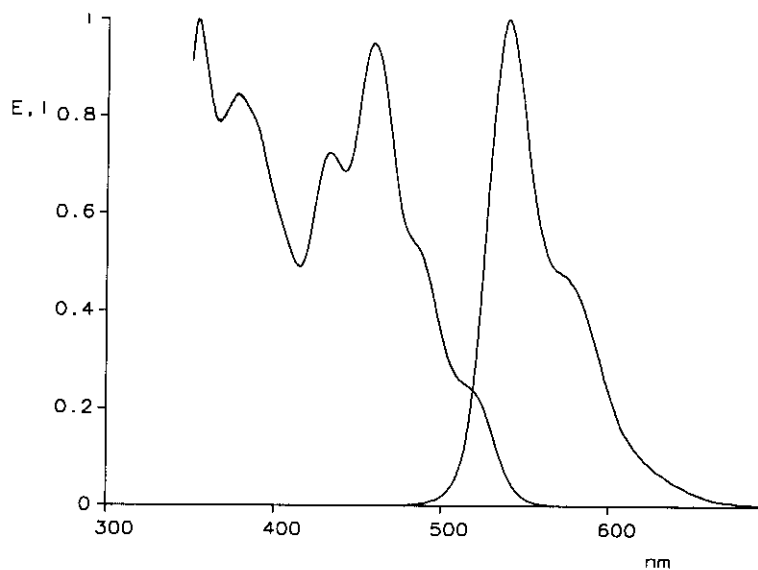
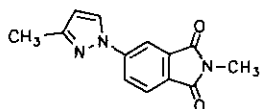
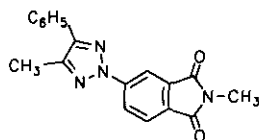


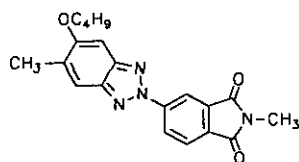
Figure 8: Uv/vis absorption and fluorescence spectrum of the 1,16-benzoperiflantheneimide (**20**) ($\lambda_{\text{max}}(\epsilon) = 458.9 (27800)$, $\Phi = 0.34$).



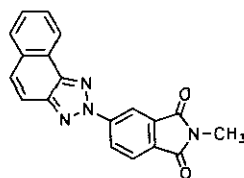
21



22



23



24

Periflanthene leads in the same way to the imide of 1,16-benzoperiflanthene (20).¹⁰ It is a fluorescent dye with a higher coefficient of absorption than the other five-ring imids (Figure 8).

Finally, phthalimides are simple derivatives of structure (1). Numerous phthalimides have been synthesized (see for example ref.^{93,94}). The phthalimides (21-24) with heterocyclic π -donor groups⁹⁵ (important for fluorescent dyes) in position 4 have been synthesized and systematically studied.⁹⁶ Highly fluorescent and photostable dyes have been obtained with this concept.

The incorporation of carboxylic imide structures into aromatic systems has proved to be a useful concept for the development of substances with a high persistency. The concept is important for dyes and it can be expected that it will become important for other areas of chemistry as well.

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 20. Anal. Calcd for $\text{C}_{24}\text{H}_{15}\text{O}_{10}\text{K}$: C 57.37, H 3.01. Found: C 58.11, H 2.82; loss of water (200°C) to

$C_{24}H_9O_7K$ calcd. 10.75 found 10.58.

21. Anal. Calcd for $C_{24}H_{10}O_9K_4$: C 48.14, H 1.68, K 26.12. Found C 48.58, H 1.60, K 27.4; H_2O determination: calcd. 3.01 found 2.82.
22. Ir (KBr): $\nu = 3600-3400\text{ cm}^{-1}$, 1592, 1563, 1510, 1461, 1417, 1388, 1352, 1322, 1271, 1204, 1133, 1115, 958, 860, 850, 811, 791, 777, 767, 650.
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