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Naphthacenequinones: synthesis and properties

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Abstract. The literature data on the methods of synthesis and the properties of naphthacenequinones and related compounds are surveyed. The tautomeric and photochromic transformations of naphthacenequinone derivatives are examined. The bibliography includes 158 references.

I. Introduction

The chemistry of polycyclic quinones is a promising and vigorously developing field of modern organic chemistry. This is associated with the fact that they have been finding increasingly wide application in many branches of science and engineering.

The first and so far the main application of quinones involves their use as organic dyes. In particular, naphthacenequinones — linear benzologues of anthraquinone — have been patented as dyes for synthetic fibres and polymeric resins.[1-10]

The study and synthesis of organic conducting materials based on certain naphthacenequinone derivatives has developed vigorously to the present time.[11-18]

Certain polycyclic quinones have found applications as pharmaceutical preparations. Thus anthracyclines, which are based on the naphthacenequinone carbon skeleton, constitute an important group of antibiotics.[19,20] Studies in the field of anthracyclines have developed vigorously in connection with the search for an alternative biochemical method of synthesis of compounds of this type in the preparation of new antitumour agents.[21-33]

It has been proposed that certain derivatives of naphthacenequinone be used in the manufacture of photochromic materials for the optical recording of information.[34]

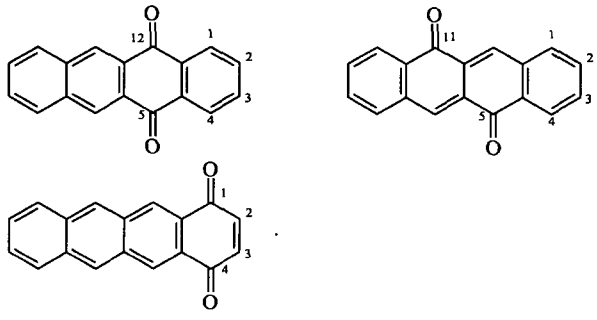
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This review surveys the literature data on the methods of synthesis and the chemical and spectroscopic properties of naphthacenequinones and presents the results of studies on the tautomeric transformations of these compounds.

II. Methods of synthesis of naphthacenequinones and their derivatives

Depending on the position of the carbonyl groups in the naphthacene nucleus, naphthacenequinones are known to include three monoquinones — 5,12-naphthacenequinone (*p*-naphthacenequinone), 5,11-naphthacenequinone (*ana*-naphthacenequinone), and 1,4-naphthacenequinone:



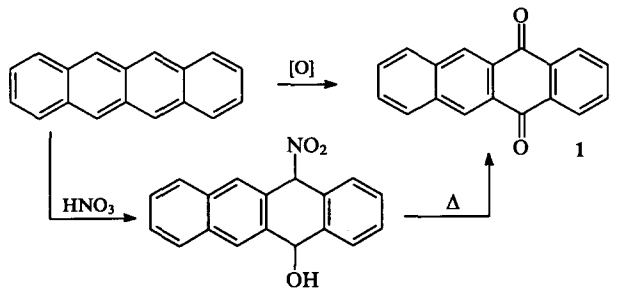
5,12-Naphthacenequinones have been most thoroughly investigated among these compounds.

1. Methods of synthesis of 5,12-naphthacenequinone and its derivatives

The existing methods of synthesis of 5,12-naphthacenequinones can be divided into two groups depending on whether they are based on the use of compounds already having the napthacene carbon skeleton or whether they involve its construction.

The first group includes the oxidation reactions of naphthacene and its derivatives. Chromium trioxide in acetic acid,[35-38] chromic acid,[39] ozone,[40] perbenzoic acid,[41] nitric acid,[42] etc. are used as oxidants.

The unsubstituted 5,12-naphthacenequinone **1** was first obtained by oxidising naphthacene with chromium trioxide in acetic acid.[43]



Substituted derivatives of 5,12-naphthacenequinone were synthesised by a similar procedure: 2-isopropyl-, 2,8-dimethyl-, and 2,9-dimethyl-naphthacenequinones.[35,36] When naphthacene is oxidised with nitric acid, an adduct is first formed, being converted on heating into 5,12-naphthacenequinone **1**.[42]

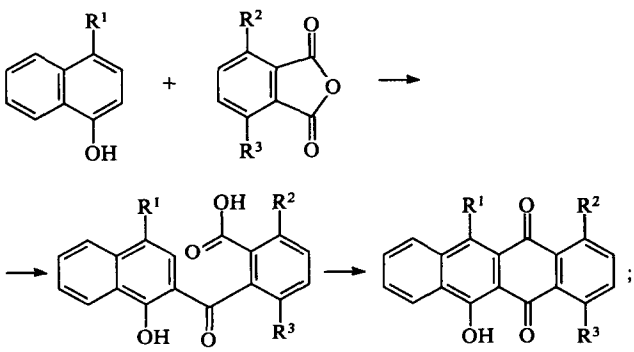
Compound **1** can also be obtained by oxidising naphthacen-5-one.[44,45]

The oxidation of 1,4-dichloronaphthacene leads to 7,10-dichloro-5,12-naphthacenequinone.[39] 6-Chloro- and 6-bromo-5,12-naphthacenequinones have been obtained from 5,11-dihalonaphthacenes.[38]

There exist data indicating the formation of 6,11-dihydroxy-5,12-naphthacenequinone in the vapour-phase oxidation of napthalene.[46,47] A method for the isolation of 6,11-dihydroxy-5,12-naphthacenequinone from the still residues remaining after the distillation of phthalic anhydride by codistillation with liquid paraffin has been proposed.[48]

The second group of methods of synthesis of 5,12-naphthacenequinone derivatives is based on cyclisation reactions, the main ones involving intramolecular acylation and diene synthesis.

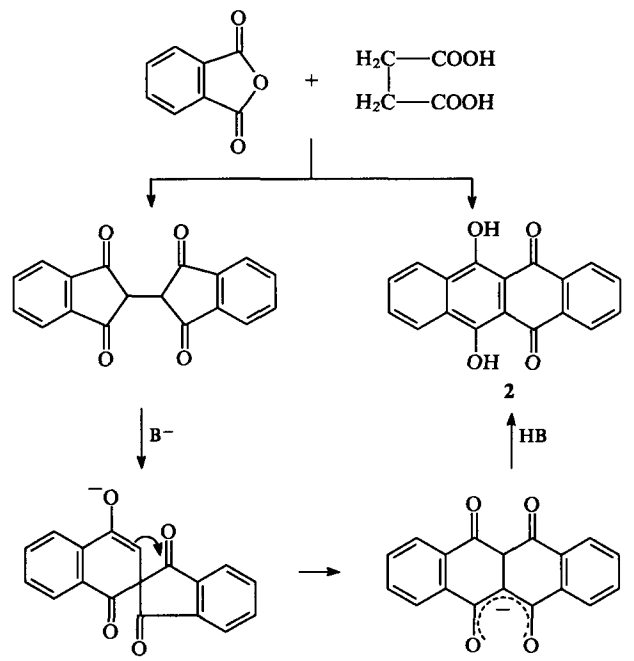
The intramolecular acylation reaction, widely used in the synthesis of anthraquinone derivatives, is also applicable to the synthesis of naphthacenequinones. Unsubstituted 5,12-naphthacenequinone **1** and many of its derivatives have been obtained by acylating naphthalene (or benzene) derivatives with phthalic anhydride (or the anhydride of naphthalene-2,3-dicarboxylic acid) by the Friedel–Crafts reaction in the presence of $AlCl_3$ or boron trioxide followed by the cyclisation of the resulting 2-(β-naphthoyl)benzoic (or 3-benzoyl-2-naphthoic) acid by a mixture of sulfuric and boric acids or in the $AlCl_3$–NaCl melt.[49,50]



R^1 = H, OH; R^2 = H, OH, NO_2, NH_2, NHAc, NMe_2, Cl;
R^3 = H, OH, Cl.

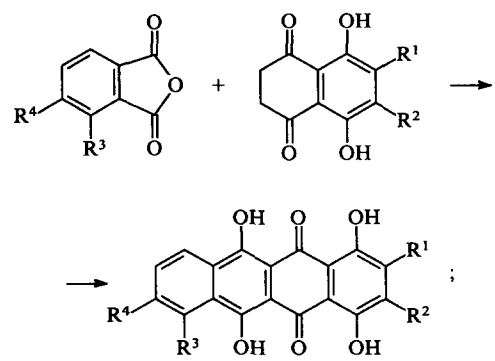
The synthesis of 6-chloro-5,12-naphthacenequinone by the cyclisation of the corresponding naphthoylbenzoic acid on treatment with P_2O_5 has been described.[57]

Condensation of phthalic anhydride with succinic acid leads[58] to diphthalideneethane, which can be readily converted into naphthacenequinone **2**, but 40% of bis-1,3-indandionyl **3** is then formed as a side product. Prolonged refluxing of compound **3** in aqueous ammonia or 10% sodium acetate solution leads to naphthacenequinone **2** in a low yield.[59] When compound **3** is fused with a mixture of sodium and potassium acetates, naphthacenequinone **2** is obtained in 50%–60% yield. A mechanism of this reaction has been proposed.[60]



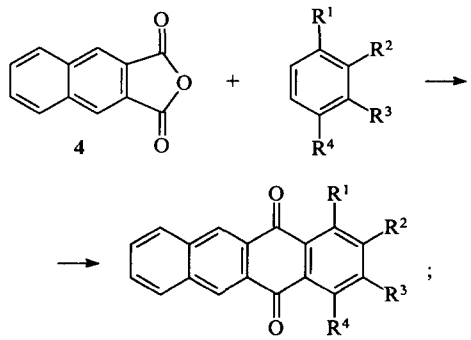
As in the case of the analogous anthraquinone derivatives, in the syntheses of a series of derivatives of 5,12-naphthacenequinone it is possible to carry out the acylation with phthalic anhydride and cyclisation of the resulting acids in a single stage in the presence of strong electron-donating substituents in the molecule to be acylated. The interaction of 1,4-dihydroxynaphthalene and 4,5-difluorophthalic anhydride with phthalic anhydride in the presence of boron trioxide afforded 6,11-dihydroxy-5,12-naphthacenequinone[52] and 2,3-difluoro-5,12-naphthacenequinone[61] respectively.

A whole series of 5,12-naphthacenequinones have been synthesised by the reactions of 3,4-disubstituted phthalic anhydride with derivatives of 2,3-dihydronaphthazarin in a melt of aluminium and sodium chlorides.[62,63]



R^1 = H, OH; R^2 = H; R^3 = OH; R^4 = Et.

A series of substituted 5,12-naphthacenequinones has been synthesised by the reaction of the anhydride of naphthalene-2,3-dicarboxylic acid **4** with substituted benzene derivatives in the presence of aluminium chloride.[49,64]

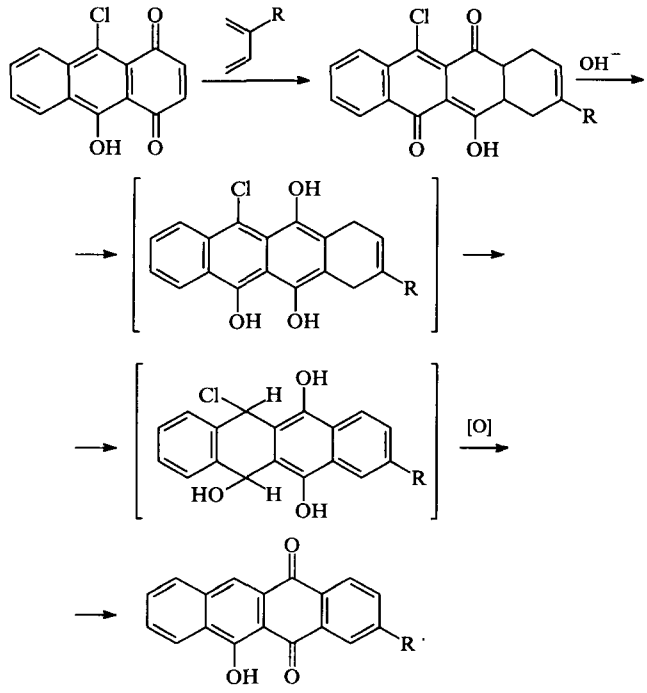


R^1 = Cl, NH_2, Me, OH; R^2 = H, Cl, Me, OH, OAlk, OPh; R^3 = OH; R^4 = H, Hal, OH, OAlk, SAlk, OPh, SPh, NH_2.

Condensation of compound **4** with substituted aminophenols in 80% – 100% sulfuric acid in the presence of boric acid at 100–200 °C afforded[65] disperse dyes which dye polyester fibres, giving rise to bright yellowish-red shades.

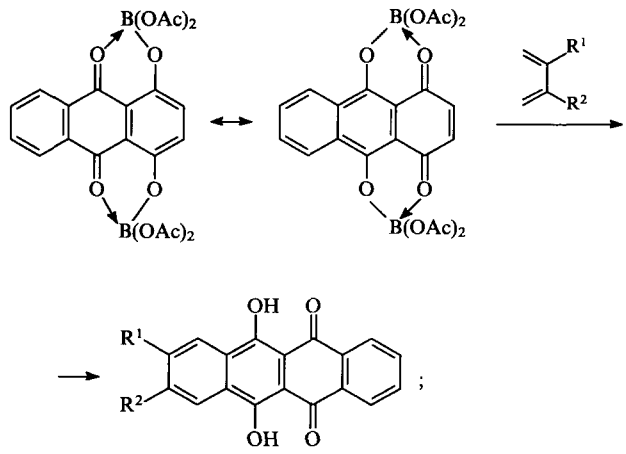
In the synthesis of 5,12-naphthacenequinones by the Diels–Alder reaction, anthraquinone derivatives, which combine with 1,3-dienes, are used as dienophiles. The adducts formed are then oxidised (Scheme 1).[66–70]

Scheme 1



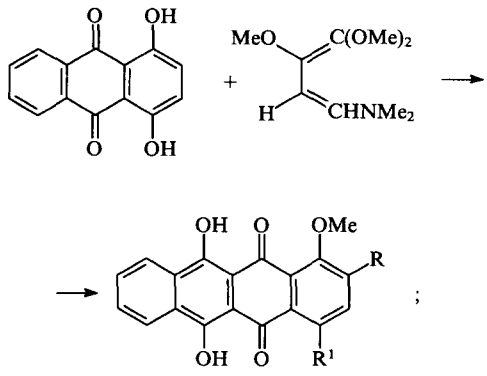
Analogues of natural antibiotics of the tetracycline series have been synthesised in this way.[71–73] There exists convincing evidence[74,75] that the dienophile enters into the reaction as a 1,4-anthraquinone.

The Diels–Alder reaction can be carried out also for the boron complexes of 1,4-dihydroxy- and 1,4-diamino-anthraquinones.[76]



R^1 = R^2 = H, Me.

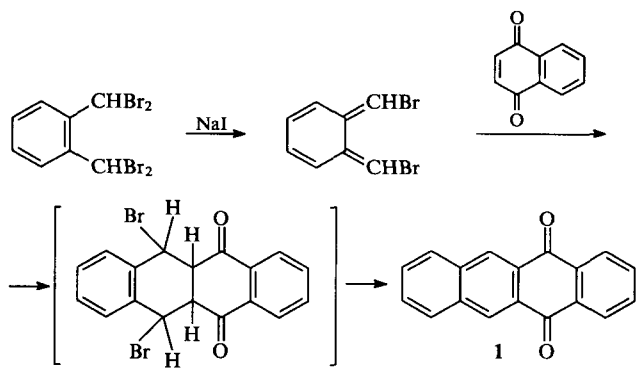
A mixture of naphthacenequinones **5a** and **5b** has been obtained from quinizarin and 4-dimethylamino-1,1,2-trimethoxybuta-1,3-diene.[77]



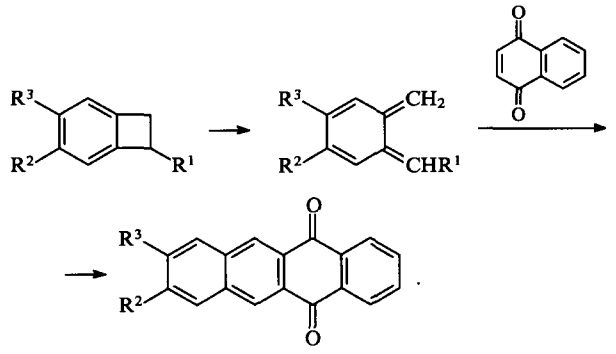
5a,b

5a: R = OMe, R^1 = H; **5b**: R = H, R^1 = NMe_2.

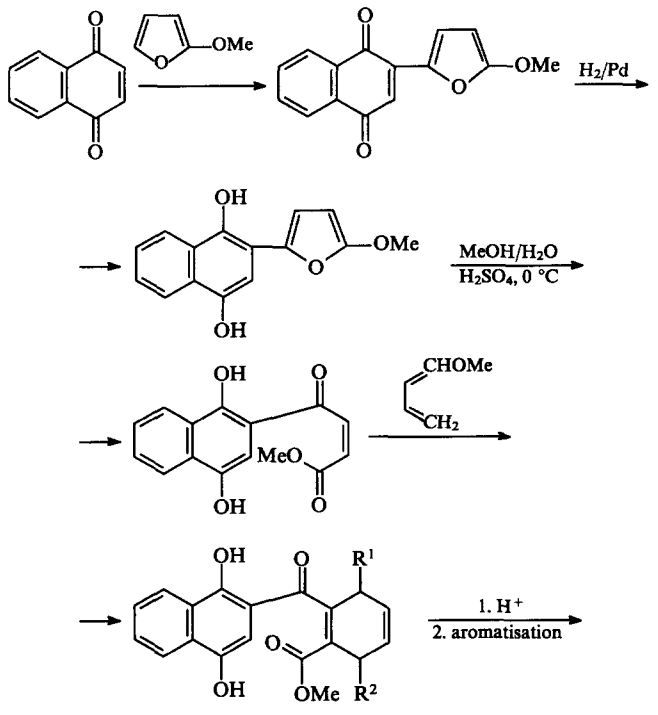
The addition of a dienophile such as dibromo-*o*-benzoquinodimethane to 1,4-naphthaquinone leads to 5,12-naphthacenequinone **1**. Dibromo-*o*-benzoquinodimethane is obtained by treating 1,2-bis(dibromomethyl)benzene with sodium iodide.[78]



The cycloaddition of benzocyclobutenes to 1,4-naphthaquinone apparently also involves the initial formation of the corresponding *o*-quinodimethanes.[79]



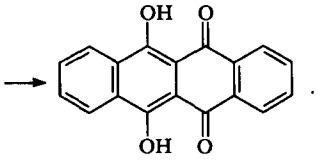
6,11-Dihydroxy-5,12-naphthacenequinone can be obtained in a low yield (13%) from 2-(5-methoxyfuryl)-1,4-naphthaquinone.[80]



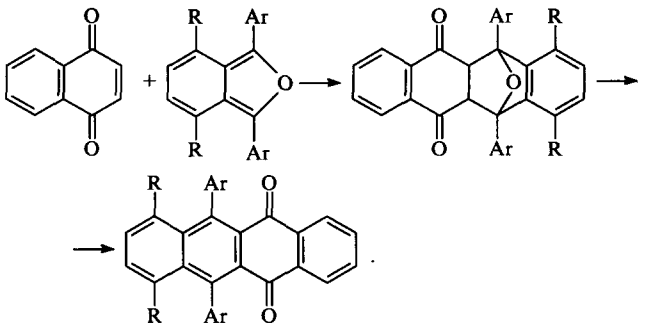
6a,b

6a: R^1 = H, R^2 = OMe; **6b**: R^1 = OMe, R^2 = H

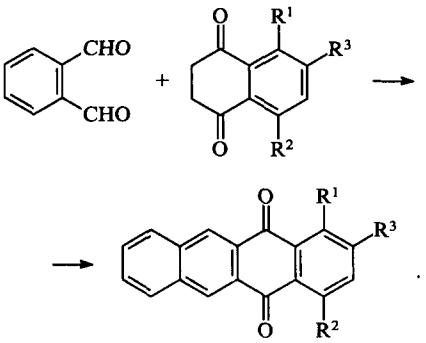
6a : **6b** = 2 : 3



The use of benzofurans in the reaction with 1,4-naphthaquinone permits the synthesis of 5,12-naphthacenequinone derivatives.[81-83]

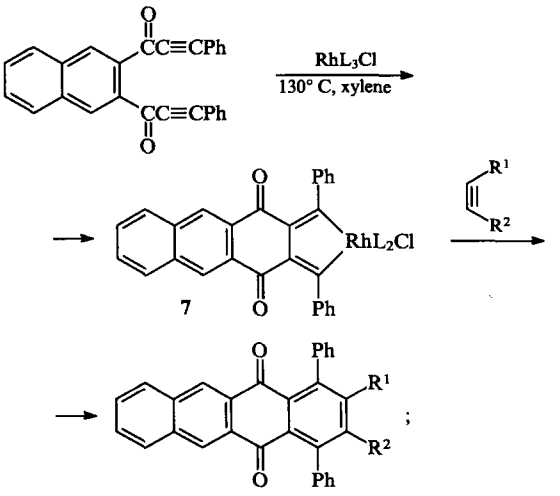


Derivatives of 5,12-naphthacenequinone have also been obtained by condensing aromatic *ortho*-dialdehydes with cyclic γ-diketones.[84-86]



1,4-Dihydroxy-5,12-naphthacenequinones can be obtained similarly from 1,2-diacylbenzenes and 2,3-dihydronaphthazarin in an acid medium.[87]

A method has been proposed for the synthesis of derivatives of 5,12-naphthacenequinone via the rhodium[88-91] and nickel[92] complexes obtained in the reaction of 1,2-bis(1-oxo-3-phenylprop-2-ynyl)naphthalene with ML_3Cl. Thus, when the rhodium complexes **7** are heated with disubstituted acetylenes, cycloaddition takes place with formation of tetrasubstituted naphthacenequinones:

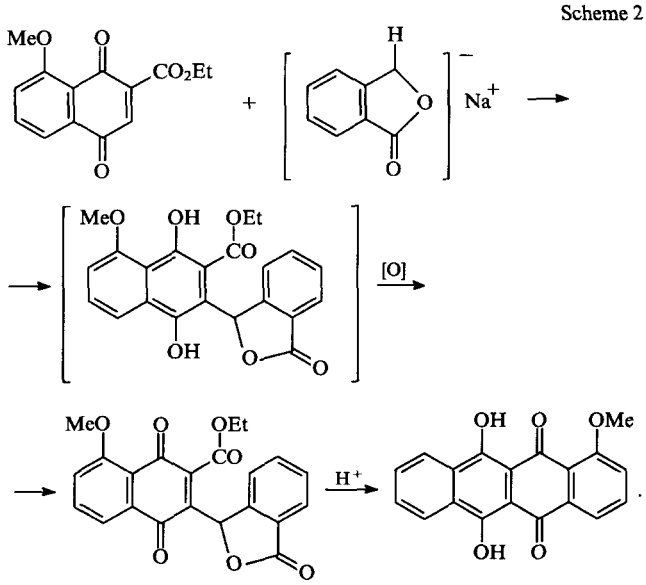


L = PPh_3; R^1 = Me, OEt, COOEt, NEt_2; R^2 = H, Me.

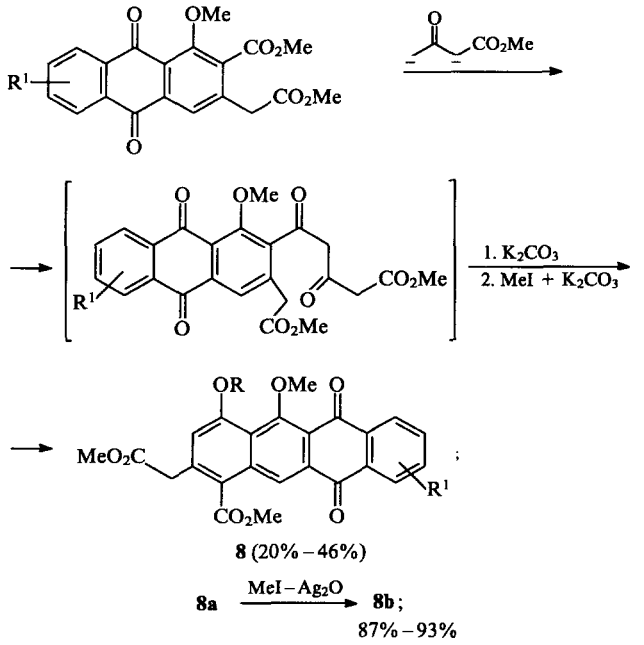
1,2-bis(1-oxo-3-phenylprop-2-ynyl)benzene isomerises to 6-phenyl-5,12-naphthacenequinone on heating or irradiation with UV light.[93]

The synthesis of 6,11-dihydroxy-1-methoxy-5,12-naphthacenequinone, the first stage of which is the addition of the phthalide ion to a substituted naphthaquinone, has been described. The adduct formed undergoes an acid-catalysed cyclisation with simultaneous decarboxylation, affording a substituted naphthacenequinone (Scheme 2).[94]

Scheme 2



Naphthacenequinone derivatives can be obtained by the Claisen condensation of substituted anthraquinones with the dianion of methyl acetoacetate and subsequent cyclisation on treatment with potassium carbonate.[95]

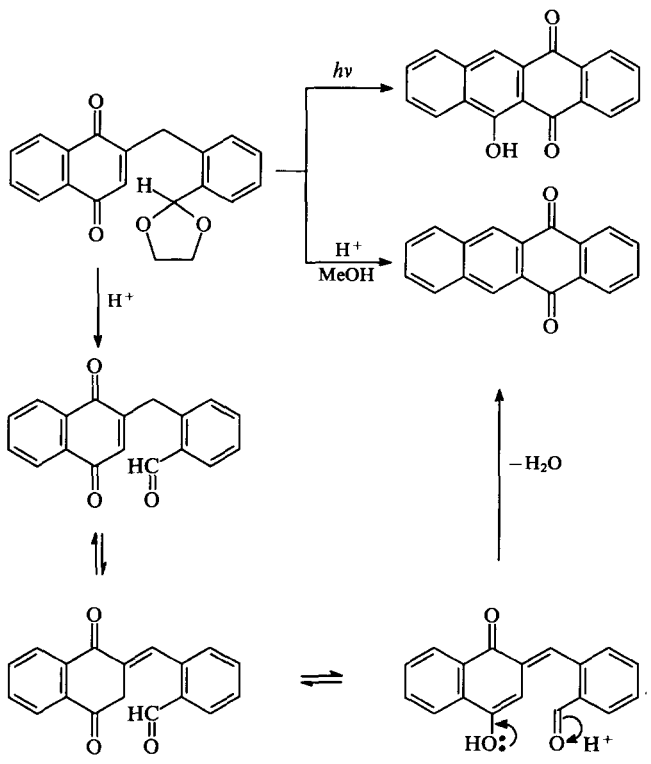


8 (20%–46%)

8a $\xrightarrow{MeI-Ag_2O}$ **8b**; 87%–93%

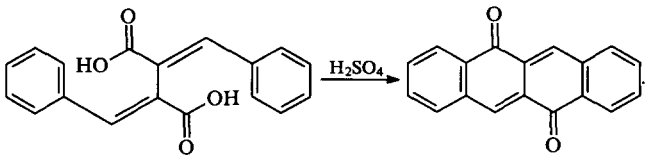
8a: R = H; **8b**: R = Me.

Irradiation of 2-[2-(1,3-dioxolan-2-yl)benzyl]-1,4-naphthaquinone in methanol (in a neutral, acid, or alkaline solution) affords a low yield of 6-hydroxy-5,12-naphthacenequinone. Hydrolysis of 1,4-naphthaquinone in sulfuric acid and methanol leads to naphthacenequinone (a mechanism is proposed for this reaction).[96]



2. Methods of synthesis of 5,11- and 1,4-naphthacenequinones

5,11-Naphthacenequinone (*ana*-naphthacenequinone), an isomer of 5,12-naphthacenequinone, was first obtained by cyclising 1,4-diphenylbuta-1,4-diene-2,3-dicarboxylic acid in concentrated sulfuric acid.[97]

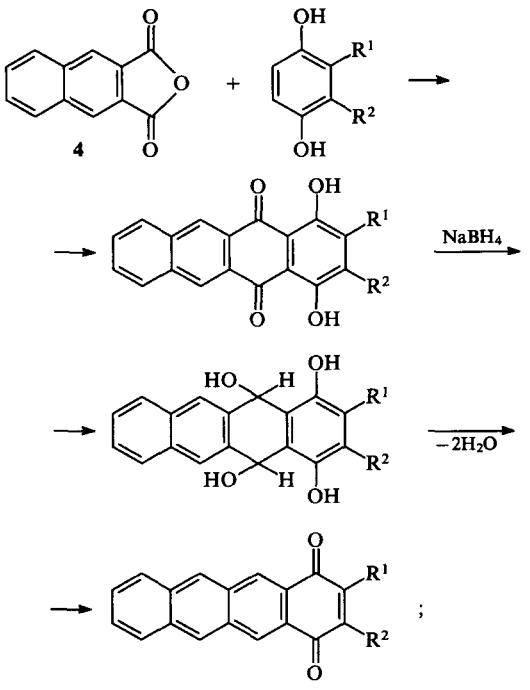


ana-Naphthacenequinone is also formed on hydrolysis of 5,11-dibromonaphthacene.[38] The synthesis of derivatives of 5,11-naphthacenequinone is described below in the section on the properties of 5,11-naphthacenequinone.

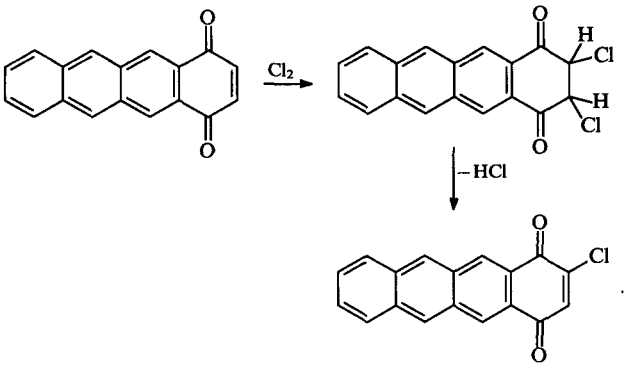
1,4-Naphthacenequinone and its derivatives have been obtained by condensing the anhydride of naphthalene-2,3-dicarboxylic acid **4** with derivatives of hydroquinones containing substituents in the 2- and 3-positions followed by the reduction of the resulting substituted 1,4-dihydroxy-5,12-naphthacenequinones with sodium tetrahydroborate and dehydration.[87,98,99]

1,4-Naphthacenequinone has many of the properties of the so called 'true' quinones having an isolated double bond, such as 1,4-naphthaquinone and 1,4-anthraquinone. Thus, 1,4-naphthacenequinone combines fairly readily with a chlorine molecule at the double bond, giving rise to 2,3-dichloro-2,3-dihydro-1,4-naphthacenequinone,[98,99] which readily splits off hydrogen chloride and is converted into the true monochloroquinone.[99]

The relatively unstable adduct was characterised in terms of the intense IR absorption band at 1721 cm^{-1} due to the carbonyl stretching vibration.



R^1 = H, Me, Cl, Br; R^2 = H, Cl, Me.



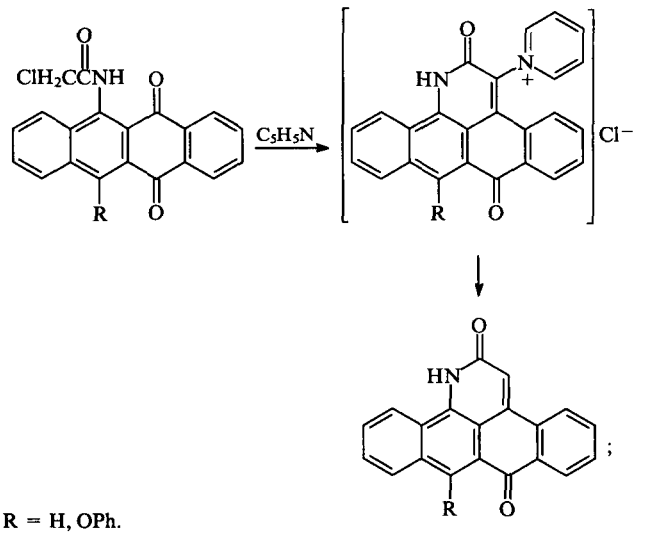
3. Methods of synthesis of heterocyclic *peri*-condensed derivatives of naphthacenequinone

In the series of naphthacenequinones, an important place is assumed by its heterocyclic *peri*-condensed derivatives. In terms of the site where the heterocycle has been added, 1,12- and 11,12-substituted derivatives are known.

As in the case of anthraquinone derivatives, the interaction of a heteroatom or functional group in the *peri*-position relative to one of the carbonyl groups of 5,12-naphthaquinone with this carbonyl group leads to the closure of a new ring beween these positions. The cyclisation reaction, leading to the formation of a new bond involving the carbon atom of the carbonyl group of naphthacenequinone, constitutes an intramolecular nucleophilic addition reaction with subsequent dehydration. The addition of a C-nucleophile and dehydration are accompanied by the replacement of a C=O bond by a C=C bond in 5,12-naphthacenequinone derivatives and the formation of a new ring.

Thus in 6-aminonaphthacenequinone the C-nucleophile bound to the nitrogen atom attacks the carbonyl group in the 5-position, which results in the closure of a six-membered nitrogen-containing ring with formation of a new heterocyclic derivative of naphthacenequinone—2*H*,8*H*-naphtho[1,2,3-*de*]-benzo[*h*]quinoline-2,8-dione (naphthacenopyridone).

Naphthacenopyridones are formed as a result of the cyclisation of 6-(*N*-chloroacetyl)amino-5,12-naphthacenequinones in pyridine to the corresponding naphthaceno(2-oxo-3-pyridyl)pyridinium chlorides[100,101] and subsequent reductive elimination of the pyridinium residue.

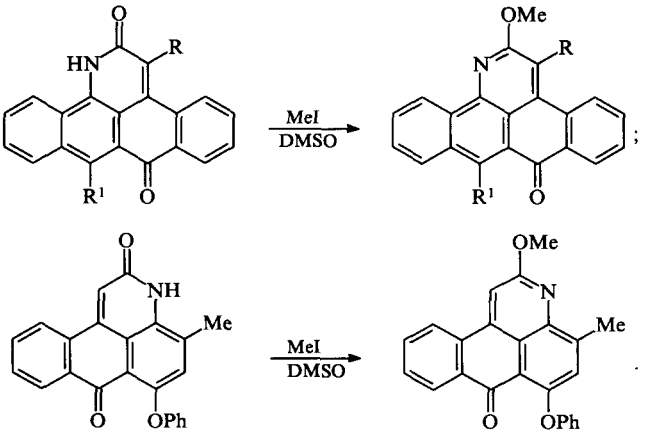


R = H, OPh.

When 6-acetamido-5,12-naphthacenequinone and its 11-chloro-derivative are heated in phenol in the presence of sodium carbonate, the elimination of the acetyl group results in the formation, together with naphthacenopyridone and its 9-phenoxy-derivative, of an appreciable amount of 6-amino- and 6-amino-11-phenoxy-5,12-naphthacenequinones.[101]

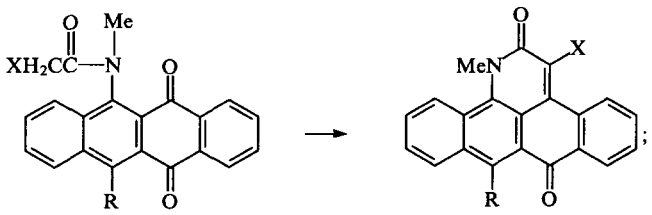
The 3-acetyl derivative of naphthacenopyridone has been obtained by the reaction of 6-amino-11-chloro-5,12-naphthacenequinone with acetoacetic ester in phenol in the presence of potassium carbonate.[101] The conditions in this reaction are the same as those used for the synthesis of anthrapyridones.[102]

Methylation of naphthacenopyridones with methyl iodide in dimethyl sulfoxide leads to 2-methoxynaphthacenopyridines (*O*-methyl derivatives), whereas methylation of anthrapyridone under the same conditions affords its *N*-methyl derivative.



This difference in the behaviour of similar structures under identical conditions is apparently associated with steric hindrance to alkylation at the nitrogen atom in the case of naphthacenopyridones. Indeed, the sterically hindered 4-methyl-6-phenoxyanthrapyridone forms on methylation 2-methoxy-4-methyl-6-phenoxyanthrapyridine (the *O*-methyl derivative), in contrast to 6-phenoxyanthrapyridone.[101]

2*H*,8*H*-Methylnaphtho[1,2,3-*de*]benzo[*h*]quinoline-2,8-diones (*N*-methylnaphthacenopyridones) are obtained by heating 6-(*N*-acetyl)methylamino-5,12-naphthacenequinone in 3% aqueous[104] or alcoholic[105] sodium hydroxide solution. 6-(*N*-Acetyl)methylamino-11-chloro- and 6-(*N*-acetyl)methylamino-11-phenoxy-5,12-naphthacenequinones are converted under these conditions into 9-hydroxy-*N*-methylnaphthacenopyridones. A convenient method of synthesis of *N*-methyl-9-phenoxynaphthacenopyridone involves heating 6-(*N*-acetylmethylamino-11-phenoxy-5,12-naphthacenequinone in phenol in the presence of potassium carbonate.[103]

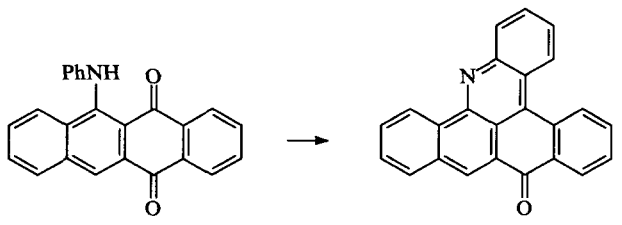


X = H: R = H, OPh, OH;
X = Cl: R = OPh.

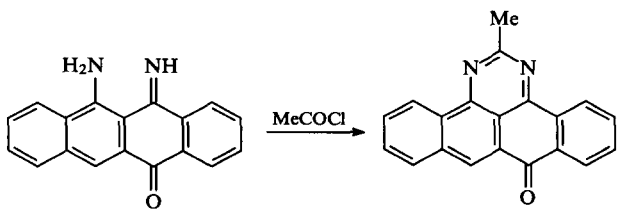
Heating of 6-(*N*-chloroacetyl)methylamino-11-phenoxy-5,12-naphthacenequinone in phenol leads to 3,9-diphenoxy-*N*-methylnaphthacenopyridone, i.e. cyclisation with simultaneous substitution in the resulting napthacenepyridone of the chlorine atom in the 3-position by a phenoxy-group takes place under these conditions.

A widely known method of synthesis of anthrapyridones, involving the cyclisation of chloroacetamidoanthraquinones in pyridine, proved to be applicable also to the synthesis of 3-chloro-*N*-methyl-9-phenoxynaphthacenopyridone.[100] 1-Methyl-9-phenoxynaphthaceno(2-oxo-3-pyridyl)pyridinium chloride, formed on heating the chloroacetamido-derivative of naphthacenequinone in pyridine, is converted into naphthacenopyridone on subsequent refluxing in nitrobenzene.[103]

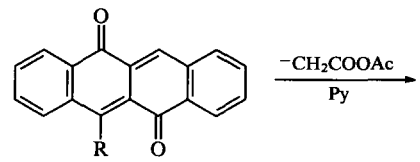
Cyclisation of 6-phenylamino-5,12-naphthacenequinone under the conditions used for the synthesis of ceramidonines, namely treatment with aluminium chloride or 75% sulfuric acid, leads to naphthacenoceramidonine[106] — 10*H*-naphtho-[*m*,*n*]benzo[*c*]-10-acridone.



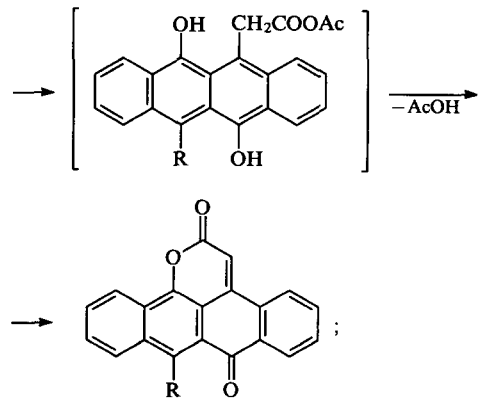
A naphthacenopyrimidine — 8*H*-dibenzo[*e*,*j*]pyrimidin-8-one — has been obtained by the reaction of 6-amino-5,12-naphthacenequinone imine with acetyl chloride in pyridine.[107]



Heterocyclic derivatives of naphthacenequinone with an oxygen-containing six-membered heterocycle — 2*H*,8*H*-naphtho[1,2,3-*de*]benzo[*h*]-1,2-chromene-2,8-diones (naphthacenopyrones) — are formed on reaction of 5,11-naphthacenequinones with acetic anhydride in pyridine or triethylamine.[108,109]



R = NAcPh (**9**), H, OPh.

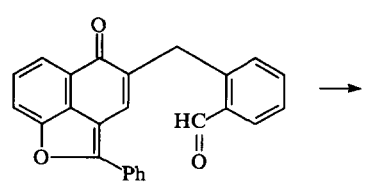


R = NAcPh, NHPh (**10**), H, OPh.

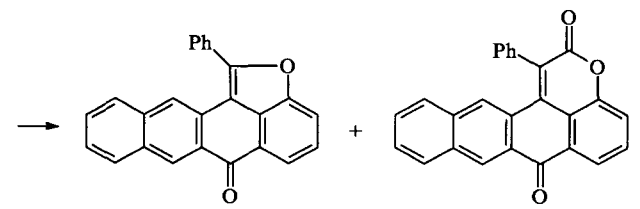
6-(*N*-Acetyl)phenylamino-5,11-naphthacenequinone interacts even more readily with malonic ester in pyridine to form 3-ethoxycarbonylnaphthacenopyrone.[108] In all the reactions enumerated above, the carbanion generated from acetic anhydride in the presence of pyridine apparently adds (via a Michael reaction) to the carbon atom in the 12-position with subsequent oxidation of the dihydro-derivative and the formation of the corresponding pyrone.

Refluxing of compound **9** (R = NAcPh) in a mixture of acetic and hydrochloric acids leads to the pyrone **10** (R = NHPh).[108]

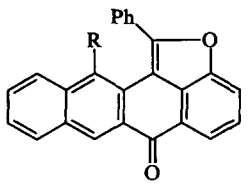
Among the heterocyclic 1,12-*peri*-condensed derivatives of naphthacenequinone, compounds containing furan and pyrone rings are known. Treatment of the aldehyde **11** with sodium cyanide leads to a mixture of 1-phenylnaphtho[2,3-*e*]-benzo-[*h*,*i*]isobenzofuran-6-one (a naphthacenofuran) and 1-phenyl-7*H*,2*H*-benzo[*cd*]naphtho[2,3-*g*]-1,2-chromene-2,7-dione (a naphthacenopyrone). The naphthacenopyrone is formed on interaction of the naphthacenofuran with sodium cyanide.[110]



11



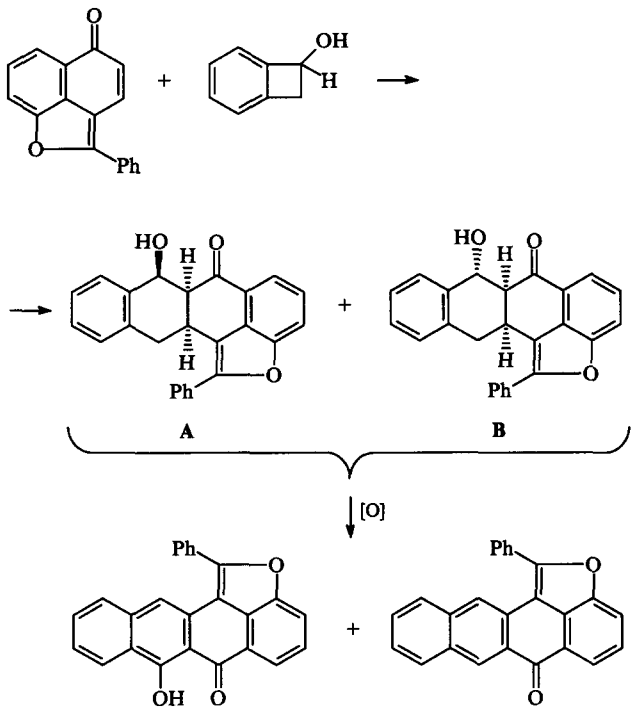
Treatment of the cyanohydrin of the aldehyde **11** with sodium hydride leads to cyano- and hydroxy-naphthacenofurans.[110]



R = OH, CN.

Thermal condensation of derivatives of naphthofuran with benzocyclobutenol in the dark results in the formation of a mixture of the stereoisomers **A** and **B**, the oxidation of which affords a mixture of naphthacenofurans (Scheme 3).[111]

Scheme 3



Treatment of the isomers **A** and **B** with a solution of alkali leads to a single naphthacenofuran.

III. Chemical properties of naphthacenequinones

1. Properties of 5,12-naphthacenequinone and its derivatives

On treatment with an alkaline solution of sodium hydrogen sulfite, 5,12-naphthacenequinone is converted into the unstable green 5,12-dihydroxynaphthacene. The latter is readily oxidised to 5,12-naphthacenequinone and also enters readily into disproportionation and ketone formation reactions.[113] The reduction potential of 5,12-naphthacenequinone has not been measured owing to the instability of the corresponding hydroquinone (the calculated value is −0.3146 V).[114] The reduction of 5,12-naphthacenequinone with tin in acetic acid leads to the stable naphthacene-5-one; refluxing with zinc dust in an alkaline alcoholic solution affords 5,12-dihydronaphthacene.[113]

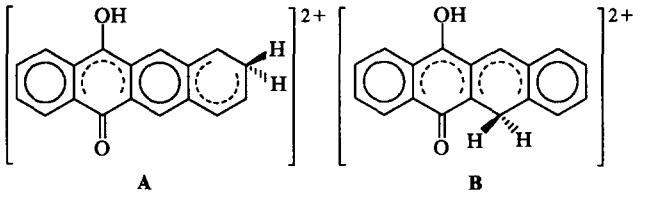
The reduction of alkylhydroxynaphthacenequinone with a cyclohexanol–aluminium cyclohexanolate mixture leads to alkylnaphthacenes.[115,116]

The polarographic behaviour of 5,12- and 5,11-naphthacenequinones in water–pyridine buffer mixtures of different composition has been investigated.[117] The reversible two-electron wave observed in acid solutions corresponds to the process[117]

$$Q + 2e^- + 2H^+ \rightleftharpoons QH_2,$$

where Q is the naphthacenequinone.

5,12-Naphthacenequinone is protonated twice in sulfuric acid. The pK_a for the first and second protonations have been determined[118] as −8.20 and −8.66 respectively. It has been suggested[118] that the second proton adds to the carbon atom of the terminal aromatic ring. Quantum-chemical calculation and ^1H NMR data indicate the formation of structures **A** and **B** on protonation.[119]

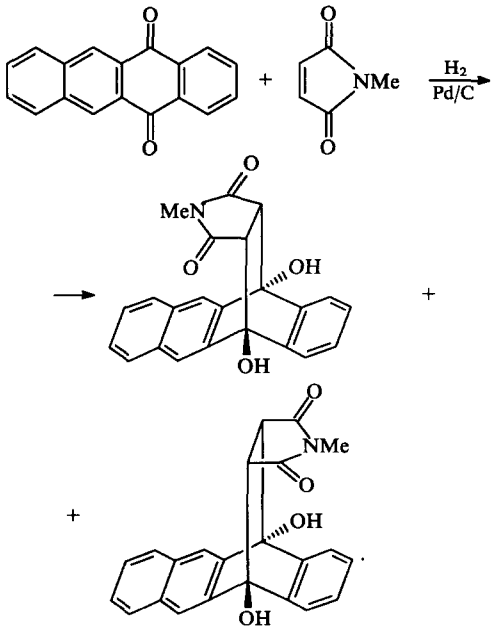


A **B**

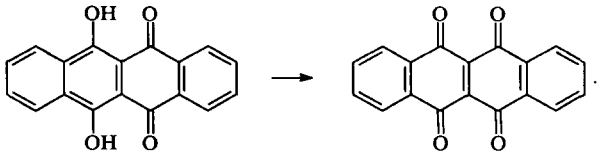
The mechanism of the electrochemical reduction in dimethylformamide of 6,11-dihydroxy-5,12-naphthacenequinone, which is reduced reversibly to 5,6,11,12-tetrahydroxynaphthacene, has been investigated by polarographic and cyclic voltammetric methods.[120]

The reduction half-wave potential of 5,12-naphthacenequinone in dimethylformamide in the presence of lithium perchlorate increases with increasing concentration of lithium ions, which has been explained by the formation of 1 : 1 and 1 : 2 ionic associated species.[121]

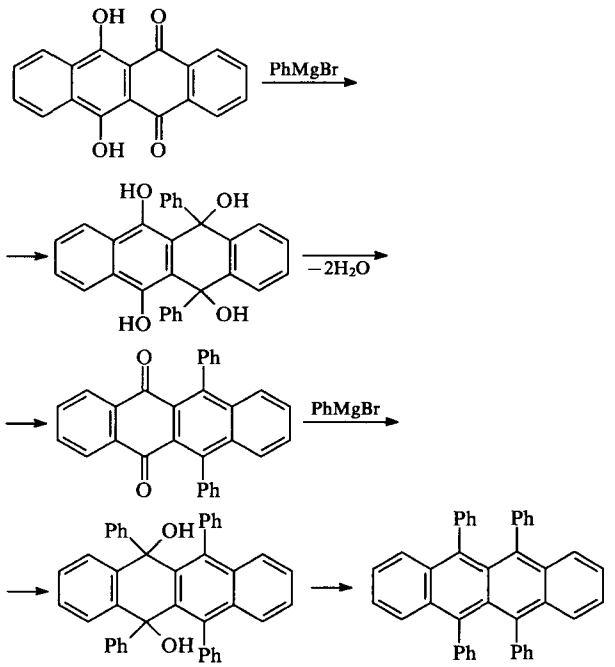
The catalytic reduction of a mixture of 5,12-naphthacenequinone and *N*-methylmaleimide in pyridine affords two products, which have been identified as the *endo*- and *exo*-adducts.[122]



Oxidation of 6,11-dihydroxy-5,12-naphthacenequinone with nitric acid leads to the formation of 5,12;6,11-naphthacenediquinone.[43]

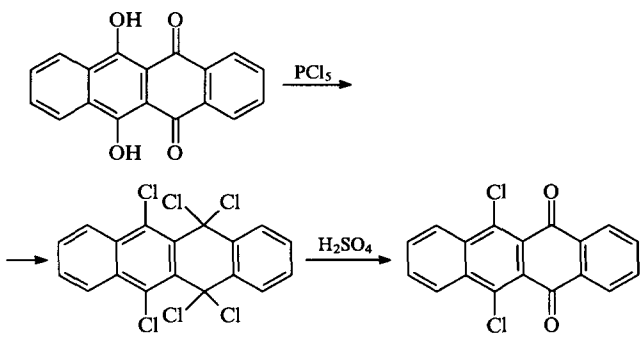


The interaction of naphthacenequinones with phenylmagnesium bromide leads to diols.



This reaction has been used in one of the syntheses demonstrating the structure of rubrene.[123]

The interaction of PCl_5 with 6-hydroxy-5,12-naphthacenequinone in nitrobenzene results in the formation of 6-chloro-5,12-naphthacenequinone,[38,57,124] while the reaction with 6,11-dihydroxy-5,12-naphthacenequinone affords 5,5,6,11,12,12-hexachlorodihydronaphthacene, the hydrolysis of which in sulfuric acid leads to 6,11-dichloro-5,12-naphthacenequinone.



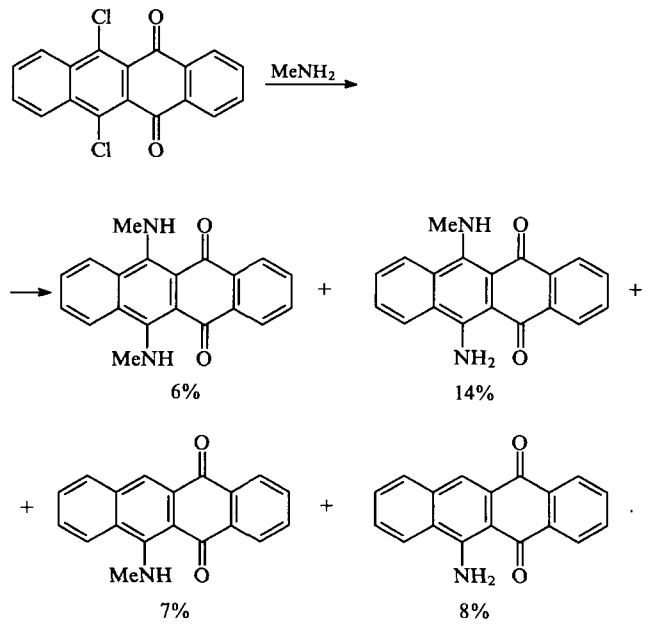
The reaction of 6,11-dihydroxy-5,12-naphthacenequinone with PCl_5 is carried out either in tetrachloroethane[125] or without a solvent in a sealed tube.[126] An improved method of synthesis of 6,11-dichloro-5,12-naphthacenequinone in a PCl_5—quinone melt has been proposed.[127]

6,11-Dichloro-5,12-naphthacenequinone is also formed on heating 5,12-naphthacenequinone with sulfuryl chloride in a sealed tube.[38,124] On reaction with thionyl chloride, 5,12-naphthacenequinone affords 11-chloro-6-hydroxy-5,12-naphthacenequinone.[128]

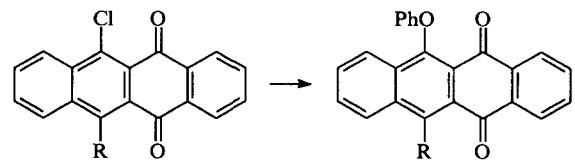
Like 1-halo- and 1,4-dihaloanthraquinones, 6-halo- and 6,11-dihalo-5,12-naphthacenequinones enter into nucleophilic substitution reactions. The mobilities of the halogen atoms in these compounds are similar.

6-Amino- and 6,11-amino-5,12-naphthacenequinones have been obtained by treating chloronaphthacenequinones with toluene-*p*-sulfonamide or benzamide in the presence of copper salts and subsequent hydrolysis of the resulting tosylamino-derivatives.[49,57] 6-Amino-5,12-naphthacenequinone can also be synthesised from 6-chloro-5,12-naphthacenequinone and ammonia under pressure.[129] The interaction of 6,11-dichloro-5,12-naphthacenequinone with one mole of toluene-*p*-sulfonamide in nitrobenzene in the presence of copper salts and subsequent hydrolysis in sulfuric acid lead to 6-amino-11-chloro-5,12-naphthacenequinone.[127]

Treatment of 6,11-dichloro-5,12-naphthacenequinone with methylamine led to the formation of a mixture of amines.[130]

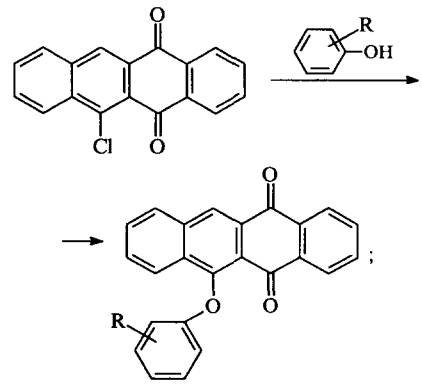


The interaction of halonaphthacenequinones with potassium phenoxide in phenol results in the formation of derivatives of 11-phenoxynaphthacenequinone.[127,129]



R = NH_2, H, NHTs, OPh.

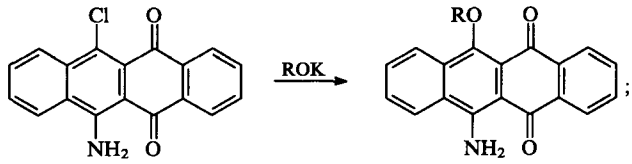
A series of 6-aryloxy-5,12-naphthacenequinones has been synthesised by the reactions of 6-chloro-5,12-naphthacenequinone with substituted phenols.



R = *p*-Br, *p*-OH, *p*-OMe, *p*-NHPh, 2,4,6-Me_3, *p*-MeCO, *p*-NO_2, *p*-NH_2.

6-(4-Aminophenoxy)-5,12-naphthacenequinone has been obtained by reducing 6-(4-nitrophenoxy)-5,12-naphthacenequinone on palladised charcoal in formic acid.[131]

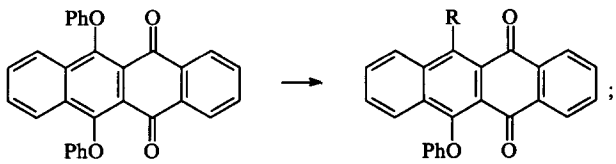
When 6-amino-11-chloro-5,12-naphthacenequinone and a substituted phenol were heated in an $ArOH-ArO^-$ melt in the presence of copper(I) chloride, 6-amino-11-aryloxy-5,12-naphthacenequinones were synthesised.[132]



R = *p*-MeC_6H_4, *p*-EtC_6H_4, *p*-$MeOC_6H_4$, *p*-$HPhNC_6H_4$, *p*-HOC_6H_4, *m*-ClC_6H_4, *p*-$O_2NC_6H_4$, α-$C_{10}H_7$.

The attempt to synthesise 6-amino-11-(4-hydroxyphenoxy)-5,12-naphthacenequinone by heating 6-amino-1-chloro-5,12-naphthacenequinone in an excess of the hydroquinone led only to the dehalogenation of the initial compound. 6-Amino-11-(4-hydroxyphenoxy)- and 6-amino-11-(4-phenylamino)-5,12-naphthacenequinones have been obtained by the reaction of 6-amino-11-chloro-5,12-naphthacenequinone with the corresponding substituted potassium phenoxide in dimethyl sulfoxide in the presence of copper(I) chloride.[132]

The interaction of 6,11-diphenoxy-5,12-naphthacenequinone with aliphatic and aromatic amines leads to 6-R-11-phenoxy-5,12-naphthacenequinone.[127]



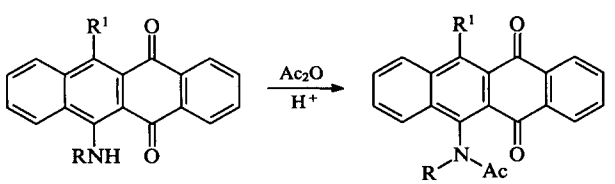
R = NHMe, NMe_2, NHPh.

6-Methoxy-11-phenoxy-5,12-naphthacenequinone has been obtained by the transesterification of diphenoxynaphthacenequinone with methanol in benzene.[127]

6-Acetoxy-11-phenoxy-5,12-naphthacenequinone has been synthesised from 6-hydroxy-11-phenoxy-5,12-naphthacenequinone and acetic anhydride in the presence of pyridine.[127]

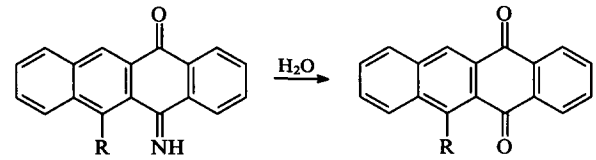
Acetoxy- and benzoyloxy-groups located in the *peri*-positions relative to the carbonyl group of naphthacenequinone are converted into hydroxy-groups on treatment with trifluoroacetic acid containing a small amount of water. With increase in the water content, the rate of the first-order reaction falls.[132]

Acetylation of aminonaphthacenequinones with acetic anhydride in the presence of sulfuric acid leads to *N*-acetyl derivatives.[127]



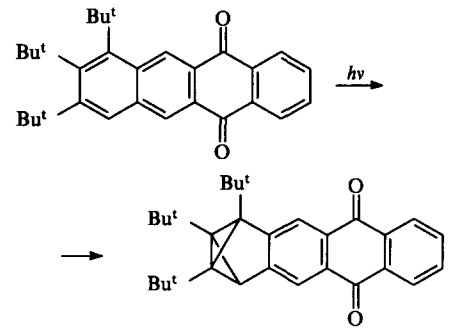
6-Nitro-11-phenoxy-5,12-naphthacenequinone has been synthesised by oxidising 6-amino-11-phenoxy-5,12-naphthacenequinone with peracetic acid.[127]

Hydrolysis of 5-iminonaphthacen-12-one leads to 5,12-naphthacenequinone.[44,45,107]



R = H, Ph, NH_2.

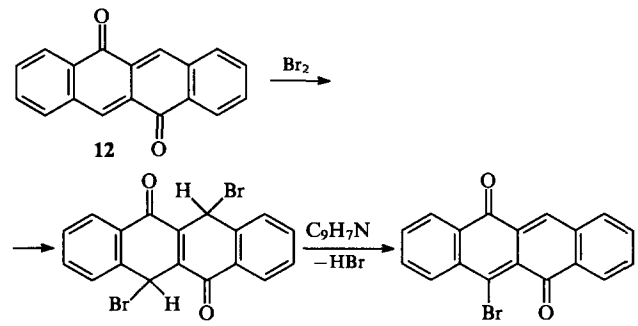
8,9,10-Tri(*tert*-butyl)naphthacenequinones have been synthesised. Under the influence of light, they undergo photovalent isomerisation with formation of a kinetically stable bicyclobutane derivative in a quantum yield of 0.09.[134]



2. Properties of 5,11-naphthacenequinones

The reduction of 5,11-naphthacenequinone **12** with zinc leads to the formation of naphthacene,[97] whilst its fusion with alkali in air gives rise to 6,11-dihydroxy-5,12-naphthacenequinone.[97]

5,11-Naphthacenequinone readily combines with bromine in the 6- and 12-positions with formation of a dibromodihydro-derivative, which on treatment with quinoline is converted into 6-bromo-5,11-naphthacenequinone.[39]



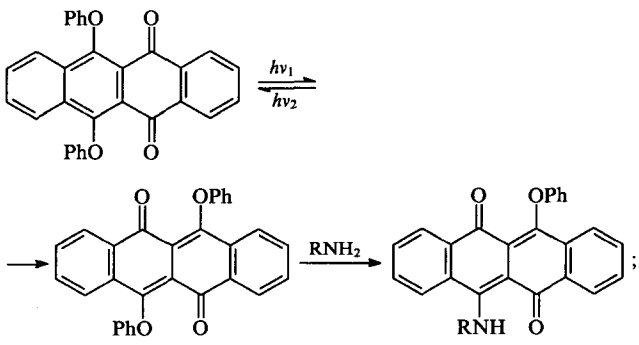
The reaction of 6-bromo-5,11-naphthacenequinone with aniline leads to 6-phenylamino-5,12-naphthacenequinone.[39]

When 5,11-naphthacenequinone is heated with sulfuryl chloride in nitrobenzene at 120–150 °C 6-chloro-5,12-naphthacenequinone is formed.[38,124] This reaction is an example of the conversion of an *ana*-quinonoid structure into a *p*-quinonoid structure. If the reaction is carried out with an excess of sulfuryl chloride in a sealed tube, 6,11-dichloro-5,12-naphthacenequinone is obtained.[38,124]

It follows from the foregoing that the 6- and 12-positions in the 5,11-naphthacenequinone molecule are reactive in relation to nucleophiles. Thus heating of 5,11-naphthacenequinone in aniline leads to 6-phenylamino-5,11-naphthacenequinone.[39]

Reactions involving the nucleophilic substitution of the halogen atom in 6-halo-5,11-naphthacenequinones proceed under much milder conditions[39] than the analogous reactions in the series of 5,12-naphthacenequinones and anthraquinones. 6-Bromo-5,11-naphthacenequinone interacts readily with primary amines at room temperature with formation of 6-amino-5,11-naphthacenequinones in quantitative yields.[39]

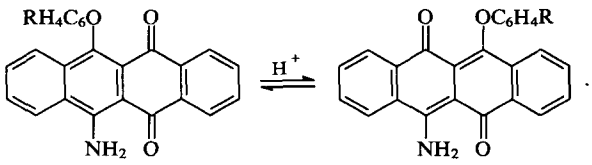
The phenoxy-group in 6-phenoxy-5,11-naphthacenequinones is extremely readily substituted by an amino-group.[135] 6-Amino-12-phenoxy-5,11-naphthacenequinones have been obtained by treating 6,12-diphenoxy-5,11-naphthacenequinone with an amine RNH_2; 6,12-diphenoxy-5,11-naphthacenequinone is formed as a result of a photorearrangement of the *p*-quinone.[127]



R = H, Me, Ph.

Treatment of 6-bromo- and 6-phenoxy-5,11-naphthacenequinones with secondary amines does not lead to tertiary amines but to 6-hydroxy-5,12-naphthacenequinone, which is probably associated with the impossibility of the existence of such tertiary amines in a stable *p*-quinone imine form.[108]

6-Amino-12-aryloxy-5,11-naphthacenequinones have been obtained by the acid rearrangement of the corresponding *p*-quinones.[132,136]



Acetylation of amino-derivatives of *ana*-naphthacenequinone with acetic anhydride leads to *N*-acetamido-5,11-naphthacenequinones.[108,127]

The interaction of 6-hydroxy- and 6,12-dihydroxy-5,11-naphthacenequinones with aniline in the presence of boric acid will be examined in the section devoted to the tautomeric transformations of naphthacenequinones.

IV. Spectroscopic properties

The IR spectra in the 1665–1678 cm^{-1} range of 5,12-naphthacenequinones contain absorption bands due to the C=O bond stretching vibrations characteristic of *p*-quinones with integral intensities $A_{C=O}$ of 2.0 for each C=O group. The presence of intramolecular hydrogen bonds lowers $\nu_{C=O}$ (the amino-group exerts a particularly strong influence). The intense absorption bands due to the stretching vibrations of the bonds of the quinonoid ring O=C–C=C–C=O in the region of 1280 cm^{-1}, which are typical of quinones, are observed in the range 1275–1290 cm^{-1} in the case of *p*-naphthacenequinones.

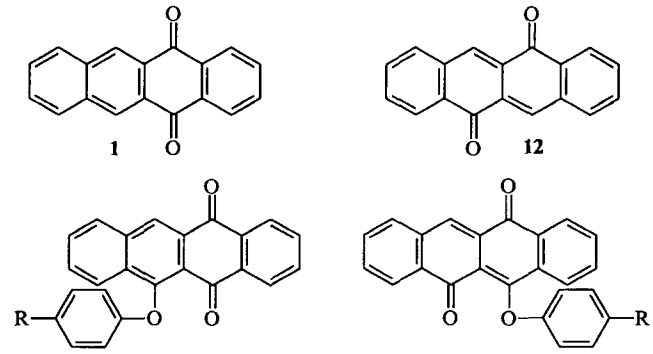
The IR spectra of 5,11-naphthacenequinones differ markedly[137] from those of 5,12-naphthacenequinones. The frequency of the stretching vibrations of the C=O bonds diminishes to 1650–1655 cm^{-1}, while the integral intensity $A_{C=O}$ falls to 1.3. In the absorption region of C=C bonds, there is only one absorption band at 1595 cm^{-1} with an enhanced intensity in the spectra of 5,11-naphthacenequinones, in contrast to 5,12-naphthacenequinones. The absorption bands due to the quinonoid ring bonds of the *ana*-isomers are displaced to 1320 cm^{-1} with retention of their intensity. The results indicate an increase in the degree of delocalisation of the π-electron density in the *ana*-isomers compared with the *para*-isomers, as suggested by Nurmukhametov et al.[138] This is confirmed both by the decrease in $\nu_{C=O}$ and $A_{C=O}$ (since the bond dipole moments, characterised by the integral intensities of the absorption bands, are reduced on delocalisation) and by the increase in the intensity of the absorption bands due to the C=C bonds in the region of 1595 cm^{-1}.

A two-dimensional electron-gas model has been used to calculate the π-electron density and spectral transition energies in naphthacenequinones; the transition energies obtained agree well with the experimental data.[139]

The localisation energies of different types have been calculated by the MO method for 5,12- and 5,11-naphthacenequinones.[140]

The main chromophore in the *p*-naphthacenequinone molecule is the naphthalene ring with two-carbonyl groups in the β-positions, while in the *ana*-naphthacenequinone molecule it is the diphenylbutadiene component with two carbonyl groups.[138,141]

The absorption spectrum of 5,12-naphthacenequinone **1** in hexane is characterised by the long-wavelength absorption band due to the π → π* transition with vibrational structure and a relatively weak shoulder corresponding to the nπ* absorption.[142] The validity of this interpretation is confirmed by the hypsochromic shift of the nπ* absorption band with increase in the number of rings in the series benzoquinone → naphthaquinone → anthraquinone. On passing from anthraquinone to naphthaquinone, there are no further changes in the system of conjugated bonds, including the carbonyl group, and hence there are no reasons for a further hypsochromic displacement of the absorption band despite the increase in the number of rings in the molecule. Therefore the lowest singlet state in naphthacenequinone is the nπ* state, as in the quinones with a smaller number of rings.[143]



R = H, NO_2, Ac.

The introduction of a phenoxy-group or of more complex substituents in the 6-position in the naphthacenequinone molecule does not induce any significant change in the position of the long-wavelength ππ* band. The nπ* band in the absorption spectra of these compounds is not observed explicitly, possibly owing to the electron-donor effect of the phenoxy-group which induces an increase in the energy of the nπ* transition.

The bathochromic shift of the long-wavelength absorption band after the introduction of hydroxy- and amino-groups in the 6-position in naphthacenequinone can be readily accounted for

in terms of the molecular orbital theory concerning the influence of electron-donating substituents on the electronic spectra of aromatic molecules. When electron-donating substituents are introduced, a higher occupied π orbital appears, which induces a decrease in the $S_1 - S_0$ transition energy. In the case of a strong electron-donating substituent (the amino-group is of this kind), this orbital corresponds to a large extent to the heteroatom and can be designated as a π_{ED} orbital, whereas in the presence of a weaker substituent (the hydroxy-group) it is the perturbed highest occupied π_{Ar} orbital. In conformity with the foregoing, the long-wavelength absorption band of 6-aminonaphthacenequinone can be assigned to the $\pi_{ED} \rightarrow \pi^*_{EA}$ transition, while the band in the range 25 000–28 000 cm^{-1} can be assigned to the $\pi_{Ar} \rightarrow \pi^*_{EA}$ transition.[138]

The long-wavelength band of 5,11-naphthacenequinone **12** is of the ππ* type. The introduction of substituents in the *para*-position of the phenoxy-group in 6-phenoxy-5,11-naphthacenequinone hardly affects the energy of the $^1\pi\pi^*$ transition, as in the corresponding *p*-naphthacenequinones.

The absorption of the *nπ** type is clearly not observed in the spectra of *ana*-naphthacenequinones. According to the results,[3] one may expect that the *nπ** absorption band in the spectra of *ana*-naphthacenequinones is in the immediate vicinity of the *nπ** levels of 1,4-naphthaquinone and benzylideneindandione. It is then found that the energy of the *nπ** level of the naphthacenequinone is very close to the energy of the $^1\pi\pi^*$ level, exceeding the latter somewhat.[143]

5,12-Naphthacenequinone does not fluoresce either at room temperature or at 77 K. At 77 K prolonged green phosphorescence of 5,12-naphthacenequinone in methylpentane has been noted.[145] In hexane, the phosphorescence spectrum has a well-resolved structure[147] with an intense peak at 1940 cm^{-1}. The appreciable gap between the absorption and phosphorescence bands (6000 cm^{-1}) and the long duration of the phosphorescence ($\tau_{ps} \simeq 0.3$ s) [145] make it possible to assign the phosphorescence to the ππ* state. A similar picture has been observed also for substituted *p*-naphthacenequinone. 6-Phenoxy-5,12-naphthacenequinone does not exhibit an intrinsic fluoresence (Fig. 1).[143]

Solutions of 5,11-naphthacenequinone do not exhibit an intrinsic luminescence either at room temperature or at 77 K. A weak fluoresence, intensifying as a function of time, has been attributed to the appearance of 6-hydroxy-5,12-naphthacenequinone — the 5,11-naphthacenequinone conversion product.

In acetic acid, which quenches the fluorescence of 6-hydroxy-5,12-naphthacenequinone, the bright green fluorescence of 5,11-naphthacenequinone was observed at 77 K. The 'activation' of the fluorescence of 5,11-naphthacenequinone by a polar solvent shows that the $^3n\pi^*$ level, located below the $^1\pi\pi^*$ level in non-polar solvents, lies above the $^1\pi\pi^*$ level in the polar acetic acid and does not participate in the non-radiative deactivation of the latter.[143]

An intrinsic fluoresence has not been observed for 6-phenoxy-5,11-naphthacenequinone in acetic acid. The introduction of substituents in the phenoxy-group does not alter appreciably the luminescence properties of the molecule. This difference in the behaviour of 5,11-naphthacenequinone and that of its 6-phenoxy-substituted derivatives is probably associated with the occurrence of the competing photoisomerisation process in the phenoxy-derivative. Fig. 2 illustrates the energy state diagram and the most probable paths leading to the degradation of the excitation energy of 5,12- and 5,11-naphthacenequinones.[143]

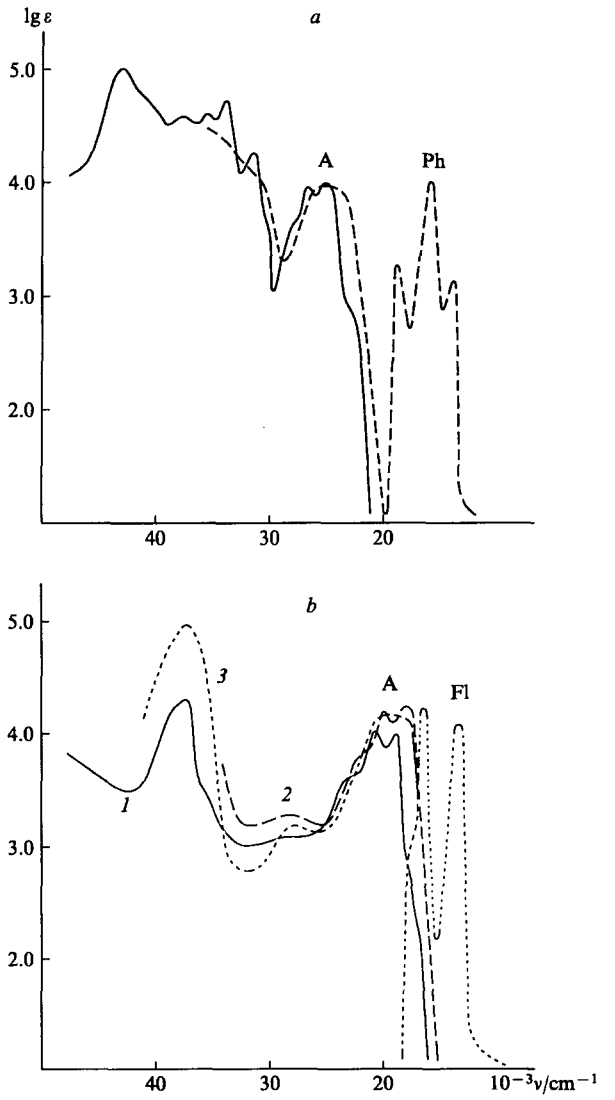


Figure 1. Absorption (A), phosphorescence (Ph), and fluorescence (Fl) spectra of the naphthacenequinones **1** (*a*) and **12** (*b*) in hexane (curve *1*), toluene (curve *2*), and acetic acid (curve *3*).[143]

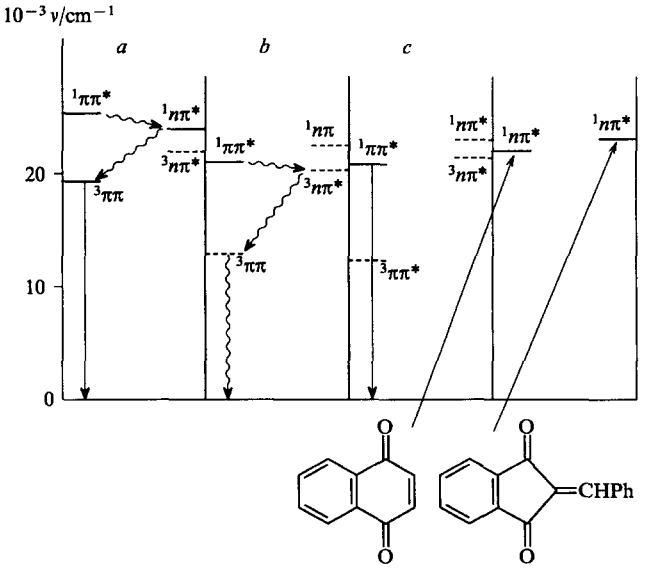
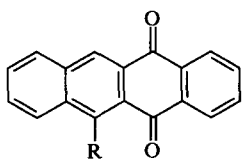
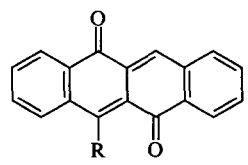
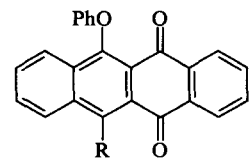
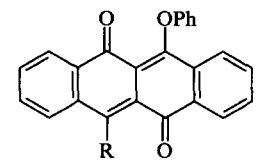


Figure 2. Electronic level diagram. The phosphorescence (Ph) (*a*, *b*) τ = 0.3 s and fluorescence (Fl) (*c*) of *p*-naphthacenequinone **1** and *ana*-naphthacenequinone **12** in hexane (*a*, *b*) and acetic acid (*c*); the dashed lines indicate the levels which are not manifested in the optical transitions.

Table 1. Electronic absorption spectra of 5,12- and 5,11-naphthacenequinones and the 6-derivatives of 11-phenoxy-5,12- and 12-phenoxy-5,11-naphthacenequinones in toluene.

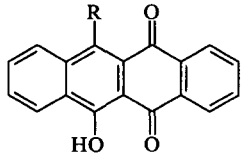
R	λ_{max}/nm (lg ε)			
				
Cl	402 (3.73)	451 (4.20)	398 (3.74) 479 (4.19)	444 (4.20) 472 (4.21)
TsNH	427 (3.77)	–	422 (3.77)	509
NH_2	382 (3.52) 474 (3.99)	490 (4.03) 513 (4.21) 522 (4.10)	389 (3.55) 468 (3.99)	474 (4.05) 503 (4.240 538 (4.17)
NHAc	436 (3.85)	509	429 (3.87)	504 (4.20)
NHCOPh	–	–	434 (3.88)	500 (4.21)
NO_2	–	–	394 (3.70)	453 (4.15) 479 (4.07)
NHMe	396 (3.52) 507 (4.09)	536 (4.11) 572 (4.01)	402 (3.73) 502 (4.09)	524 (4.15) 559 (4.07)
NMe_2	393 (3.69) 408 (3.68) 469 (3.57)	–	408 (3.78)	– 465 (3.60)
NHPh	401 (3.85) 504 (4.00)	472 (3.91) 536 (3.92) 572 (3.82)	404 (3.84) 496 (3.95)	525 (3.94) 558 (3.86)
OMe	401 (3.77)	–	400 (3.82)	447 (4.16) 469 (4.16)
NAcMe	397	455 (4.20) 485 (4.20)	396 (3.85)	448 (4.19) 476 (4.20)
OH	447 (3.98)	–	443 (4.00)	–
OCOMe	397 (3.86)	–	396 (3.89)	–

The electronic absorption spectra of 6-substituted naphthacenequinones[129] are very similar (as regards the position of λ_{max}) to the analogous spectra of the 6-derivatives of 11-phenoxynaphthacenequinone.[127] A definite analogy in the influence of the substituents in the 6-position in naphthacenequinone and in the 1-position in anthraquinone on the colour of these compounds can be traced.

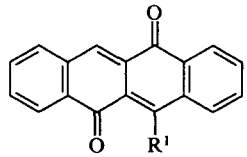
The nature of the substituents in the arene nucleus of 6-aryloxy-5,12-,[131] 6-amino-11-aryloxy-5,12-,[132] 6-aryloxy-5,11-naphthacenequinone[131] exerts little influence on the positions of the long-wavelength absorption maxima and the molar absorption coefficient (Table 1).

Comparison of the long-wavelength absorption band maxima of 6-R-11-phenoxy-5,12- and 6-R-11-phenoxy-5,11-naphthacenequinones by the proportional response method indicates the existence of a linear correlation (r = 0.992), which may apparently indicate that the nature of the bands is identical.[127]

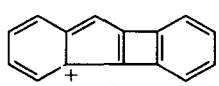
The study of the mass spectra of compounds **13–18** showed[146] that the main process involving the dissociative ionisation of compounds **13** and **16** is the consecutive removal of



13–15



9, 16–18

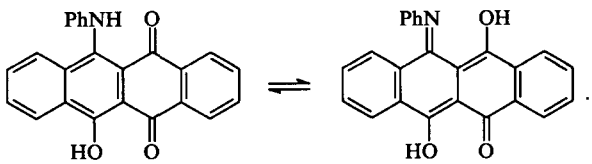


19

R = H (**13**); NHPh (**14**); NAcMe (**15**); R^1 = NH_2 (**16**); NHPh (**17**); NAcPh (**9**); MeNCPh (**18**).

O

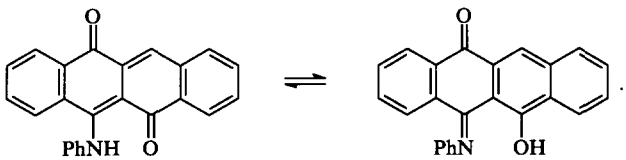
the two carbonyl groups, i.e. an anthraquinone type of decomposition leading to the formation of the stable structure **19**. The similar type of fragmentation of compounds **13** and **16** constitutes indirect evidence for the existence of 6-amino-5,11-naphthacenequinone **16** in an excited state following ionisation by electron impact in the *p*-quinonoid form. Together with the fragments characterising the *p*-quinonoid form **14a**, the mass spectrum of compound **14** contains a fairly large number of specific fragments corresponding to the *ana*-quinone imine form **14b**.



14a **14b**

The disporportionation of compound **15** after the removal of the acetyl group probably takes place in the *ana*-quinone imine form.

The successive elimination of the two carbonyl groups, characteristic of compounds with the *p*-quinonoid structure **13–15** is not observed in the dissociative ionisation of the *ana*-quinones **16–18**. The specific fragmentation processes are in all probability due to the fact that in the excited state, arising on ionisation by electron impact, 6-phenylamino-5,11-naphthacenequinone exists predominantly in the *p*-quinone imine form **17b**.



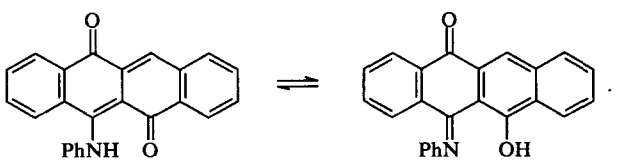
17a **17b**

Analysis of the mass spectra of compounds **17** and **18** also confirm this decomposition pathway for *ana*-phenylaminonaphthacenequinones.[147]

V. Tautomerism of naphthacenequinone derivatives

1. Prototropic and acylotropic rearrangements

The electronic absorption spectra of 6-phenylamino-5,11-naphthacenequinone **17** vary as a function of the polarity of the solvent employed. The family of spectral curves in CCl_4–EtOH mixtures of different composition is characterised by the presence of an isosbestic point, which indicates the presence of two coloured forms in solution (Fig. 3). The characteristic features of the spectroscopic properties of compound **17** can be explained[131] by the tautomerism due to the migration of a proton between the O and N atoms in the *peri*-positions.



17a **17b**

Bearing in mind the similarity of the absorption characteristics of the isoelectronic molecules, one might expect that the spectrum of the *p*-quinone imine tautomer would be similar to that of 6-hydroxy-5,12-naphthacenequinone and for this reason the shorter-wavelength absorption band, appearing in non-polar solvents, was assigned to 6-hydroxy-5-phenyliminonaphthacen-12-one **17b**, while the longer-wavelength band was assigned to the amino-derivative of *ana*-naphthacenequinone **17a**.

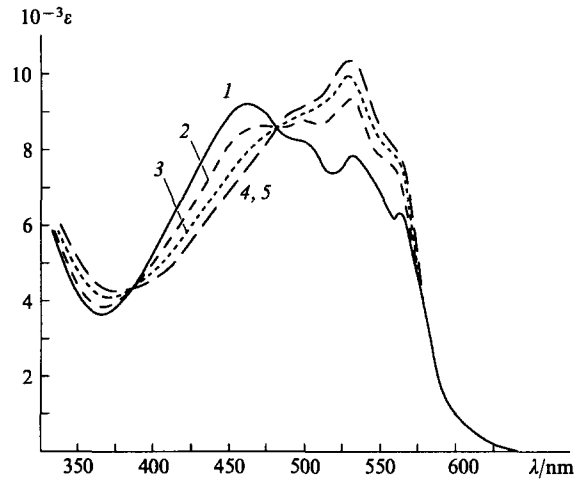
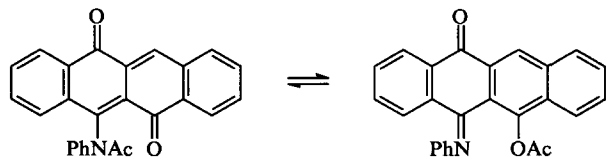


Figure 3. Electronic absorption spectra of 6-phenylamino-5,11-naphthacenequinone in CCl_4 (curve *1*), in C_2H_5OH (curve *5*), and in CCl_4–C_2H_5OH mixtures in different proportions: (*2*) 4 : 1; (*3*) 1 : 1; and (*4*) 1 : 4.

Similar prototropic transformations are characteristic also of 6-phenylamino-12-phenoxy-5,11-naphthacenequinone. 6-Amino- and 6-alkylamino-5,11-naphthacenequinones exist predominantly in the *ana*-quinonoid form in solvents of different polarity.[131]

A capacity for N,O-acylotropism has been observed for certain derivatives of 6-phenylamino-5,11-naphthacenequinone. Depending on the solvent used for recrystallisation, 6-(*N*-acetyl)-phenylamino-5,11-naphthacenequinone **9** can be isolated in two forms differing in the colour of the crystals. Analysis of the IR spectroscopic data led to the structure of the *ana*-quinone **9a** being attributed to the 'red' form, while the structure of the *p*-quinone imine **9b** was assigned to the 'yellow' form.

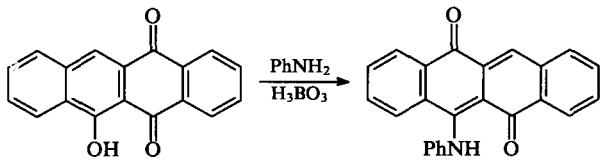


9a **9b**

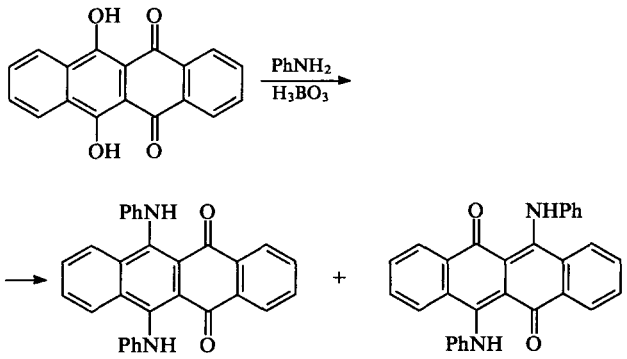
The electronic absorption spectra of compounds **9a** and **9b** in the same solvents are identical. The family of spectral curves of both compound **9a** and compound **9b** in decane–ethanol mixtures with different proportions of the individual solvents show isosbestic points, a consequence of the acylotropic equilibrium **9a** ⇄ **9b**. The tautomeric equilibrium constants were estimated approximately by the method of model compounds as 2.0 in ethanol and 0.4 in decane.[108]

6-Benzoylphenylamino-5,11-naphthacenequinone also exists in solution in two forms, but, in contrast to the acetyl derivative, the *p*-quinone imine form predominates in both polar and non-polar solvents.[108] 6-(*N*-Acetyl)methylamino-5,11-naphthacenequinone does not exhibit acylotropic properties.[108]

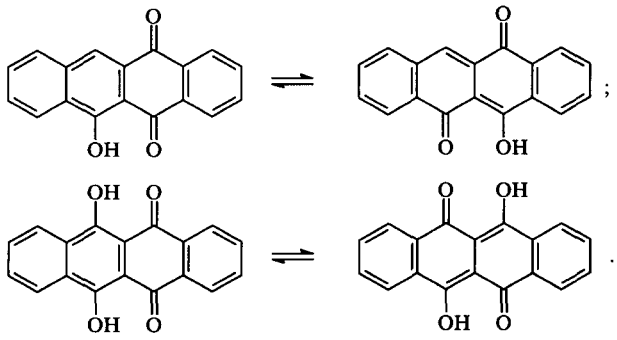
Instead of the expected 6-phenylamino-5,12-naphthacenequinone, its isomer 6-phenylamino-5,11-naphthacenequinone is formed on refluxing 6-hydroxy-5,12-naphthacenequinone with aniline in the presence of boric acid.[39]



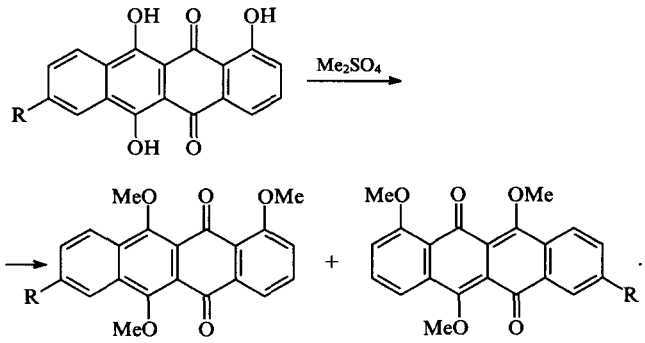
The analogous reaction of 6,11-dihydroxy-5,12-naphthacenequinone leads to a mixture of two isomers.[124,125]



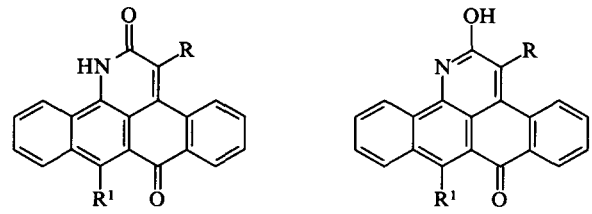
These facts suggested the existence of a tautomeric equilibrium.[39,124]



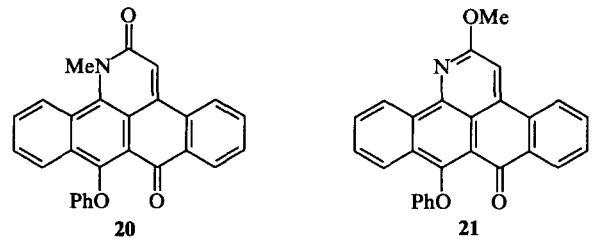
Methylation of derivatives of trihydroxynaphthacenequinone afforded isomeric compounds with *para*- and *ana*-quinonoid structures.[148]



Lactim–lactam tautomerism of naphthacenopyridones has been observed[101] for heterocyclic *peri*-condensed derivatives of naphthacenequinone, in contrast to the analogous derivatives of anthrapyridones which are incapable of this type of prototropism.



R = R¹ = H; R = H, R¹ = OPh; R = Ac, R¹ = OPh



20 **21**

It follows from the analysis of spectroscopic data for naphthacenopyridone and its fixed lactam (compound **20**) and lactim (compound **21**) forms that in polar solvents (*N*-methylpyrrolidone, hexamethylphosphoramide, dimethyl sulfoxide) pyridones exist mainly in the lactim form. The approximate constant of the lactam ⇄ lactim tautomerism for the unsubstituted naphthacenopyridone in *N*-methylpyrrolidinone is 0.4 at 25 °C.[101]

2. Arylotropic rearrangement of *peri*-aryloxynaphthacenequinones

One of the most interesting properties of derivatives of naphthacenequinone is the capacity of the *peri*-aryloxy-substituted 5,12-naphthacenequinones to undergo a reversible colour change in their solutions on exposure to light at different wavelengths, i.e. a capacity for photochromic transformations (Fig. 4).[135,149]

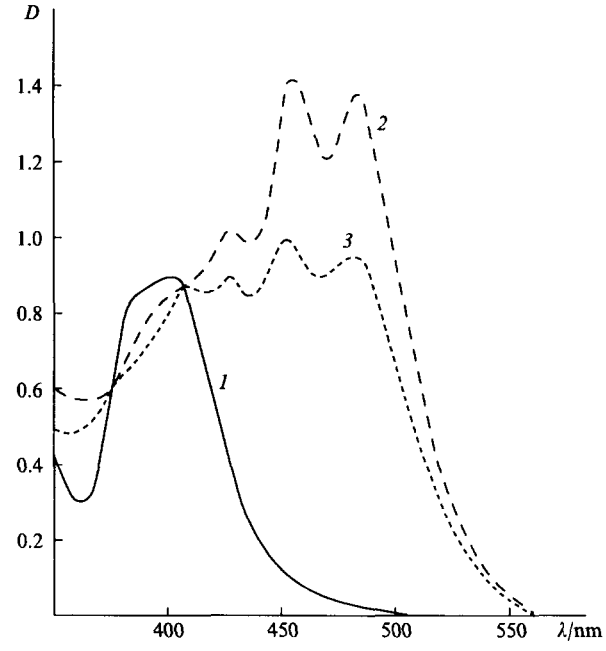
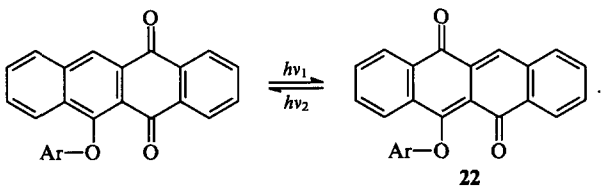


Figure 4. Electronic absorption spectra of 6-(β-naphthoxy)-5,12-naphthacenequinone in toluene ($c = 7.6 \times 10^{-5}$ M, $l = 2$ cm). (*1*) Initial solution prepared in the dark; (*2*) solution *1* irradiated for 2 min through a UFS-1 light filter; (*3*) solution *2* irradiated for 5 min through a ZhS-16 light filter. Source of radiation — DRK-120 mercury lamp.

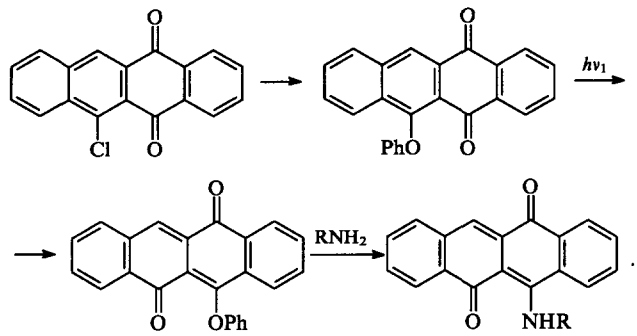
The photochromism of *peri*-aryloxynaphthacenequinones is due to the photoisomerisation of the *p*-quinonoid structure to the *ana*-quinonoid structure on exposure to light as a result of the migration of the arene nucleus to the oxygen atom of the carbonyl group in the *peri*-position relative to the ArO group.[149]



22

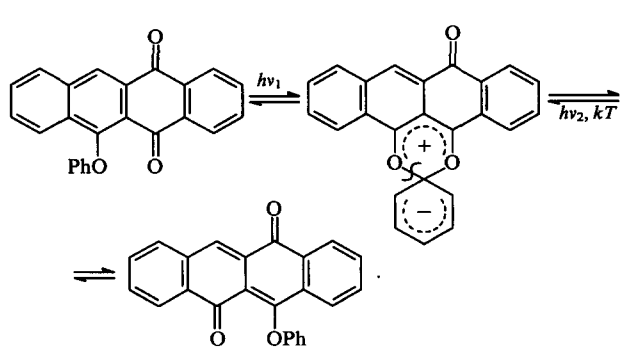
The formation of the *ana*-quinonoid structure as a result of the photorearrangement of 6-phenoxy-5,12-naphthacenequinone is confirmed by the similarity of the electronic absorption spectra of the photoinduced form **22** and those of 5,11-naphthacenequinone and 6-bromo-5,11-naphthacenequinone.[135] Furthermore, the intensities of the C=O stretching vibration bands (1685 and 1682 cm^{-1}) of 6-phenoxy-5,12-naphthacenequinone diminish after irradiation and new C=O absorption bands (1635 and 1660 cm^{-1}), characteristic of *ana*-naphthacenequinones, appear.[150]

The photoinduced form of 6-phenoxy-5,12-naphthacenequinone is stable under the usual conditions and is readily converted on treatment with ammonia and aniline into the nitrogen-containing derivatives **16** and **17** of *ana*-naphthacenequinone.[135]



16, 17

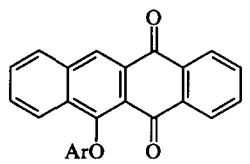
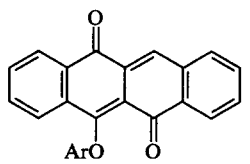
The unambiguous synthesis of compounds **16** and **17** from bromo-5,11-naphthacenequinone has been achieved.[39,97,151] It has been suggested that the intramolecular photoarylotropic rearrangement of naphthacenequinone most probably proceeds via an associative mechanism, although one cannot fully rule out the possibility of a dissociative mechanism with the intermediate formation of a contact ion or radical pair. The absence of radicals on irradiation of the *p*-quinone ⇄ *ana*-quinone system constitutes indirect evidence (obtained by the EPR method) for the heterolytic dissociation of the C=O bond. The dissociation of the C=O bond is preceded by the formation of a σ-complex, the stabilisation of which may lead to either the *p*- or *ana*-quinonoid structure.[149]



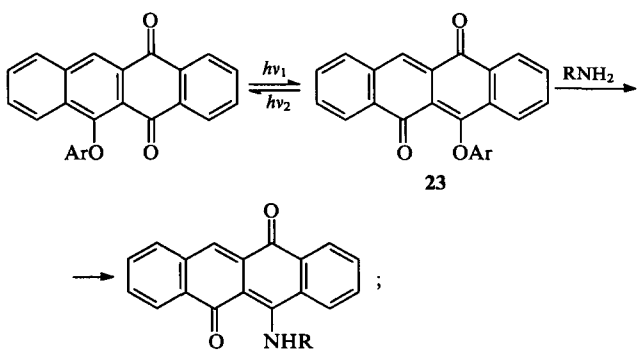
A mechanism of the isomerisation of 6-phenoxy-5,12-naphthacenequinone in solutions in organic solvents at room temperature has been proposed based on a comparative analysis of the spectral-kinetic behaviour of the intermediates and T-states of the nonphotochromic *p*- and *ana*-naphthacenequinones arising on laser photoexcitation. The photoexcitation of the initial form of 6-phenoxy-5,12-naphthacenequinone by radiation at a wavelength of 347 nm induces a transition of the molecule to a coloured form via an intermediate triplet photoproduct. The photoexcitation of the coloured form leads to the population of the T-state of this form, its deactivation not being accompanied by a transition of the molecule to the initial form.[152]

The nature of the substituent in the arene ring has little influence on the positions of the long-wavelength absorption maxima and the molar absorption coefficient but it does affect significantly the quantum yields of the forward and reverse reactions of aryloxynaphthacenequinones. However, a dependence of the quantum yields on the electronic structure of the substituent has not been observed (Table 2).[131]

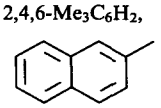
Table 2. Molar absorption coefficients and quantum yields of the forward (φ_B) and reverse (φ_A) photoisomerisation of 6-aryloxy-5,12- and 6-aryloxy-5,11-naphthacenequinones in toluene (λ_{act} = 366 nm).

Ar						
	λ_{max}/nm	$10^3\varepsilon$	φ_B	λ_{max}/nm	$10^3\varepsilon$	φ_B
C_6H_5	400	6.0	0.3	480	1.7	0.05
p-BrC_6H_4	397	5.9	0.36	480	1.8	0.10
p-OHC_6H_4	400	5.2	0.06	480	1.7	0.32
p-$OMeC_6H_4$	400	5.8	0.08	480	1.6	0.03
p-$PhNHC_6H_4$	396	6.4	0.02	476	1.8	0.01
2,4,6-$Me_3C_6H_2$	410	6.7	0.08	498	1.3	0.05
p-$MeCOC_6H_4$	400	6.0	0.27	480	1.8	0.10
p-$NO_2C_6H_4$	395	6.0	0.20	480	1.9	0.05
p-$NH_2C_6H_4$	395	5.5	0.13	480	1.7	0.07
β-$C_{10}H_7$	398	5.7	0.16	478	1.7	0.07
p-PhC_6H_4	398	5.4	0.20	478	1.8	0.10

The ability of the photoinduced form of aryloxynaphthacenequinones to react with amines at room temperature has been used to determine the molar absorption coefficients ε of *ana*-aryloxynaphthacenequinones **23** without their isolation in a pure form.[153]

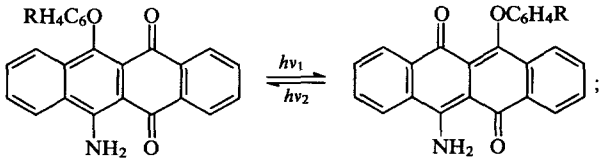


23

Ar = Ph, *p*-HOC_6H_4, *p*-$MeOC_6H_4$, *p*-$PhHNC_6H_4$, 2,4,6-$Me_3C_6H_2$, *p*-$MeCOC_6H_4$, *p*-$NO_2C_6H_4$, *p*-$NH_2C_6H_4$, *p*-PhC_6H_4, .

Solutions of 11-phenoxy-5,12-naphthacenequinones containing substituents of different electronic nature (Cl, NO_2, OMe, NH_2, NHTs, NHAc, NAcMe), in the 6-position in the naphthalene nucleus exhibit photochromic properties in polar and non-polar solvents. 6-Dimethylamino-, 6-phenylamino-, 6-hydroxy-, and 6-acetoxy-11-phenoxynaphthacenequinones proved to be non-photochromic. In the series of 6-(*N*-acetyl)-methylamino-, 6-amino-, and 6-methylamino-11-phenoxy-5,12-naphthacenequinones, the photosensitivity of the compounds diminishes with enhancement of the electronic-donating properties of the substituent. 6-(*N*-Acetyl)methylamino-11-phenoxy-5,12-naphthacenequinone is photochromic, in contrast to the 6-methylamino-derivative, the photoinduced form of which is hardly observable spectroscopically after prolonged irradiation, while the reverse photochemical reaction does not occur. Substituents such as NO_2 and MeO, which exert very different electronic influences, also diminish the stability of the photoinduced form, which cannot be isolated in an analytically pure form owing to its degradation on contact with silica gel.[127]

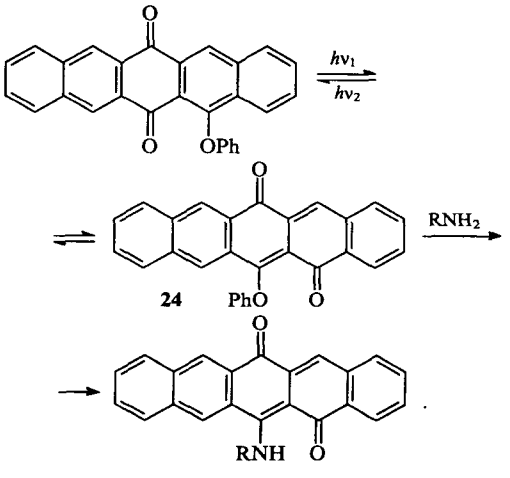
The presence of electron-donating substituents in the migrating group of 6-amino-11-aryloxy-5,12-naphthacenequinones promotes the occurrence of the photorearrangement in these compounds, in contrast to 6-amino-5,12-naphthacenequinone. 6-Amino-11-aryloxy-5,12-naphthacenequinones, containing electron-accepting substituents in the arene nucleus, isomerise under the influence of light less effectively than the unsubstituted 6-amino-11-phenoxy-5,12-naphthacenequinone.[132]



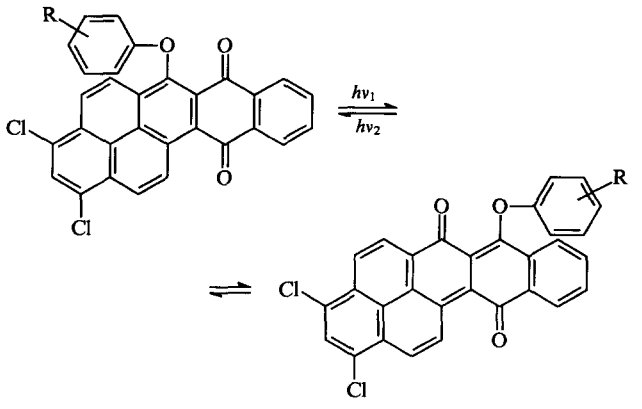
R = *p*-Me, *p*-Et, *p*-OMe, *p*-NHPh, *p*-OH, *p*-NO_2, *m*-Cl.

These data are consistent with experimental findings on substituent effects in photonucleophilic substitution and do not conflict with the hypothesis according to which the photoarylotropic rearrangement of *peri*-aryloxynaphthacenequinones is regarded as intramolecular photonucleophilic substitution.[149]

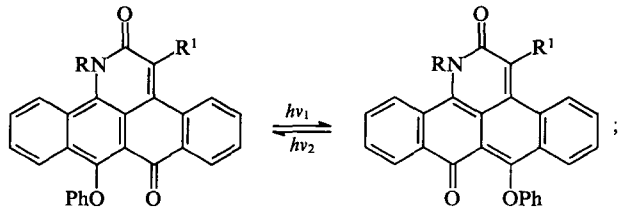
Derivatives of 5,12-naphthacenequinone with a linearly condensed benzene ring—5-phenoxy-6,13-pentacenequinone—isomerise reversibly under the influence of UV radiation to 6-phenoxy-5,13-pentacenequinone **24**. The photoinduced form was isolated in a pure form by virtue of the low rate of the dark isomerisation of the *ana*-quinone to the *p*-quinone. The high reactivity of the photoinduced form made it possible to obtain the first, previously unavailable, amino-derivatives of 5,13-pentacenequinone.[154]



Aryloxy-derivatives of a more complex polycyclic quinone—6,8-dichloro-2,3-phthaloylpyrene (structurally similar to 5,12-naphthacenequinone) are capable of arylotropism.[155,156]



peri-Phenoxy-substituted *N*-methylnaphthacenopyridones are photochromic, like their anthrone analogues—*N*-methylanthrapyridones.[103]

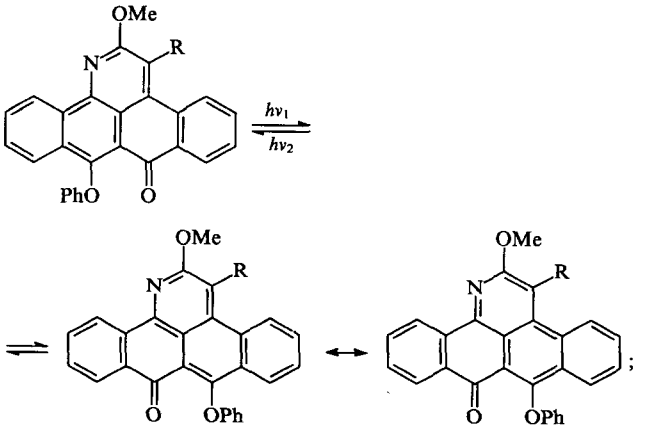


R = Me, R^1 = H, Cl, OPh, ; R = H, R^1 = H, MeCO.

Naphthacenopyridones, which have no methyl group attached to the nitrogen atom of the heterocyclic fragment of the molecule, undergo in chloroform photochromic transformations similar to those of phenoxyanthrapyridones,[157] but, together with the photochromic transformations, the decomposition of the photoinduced form under the influence of light is also observed.[101]

In contrast to *N*-methylnaphthacenopyridones,[103] alcoholic solutions of *NH*-naphthacenopyridones are not photochromic, which may be associated with the occurrence in alcohol of the photoinduced prototropic transformation of the *NH*-naphthacenopyridone into the lactim form, which rapidly isomerises to the initial pyridone.[101]

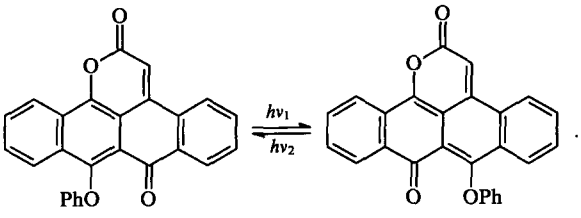
The ability to undergo the photophenyltropic rearrangement has been observed also in toluene solutions of naphthacenopyridones.[101]



R = H, COMe.

The photoinduced forms of naphthacenopyridines exist in solutions probably in the *p*-quinone imine forms, since the absorption band of the photoinduced form of naphthacenopyridines has undergone a hypsochromic shift relative to the band of the photoinduced form of naphthacenopyridones.[101]

9-Phenoxynaphthacenopyridone undergoes a reversible arylotropic rearrangement on exposure to light (Fig. 5).[109]



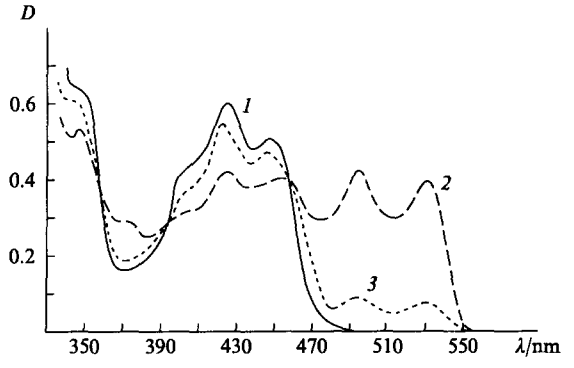
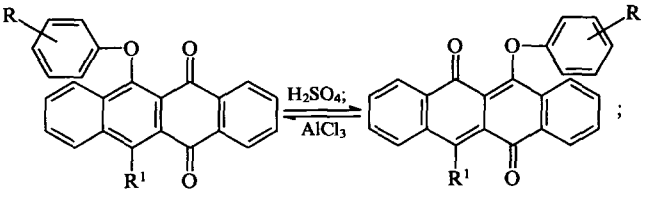


Figure 5. Electronic absorption spectra of 9-phenoxynaphthacenopyrone in toluene ($c = 6.97 \times 10^{-5}$ mol litre^{-1}). (*1*) Initial solution prepared in the dark; (*2*) solution *1* irradiated for 3 min through a SS-8 light filter; (*3*) solution *2* irradiated for 5 min through a ZhS-16 light filter. Source of radiation—DRK-120 mercury lamp.

The arylotropic rearrangement in the series of *peri*-phenoxynaphthacenequinones takes place not only under the influence of light but also in the dark. Treatment of *peri*-phenoxynaphthacenequinones with sulfuric acid or aluminium chloride leads to the corresponding *ana*-naphthacenequinones.[136]



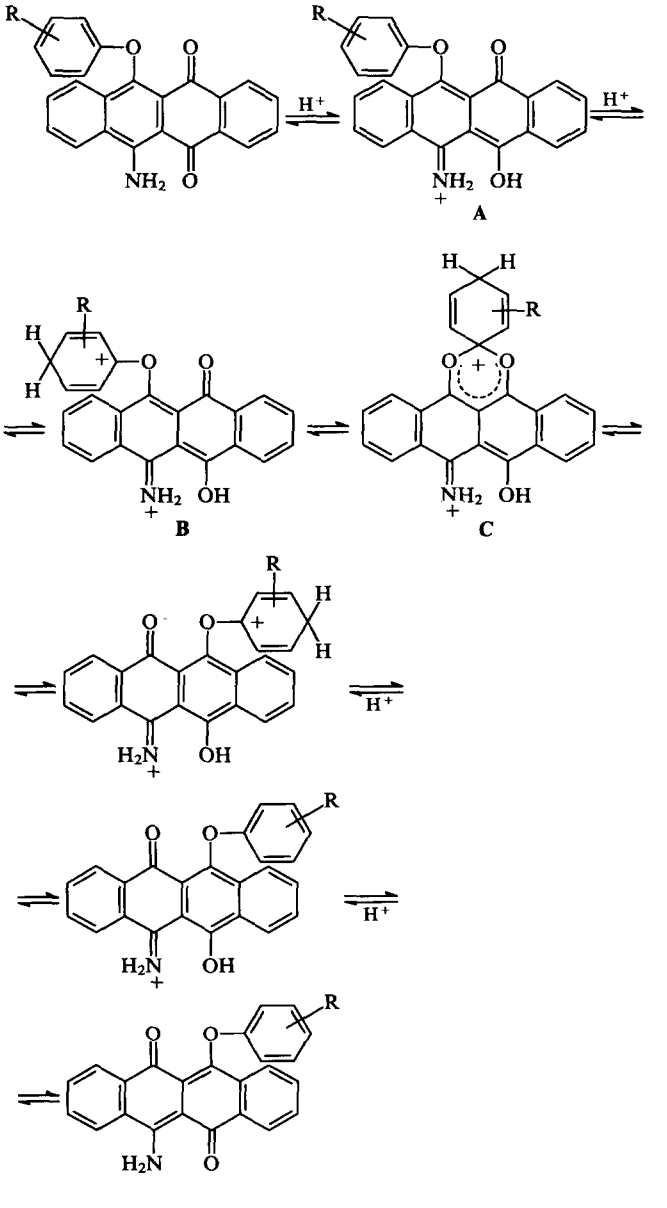
R^1 = NH_2, NHMe, NHPh, NHAc, H, OPh, OMe, Cl.

When naphthacenequinones containing an amino- or a substituted amino-group in the 6-position isomerise, the *ana*-isomer predominates in the equilibrium mixture; in the case of the remaining derivatives, the *p*-isomer predominates.[136]

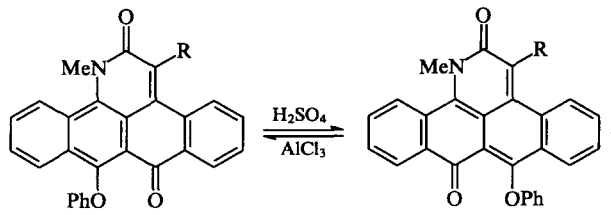
6-Amino-11-aryloxy-5,12-naphthacenequinones, containing electron-accepting substituents in the migrating group, isomerise in sulfuric acid with a higher yield than derivatives having electron-donating substituents.[132]

The *p*-quinone ⇄ *ana*-quinone rearrangement in sulfuric acid proceeds intramolecularly, which is indicated by the results of the cross-experiment: treatment of a mixture of 6-amino-11-(4′-ethylphenoxy)-5,12-naphthacenequinone and 6-phenylamino-11-phenoxy-5,12-naphthacenequinone with sulfuric acid at room temperature leads to the corresponding *ana*-isomers without admixture of intermolecular reaction products. The isomerisation of *peri*-aryloxynaphthacenequinones under the influence of sulfuric acid can apparently be represented as intramolecular nucleophilic substitution (Scheme 4). Protonation of the amino-group of *peri*-phenoxynaphthacenequinone and the appearance of the cation **A** with the *ana*-quinone imine structure in the equilibrium mixture apparently constitute an essential condition for the rearrangement. *peri*-Phenoxynaphthacenequinones, for which such protonation is impossible, for example 6-nitro-11-phenoxy-5,12-naphthacenequinone, do not isomerise under these conditions. In concentrated sulfuric acid, a second proton adds to the phenoxy-group of the monocation **A** with formation of the cation **B**. The latter is stabilised in the form of the spiro-complex **C**. Depending on which oxygen—carbon bond dissociation predominates in the spiro-complex **C**, both the *ana*-isomer and the initial quinone may be formed.[132]

Scheme 4

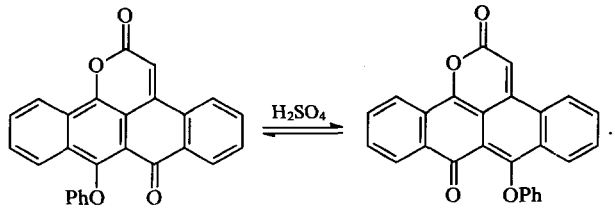


9-Phenoxy-derivatives of *N*-methylnaphthacenopyridone undergo an arylotropic rearrangement on treatment with sulfuric acid or aluminium chloride. The *para*-isomer predominates in the equilibrium mixture. The isomerisation is accompanied by degradation processes.



Phenoxynaphthacenopyridones without a methyl group at the nitrogen atom of the heterocyclic fragment as well as phenoxy-derivatives of *N*-methylanthrapyridones, anthrapyridines, and naphthacenopyridines do not isomerise under these conditions. 8-Phenoxy-derivatives of *N*-methylnaphthacenopyridones with the *ana*-quinonoid bond distribution have been obtained in a pure form by acid isomerisation.[158]

The acid arylotropic rearrangement is also characteristic of 9-phenoxynaphthacenopyrone.[109]



VI. Conclusion

The present review constitutes the first attempt to survey the literature data on the methods of synthesis and properties of naphthacenequinones and their derivatives. The observation of photochromism of a new type, involving the reversible photoarylotropic rearrangement of 6-phenoxy-5,12-naphthacenequinone to 6-phenoxy-5,11-naphthacenequinone, is especially interesting. The undoubted value of these data lies in the fact that the photochromism discovered for 6-phenoxy-5,12-naphthacenequinone proved to be general for the whole series of aryloxy-derivatives of polycyclic quinones (anthraquinone, pentacenequinone, and phthaloylpyrene) and also for heterocyclic derivatives based on them.

A high photostability and pronounced cyclic behaviour are characteristic of this class of photochromic materials. The photochromic materials obtained after the introduction of 6-phenoxy-5,12-naphthacenequinone into poly(methyl methacrylate) and other polymers can be used to record holograms with the aid of a helium-cadmium laser (λ = 441.6 nm) and for the non-disruptive recovery of the image from the holograms by means of the radiation from a helium-neon laser (λ = 632.8 nm).

Photochromism of this type can be used as a photochromic method of synthesis of compounds with the *ana*-quinoid structure, the synthesis of which by traditional methods is extremely difficult or impossible.

Data concerning the ability of 11-substituted derivatives of 6-phenoxy-5,12-naphthacenequinones to undergo the phenylotropic rearrangement under the influence of Lewis acids are extremely interesting.

It is noteworthy that the widely known reactions leading to the formation of heterocyclic derivatives based on 9,10-anthraquinone are also applicable to the synthesis of the analogous derivatives based on 5,12-naphthacenequinone, which makes it possible to synthesise a whole series of new heterocyclic derivatives with interesting properties.

Thus it may be hoped that the data presented in this review will attract the attention of investigators and that the chemistry of naphthacenequinones will undergo a new development.

References

1. Jpn. Appl. 74-81 440; *Chem. Abstr.* **83** 115 804w (1975)
2. Jpn. Appl. 75-53 684; *Chem. Abstr.* **83** 116 809p (1975)
3. Jpn. Appl. 75-53 685; *Chem. Abstr.* **83** 133 380j (1975)
4. Jpn. Appl. 75-65 539; *Chem. Abstr.* **84** 194 459p (1976)
5. Jpn. Appl. 75-121 580; *Chem. Abstr.* **84** 61 056d (1976)
6. Jpn. Appl. 77-40 684; *Chem. Abstr.* **87** 2 030 605u (1977)
7. Jpn. Appl. 77-94 326; *Chem. Abstr.* **88** 38 935t (1978)
8. Jpn. Appl. 49-14 892; *Ref. Zh. Khim.* 5N187P (1979)
9. Jpn. Appl. 54-17 877; *Ref. Zh. Khim.* 10N279P (1980)
10. German P. 138 325; *Frdl.* 241 (1905)
11. R Medne, V Kampar, O Neilands *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* (4) 465 (1972)
12. R Medne, A Livdane, V Kampar, O Neilands *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* (1) 83 (1975)
13. O Neilands, R Medne, A Okman, A Daneberg, V Kampar *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* (1) 69 (1975)
14. R Medne, I Kraupsa, O Neilands *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* (5) 633 (1989)
15. USSR P. 767 106; *Ref. Zh. Khim.* 11N122P (1981)
16. R P Shibaeva, V F Kaminskii *Cryst. Struct. Commun.* **10** 633 (1981)
17. Y Matsunaga, K Takayanagi *Bull. Chem. Soc. Jpn.* **53** 2796 (1980)
18. T Inabe, T Mitsuhashi, Y Maruyama *Chem. Lett.* **3** 129 (1988)
19. W A Remers *The Chemistry of Antitumor Antibiotics* (New York: Wiley, 1979) Vol. 1, p. 63
20. F Arcamone, in *Topics in Antibiotic Chemistry* Vol. 2 (Ed. P G Sammes) (Chichester: Ellis Horwood, 1978) p. 99
21. H Brokmann, I Hiemeyer *Naturwissenschaften* **48** 570 (1961)
22. H Brokmann, H Brokmann *Chem. Ber.* **94** 2681 (1961)
23. H Brokmann, P Boldt, J Niemeyer *Chem. Ber.* **96** 1356 (1963)
24. V M Bakshi, A B Kulkarni *Indian J. Chem.* **1** 215 (1963)
25. K Krohn *Tetrahedron* **46** 291 (1990)
26. N Gupta Dharmendra, P Hodge, N Khan *J. Chem. Soc., Perkin Trans. 1* 689 (1981)
27. Jpn. Appl. 63-188 674; *Ref. Zh. Khim.* 3O100P (1990)
28. T Antonsson, P Vogel *Tetrahedron Lett.* **31** 89 (1990)
29. G Sartori, G Casnati, F Bigi *Gazz. Chim. Ital.* **120** 13 (1990)
30. M H Frank, S Prasanna *J. Am. Chem. Soc.* **103** 6378 (1981)
31. Jpn. Appl. 63-188 694; *Ref. Zh. Khim.* 12O109P (1990)
32. H Fujioka, H Yamamoto, H Kondo, A Hirokazu, K Vasuyuki *J. Chem. Soc., Chem. Commun.* 1509 (1989)
33. Zheng Gihuang, Sui Leshu *Guo Gizxiamen Univ. Nat. Sci.* **28** 401 (1989); *Ref. Zh. Khim.* 11Zh193 (1990)
34. USSR P. 798 139 CCCP; *Ref. Zh. Khim.* 16N254P (1981)
35. E A Coulson *J. Chem. Soc.* 1406 (1934)
36. J W Cook *J. Chem. Soc.* 1412 (1934)
37. L F Fiser, E B Hershberg *J. Am. Chem. Soc.* **62** 49 (1940)
38. C Marschalk, C Stumm *Bull. Soc. Chim. Fr.* **15** 418 (1948)
39. C Marschalk *Bull. Soc. Chim. Fr.* **19** 155 (1952)
40. P G Copeland, R E Deen, L McNeil *J. Chem. Soc.* 3858 (1961)
41. J M Roitt, W A Waters *J. Chem. Soc.* 3060 (1949)
42. N P Bednyagina, G A Panfilov, I Ya Postovskii *Zh. Obshch. Khim.* **28** 365 (1958)
43. S Gabriel, E Leupold *Chem. Ber.* **31** 1272 (1898)
44. C Dufraisse, A Etienne, B Rütimeyer *C. R. Acad. Sci.* **236** 641 (1953)
45. C Dufraisse, A Etienne, B Rütimeyer *C. R. Acad. Sci.* **237** 1601 (1953)
46. H Oka *J. Jpn. Tar Ind. Assoc.* **3** 267 (1951); *Chem. Abstr.* **47** 3839c (1953)
47. V Kratochvil *Chem. Prum.* **23** 506 (1973)
48. USSR P. 505 623; *Ref. Zh. Khim.* 4N207P (1977)
49. H Waldmann, H Mathiowitz *Chem. Ber.* **64** 1713 (1931)
50. C Weizmann, E Bergmann, F Bergmann *J. Chem. Soc.* 1367 (1935)
51. C Deichler, C Weizmann *Chem. Ber.* **36** 547 (1903)
52. C Weizmann, L Haskelberg, T Berlin *J. Chem. Soc.* 398 (1939)
53. H Brokmann, W Müller *Chem. Ber.* **92** 1164 (1959)
54. J Finkelsteein, J A Romano *J. Med. Chem.* **13** 568 (1970)
55. D Harrop, R V Norris, C Weismann *J. Chem. Soc.* 279 (1909)
56. W H Bentley, A Fridl, F Tomas *J. Chem. Soc.* 411 (1907)
57. H Waldmann, G Polak *J. Prakt. Chem.* **150** 113 (1938)
58. S Gabriel, E Leupold *Chem. Ber.* **31** 1127 (1898)
59. G Wanag *Chem. Ber.* **10** 274 (1936)
60. R Medne, L Stradyns, O Neilands *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* (6) 698 (1979)

61. Swiss P. 664 963; *Ref. Zh. Khim.* 1N199P (1989)
62. K Zahn, P Ochwat *Liebigs Ann. Chem.* **462** 72 (1928)
63. H Brocmann, E Winner *Chem. Ber.* **96** 2399 (1963)
64. Jpn. Appl. 54-38 620; *Ref. Zh. Khim.* 23N213P (1980)
65. Jpn. Appl. 52-94 326; *Ref. Zh. Khim.* 15N209P (1978)
66. K Zahr *Chem. Ber.* **64** 2063 (1934)
67. Swiss P. 470 334; *Chem. Abstr.* 125 999c (1969)
68. Swiss P. 514 530; *Chem. Abstr.* 85 601p (1972)
69. R Winkler *Chimia* **20** 122 (1966)
70. R Winkler *Helv. Chim. Acta* **50** 2497 (1967)
71. K Yamamoto, E M Acton, D Henry *J. Med. Chem.* **15** 872 (1972)
72. A Di Marco, C Sjranco, A M Casazza *Cancer Chemother. Rep.* **53** 269 (1973)
73. W W Lee, A B Martinez, M T Smith, D W Henry *J. Org. Chem.* **41** 2296 (1976)
74. H Muxfeldt, V Koppe *Chem. Ber.* **91** 838 (1958)
75. M V Gorelik, S P Titova, V A Trdatyan *Zh. Org. Khim.* **15** 157 (1979)
76. A M Birch, A J M Mercer, A M Chippendale, C W Greenhalgh *J. Chem. Soc., Chem. Commun.* 745 (1977)
77. R Gompper, M Sramek *Synthesis (BRD)* 649 (1981)
78. M P Cava, A A Deana, K Muth *J. Am. Chem. Soc.* **81** 6458 (1959)
79. T Kametani, T Takanashi, M Kajiwara *Chem. Pharm. Bull.* **22** 2159 (1974)
80. J N Bridson, S M Bennet, G Butler *J. Chem. Soc., Chem. Commun.* 413 (1980)
81. W C Christopfel, L L Miller *Tetrahedron* **43** 3681 (1987)
82. J A Dodge, A R Chamberlin *Tetrahedron Lett.* **29** 1359 (1988)
83. J A Dodge, A R Chamberlin *J. Org. Chem.* **55** 4190 (1990)
84. Y Lepage, A Verine *C. R. Acad. Sci., Ser. C* **274** 1534 (1972)
85. A Verine, Y Lepage *Bull. Soc. Chim. Fr.* **3** 1154 (1973)
86. W Lange *Z. Naturforsch. B, Chem. Sci.* **31** 398 (1976)
87. M Peyrot, Y Lepage *Bull. Soc. Chim. Fr.* **9–10** 2856 (1973)
88. BRD P. 2 011 920; *Chem. Abstr.* **76** 14 189v (1972)
89. E Müller, E Langer. *Tetrahedron Lett.* **11** 989 (1970)
90. E Müller, H Muhm, E Langer *Chem.-Ztg.* **95** 525 (1971)
91. E Müller, G Odenigbo *Liebigs Ann. Chem.* 1435 (1975)
92. E Müller, A Scheller, R Winter *Chem.-Ztg.* **99** 155 (1975)
93. H A Staab, B Draeger *Chem. Ber.* **105** 2320 (1972)
94. W Trueb, E H Eugster *Helv. Chim. Acta* **55** 969 (1972)
95. M Yamaguchi, K Hasebe, H Higasi *J. Org. Chem.* **55** 1611 (1990)
96. D H R Barton, J H Bateson, S C Datta *J. Chem. Soc., Perkin Trans. 1* 503 (1976)
97. C Dufraisse, J Houpillart *C. R. Acad. Sci.* **206** 756 (1938)
98. J Deschamps, A Cohen, J Abbound *Bull. Soc. Chim. Fr.* **10** 2694 (1965)
99. A Cohen, J Deschamps *Tetrahedron* **42** 4409 (1968)
100. C Marschalk *Bull. Soc. Chim. Fr.* **1–2** 952 (1952)
101. Yu E Gerasimenko, N T Sokolyuk, L P Pisulina *Zh. Org. Khim.* **20** 1078 (1984)
102. Swiss P. 286 502; *Zbl.* **126** 2081 (1955)
103. Yu E Gerasimenko, N T Poteleshchenko *Zh. Org. Khim.* **18** 1039 (1982)
104. German P. 192 201; *Frdl.* **9** 732 (1908)
105. V P Shapkin, S I Popov *Zh. Org. Khim.* **16** 230 (1980)
106. H Waldmann, K G Hindenburg *J. Prakt. Chem.* **156** 157 (1940)
107. C Dufraisse, A Etienne, B Rutimeyer *C. R. Acad. Sci., Ser. C* **243** 878 (1956)
108. Yu E Gerasimenko, N T Poteleshchenko, V V Romanov *Zh. Org. Khim.* **16** 1933 (1980)
109. Yu E Gerasimenko, N T Sokolyuk, L P Pisulina *Zh. Org. Khim.* **21** 453 (1985)
110. E Aufderhaar, I E Baldwin, D H R Barton *J. Chem. Soc. C* 2175 (1971)
111. J A Barry, P G Sammes, T W Wallace *J. Chem. Soc., Perkin Trans. 1* 409 (1974)
112. D H R Barton, D L J Clive, P D Magnus *J. Chem. Soc. C* 2193 (1971)
113. L F Fiser *J. Am. Chem. Soc.* **53** 2329 (1931)
114. E Clar *Polycyclic Hydrocarbons* (Translated into Russian; Moscow: Khimiya, 1971) Vol. 1
115. USSR P. 406 821; *Byull. Izobret.* **46** 66 (1973)
116. R Medne, A Livdane, O Neilands *Zh. Org. Khim.* **13** 624 (1977)
117. J L Brisset *J. Electroanal. Chem.* **60** 217 (1975)
118. M Nepraš, V Kratochvil, M.Titz *Collect. Czech. Chem. Commun.* **38** 1003 (1973)
119. M Nepraš, M Titz, D Šnobl *Collect. Czech. Chem. Commun.* **38** 2397 (1973)
120. C Y Li, F M Whitehurst *Electrochim. Acta* **27** 601 (1982)
121. T Nagaoka, S Okaraki, T Fujinaga *Bull. Chem. Soc. Jpn.* **55** 1967 (1982)
122. M Roerner, B Rickborn *J. Org. Chem.* **56** 1373 (1991)
123. C Dufraisse, L Vellus *C. R. Acad. Sci., Ser. C* **201** 1394 (1945)
124. I Ya Postovskii, L N Goldyrev *Zh. Obshch. Khim.* **11** 429 (1941)
125. I Ya Postovskii, R G Beiles *Zh. Obshch. Khim.* **20** 522 (1950)
126. USSR P. 535 273; *Ref. Zh. Khim.* 14N204P (1978)
127. Yu E Gerasimenko, N T Poteleshchenko, V V Romanov *Zh. Org. Khim.* **16**, 1938 (1980)
128. H Waldmann, E Ulsperger *Chem. Ber.* **83** 178 (1950)
129. N T Poteleshchenko, Candidate's Thesis in Chemical Sciences, NIOPiK, Moscow, 1971
130. M Matsuoka, K Yoshida, M Kishimoto *Bull. Univ. Osaka Prefect.* **28** 33 (1979)
131. V V Romanov, Candidate's Thesis in Chemical Sciences, NIOPiK, Moscow, 1981
132. Yu E Gerasimenko, N T Sokolyuk, L P Pisulina *Zh. Org. Chem.* **26** 1100 (1990)
133. C R Harrison, P Hodge, N Khan *J. Chem. Soc., Perkin Trans. 1* 1592 (1980)
134. S Miki, H Kagawa, K Matsuo *Chem. Runct. Dyes* (First International Symposium, Osaka, June 5th–9th 1989) Tokyo, 1989, p. 299
135. Yu E Gerasimenko, N T Poteleshchenko *Zh. Org. Khim.* **7** 2413 (1971)
136. Yu E Gerasimenko, N T Poteleshchenko, V V Romanov *Zh. Org. Khim.* **16** 2014 (1980)
137. G N Rodionova, N I Karpova, V V Romanov, N T Sokolyuk, Yu E Gerasimenko *Zh. Fiz. Khim.* **58** 2323 (1984)
138. R N Nurmukhametov, G N Rodionova, V V Romanov, N T Poteleshchenko, Yu E Gerasimenko *Zh. Prikl. Spektrosk.* **30** 856 (1979)
139. L Navangu, V Himanskoo *Indian J. Chem.* **6** 85 (1968)
140. H Hopff, H R Schweirer *Helv. Chim. Acta* **45** 1044 (1962)
141. A Novak, M Titz, M Nepraš *Collect. Czech. Chem. Commun.* **39** 1532 (1974)
142. I L Belaits, N I Kunavin, R N Nurmukhametov, A E Podorol'skaya *Opt. Spektrosk.* **38** 908 (1975)
143. I L Belaits, N T Sokolyuk, A A Parshutkin, L P Samsonova, Yu E Gerasimenko *Zh. Fiz. Khim.* **50** 640 (1986)
144. M Nepraš, A Novak *Collect. Czech. Chem. Commun.* **42** 2343 (1977)
145. R N Nurmukhametov *Pogloshchenie i Lyuminestsentsiya Aromaticheskikh Soedinenii* (The Absorption and Luminescence of Aromatic Compounds) (Moscow: Khimiya, 1971)
146. A D Vasil'eva, N T Poteleshchenko, Yu E Gerasimenko *Zh. Org. Khim.* **19** 1529 (1983)
147. Z Horii, Y Osaki, S Yamamura *Chem. Pharm. Bull.* **22** 93 (1974)
148. Yu E Gerasimenko, N T Poteleshchenko *Zh. Vses. Khim. O-va im. D. I. Mendeleeva* **16** 105 (1971)
149. L V El'tsov (Ed.) *Organicheskie Fotokhromy* (Organic Photochromic Materials) (Leningrad: Khimiya,1982)
150. V N Kostylev, B E Zaitsev, V A Barachevskii, N T Poteleshchenko, Yu E Gerasimenko *Opt. Spektrosk.* **30** 86 (1971)
151. H Stobbe, P Haoum *Chem. Ber.* **37** 2240 (1904)
152. Yu P Strokach, B A Barachevskii, N T Sokolyuk *Khim. Fiz.* **6** 320 (1987)
153. Yu E Gerasimenko, A A Parshutkin, N T Poteleshchenko, V P Poteleshchenko, V V Romanov *Zh. Prikl. Spektrosk.* **30** 954 (1979)
154. Yu E Gerasimenko, N T Poteleshchenko *Zh. Org. Khim.* **15** 393 (1979)
155. Yu E Gerasimenko, N T Poteleshchenko *Zh. Org. Khim.* **4** 1473 (1968)
156. Yu E Gerasimenko, N T Poteleshchenko *Zh. Org. Khim.* **9** 2392 (1973)
157. Yu E Gerasimenko, N T Sokolyuk, L P Pisulina *Zh. Org. Khim.* **19** 1312 (1983)
158. Yu E Gerasimenko, N T Sokolyuk, L P Pisulina *Zh. Org. Khim.* **21** 2236 (1985)