Photo-, Thermo-, Solvato-, and Electrochromic Spiroheterocyclic Compounds

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Vladimir Minkin received his Candidate (Ph.D.) and Doctor of Science (chemistry) degrees from Rostov on Don State University. In 1967, he was appointed Professor at the same University, and since 1981 he has held the position of Head of the Institute of Physical and Organic Chemistry. He was a visiting professor or visiting scientist at the Havana, Strathclyde, Cornell, Florida, Regensburg, and Humboldt Universities, received his Dr. h.c. degree from the University of Aix-Marseille, and was elected a member of the Russian Academy of Sciences. Among his awards are the State Prize of USSR (chemistry), the Butlerov and Chugaev Prizes of the Russian Academy of Sciences, and the Senior Humboldt Award. His research interests include quantum organic chemistry, photochemistry, stereodynamics of metal coordination compounds, new types of tautomeric rearrangements, and organotellurium chemistry.

1. Introduction

During the past few decades, interest has been rapidly growing in gaining insight into the properties and transformations of the so-called bistable compounds and molecular systems, i.e., the chemical species and assembles that may exist in two thermodynamically stable states and are capable of interconversion under the action of various external sources. This interest is highly motivated by the fact that the bistable molecules and molecular systems represent, in effect, two-bit logic elements of nanoscopic size and have diverse potential applications in the areas of molecular electronics, photonics, and computing,[1] as well as by the role they play in the transport of biochemical information and signal transmission across biological membranes and photochemically switched enzymatic systems.[2] The most efficient and technologically adaptable way to address bistable molecules and systems from the macroscopic level is the use of light. Reversible rearrangements of a chemical species between two forms, **A** and **B**, induced in one or both directions by absorption of electromagnetic radiation and resulting in changes in the absorption spectra (and other physical properties as well), form the basis of the extensively studied phenomenon of photochromism[3] (eq 1). Thermally induced rearrangements accompanied by reversible color change are assigned to thermochromism[4] (eq 2). In solution, the position of the equilibrium described by this equation and, thus, the color of the solution may be affected by polarity or other properties of the solvent. In this case one deals with a version of the more general phenomenon of solvatochromism.[5] Electrochemical switching between different colors (eq 3), resulting from the generation of different redox states of a chemical species possessing different electronic absorption bands, underlies the phenomenon of electrochromism.[6]

$$\mathbf{A} \underset{h\nu_1,\Delta}{\overset{h\nu}{\rightleftharpoons}} \mathbf{B} \tag{1}$$

$$\mathbf{A} \overset{\Delta}{\rightleftharpoons} \mathbf{B} \tag{2}$$

$$\mathbf{A} \underset{-e}{\overset{+e}{\rightleftharpoons}} \mathbf{A}^{\bullet -}; \quad \mathbf{A} \underset{+e}{\overset{-e}{\rightleftharpoons}} \mathbf{A}^{\bullet +} \tag{3}$$

Although several thousand photo- and thermochromic compounds and materials based on the properties of these compounds have been already prepared and investigated for various applications, such as eye-protective glasses, filters and lenses of variable optical density, emissive displays, fluid flow field

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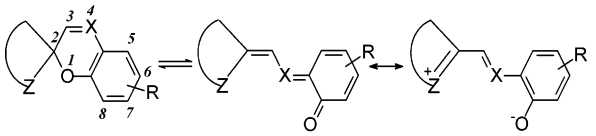
visualization, recording, and optical data storage and retrieval, their performance matching to transformations schematized by eqs 1 and 2 is limited to a few reaction mechanisms. The principal ones include *cis*−*trans* isomerization, excited-state proton or electron transfer, and $2_\pi + 2_\pi + 2_\pi$ pericyclic reactions. The latter mechanism (1,6-electrocyclization) is at the root of photo- and thermochromic behavior of spiropyrans and spiro[1,4]oxazines—spiroheterocyclic compounds capable of interconversion between two valence isomeric forms—colorless or slightly colored spirocyclic **1** and deeply colored merocyanine **2**. Photochemical or, respectively, thermal cleavage of the C−O bond in the 2*H*-pyran or 2*H*-4-azapyran rings is the rate-controlling stage of the reaction shown in Scheme 1.

Scheme 1



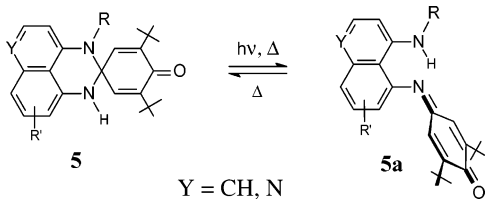
1 **2a** **2b**

Discovery of the photochromic behavior of spiropyrans[7a−c] and recognition of the significance of their bistability for a "photochemical erasable memory" [7d,e] spurred active research on the general phenomenon of photochromism. Until recently, spiropyrans **1** (X = CH, CR′) comprised the most amply studied family of photochromic compounds, and only during the past decade have these given way to their more practicable congeners, spirooxazines **1** (X = N) and also to diarylethenes with heterocyclic aryl groups.[8] The synthesis and the spectral and photochemical properties of spiropyrans and spirooxazines, particularly in the context of their application in a variety of photo- and thermochromic materials and devices, have become the subject of a number of comprehensive reviews[9] and will not be considered in detail in the present paper. Instead, this review is focused on studies aimed at gaining insight into the mechanisms governing photo- and thermally driven rearrangements (eqs 1 and 2) and structure−property relationships important for optimization of thermodynamic, kinetic, spectral, and other important parameters of the photochromic systems of this type, which include also thio and recently discovered[10] carbon analogues of spiropyrans **3** and **4**, respectively.

3 **4**

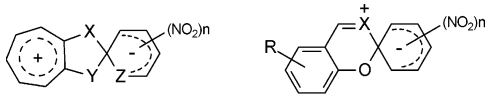
The photo-, thermo-, and electrochromic behavior of the next group of spiroheterocyclic compounds, derivatives of 2,3-dihydro-2-spiro-4′-(cyclohexadien-2′,5′-one)perimidine and their analogues **5**,[11] is determined by a combination of two principal reaction mechanisms involving cleavage of a C−N bond occurring in the first singlet excited state and the intramolecular proton transfer (Scheme 2).

Scheme 2



5 Y = CH, N **5a**

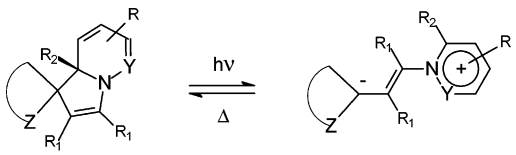
As for the compounds **1** and **3**−**5**, molecules of neutral spiro-σ-complexes **6** and **7** and their analogues, considered in section 8, contain a spiro-carbon center incorporated into a conjugated system. The structural similarity defines the similarity in the mechanisms of the photo- and thermochromic rearrangements, which involve dissociation of a C_{spiro}−X bond in the electronic excited or ground state, respectively.[12]



6 X, Y = O, S, NR; Z = N **7** X = O, NR

Dihydroindolizines **8** is another important class of photo- and thermochromic spiroheterocyclic compounds. As for spiropyrans and spirooxazines, the photochemical and thermal rearrangements of **8** are driven by a 6π-electron pericyclic reaction (Scheme 3), with the difference that one pair of π-electrons in

Scheme 3



8 Y = CR', N **8a**

their electronic system is located on a nitrogen or a carbanionic center. This leads to a 1,5-, instead of a 1,6-, electrocyclic route.

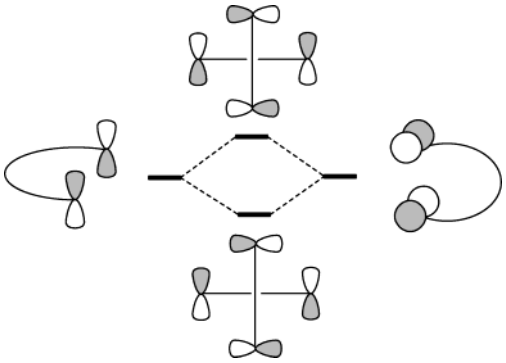
The photochromism of dihydroindolizines was discovered in 1979.[13] Their synthesis, photochemical and photophysical parameters, and areas of application have been thoroughly studied and described in several reviews.[14] This family of photo- and thermochromic spiroheterocyclic compounds will not be considered herein.

2. Spiroconjugation and Negative Hyperconjugation in Spiroheterocyclic Compounds

In compounds **1** and **5**−**7**, the through-space interaction of two orthogonal π-networks connected by a tetrahedral carbon center, i.e., spiroconjugation, may lead to nonadditivity of the photoelectron, electronic absorption spectra, and some other properties of the compounds.[15] Contrary to expectations, no such effect had been revealed in studies of the absorption spectra of various spiropyrans and spirooxazines **1** (X = CR, N), which were found to consist of localized transi-

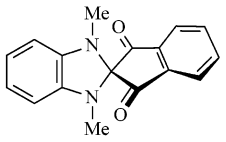
tions belonging to the two orthogonal halves of their molecules.[9b,f,16] This result can be explained in terms of the qualitative MO analysis of the factors determining the effects of spiroconjugation. The nonzero overlap between MOs of the two π-subsystems leading to the formation of MOs spanning the entire system and, thus, to delocalization of the electronic density over this system is achieved, provided that the interacting MOs have the same symmetry. For the spiroconjugated π-subsystems, this requirement must be supplemented with the condition that the MOs of the mutually perpendicular fragments are antisymmetric with respect to the two perpendicular bisecting planes,[15] as shown by the relative phases of the atomic orbitals at the centers adjacent to the spiro atom in Scheme 4.

Scheme 4

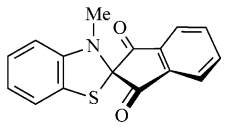


On the basis of this concept, and restricting themselves to consideration of only frontier orbitals of fragments of the spiroconjugated systems, Maslak and coauthors[17a,b] designed a number of spiroheterocyclic dyes **9** with useful optical properties, in which interaction of the antisymmetric LUMO of the acceptor part (1,3-indandione) with the HOMO of the donor part (aromatic diamines) results in the appearance of new absorption bands in the visible region due to the intramolecular charge transfer between the spiroconjugated fragments. For **9a**,**b**, the intensity of these charge-transfer bands is low because 1,2-phenylene derivatives possess symmetrical HOMOs, the symmetry of which is mismatched with that of the acceptor's LUMO. In contrast, 1,8-naphthylene derivatives **9c**,**d** have antisymmetric HOMOs overlapping with the acceptor's LUMO, which provides for spiroconjugation and rather intense charge-transfer bands in the absorption spectra of these compounds[17a,b] and some of their close analogues.[17c]

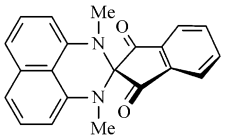
In spiropyrans and spirooxazines **1**, LUMOs of the 2*H*-chromene and 2*H*-4-azachromene fragments are conceptually (no strict symmetry) antisymmetric,[18] whereas HOMOs of 1,2-phenylenediamine, 1,2-phenylenedithiol, and other 1,2-phenylene moieties of various five-membered heterocycles constituting the "left" part of **1** are symmetric. Such a combination does not fit the requirements of spiroconjugation. On the other hand, in the spiroheterocyclic compounds **5**−**7**, both conjugated fragments linked by a spiro carbon atom possess antisymmetric frontier orbitals, and their spectra contain additional red-shifted absorption bands (section 6) originated from the charge transfer between the orthogonal fragments.



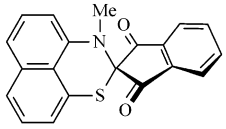
9a



9b



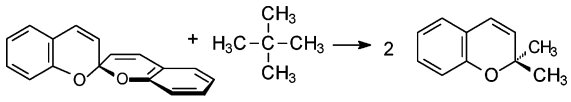
9c



9d

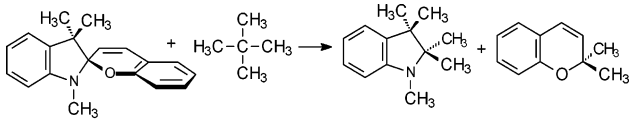
While the compatibility in the HOMO−LUMO symmetry properties depicted by Scheme 4 seems to be an essential factor accounting for the occurrence of the electronic transitions unobserved in the separated conjugated moieties of certain spiroheterocyclic compounds, it should not be considered as the dominant factor defining other consequences of spiroconjugation. As stems from the DFT (B3LYP/6-31G**) calculations[18d] presented in Schemes 5−10, such an integral property of a spiroheterocyclic system as net stabilization (or destabilization) related to the spirointeraction cannot be reduced to a simple HOMO−LUMO symmetry relationship. On the basis of the homodesmotic stabilization energies (HSEs), the calculations predict weak stabilization of the spiropyran and spirooxazine systems **10**−**12**, whose electronic absorption spectra do not display spatial interaction between the two orthogonal π-systems, and somewhat larger stabilization for perimidinespirocyclohexadienone **5b**, for which a long-wavelength

Scheme 5



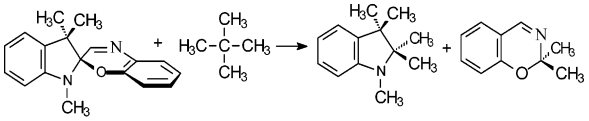
10 HSE = Δ (E_{total} + ZPE) = - 2.2 kcal mol^{-1}

Scheme 6



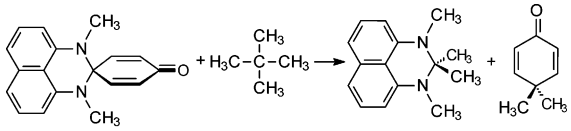
11 HSE = Δ (E_{total} + ZPE) = - 0.7 kcal mol^{-1}

Scheme 7



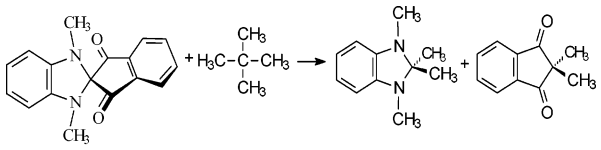
12 HSE = Δ (E_{total} + ZPE) = - 3.0 kcal mol^{-1}

Scheme 8



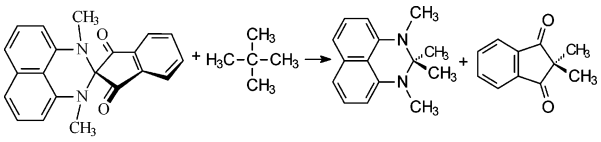
5b HSE = Δ (E_{total} + ZPE) = - 0.7 kcal mol^{-1}

Scheme 9



9a HSE = Δ (E_{total} + ZPE) = + 9.3 kcal mol^{-1}

Scheme 10

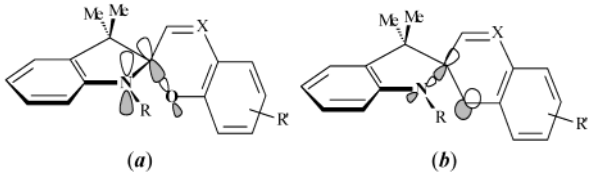


9c HSE = Δ (E_{total} + ZPE) = + 5.6 kcal mol^{-1}

charge-transfer band appears in the spectrum. At the same time, both spirocyclic systems **9a** and **9c**, the spectral behavior of which was considered[17a,b] as providing examples for, correspondingly, the nonexistence and the manifestation of the effects of spiroconjugation, are significantly destabilized (positive HSE values) compared to the isolated fragments.

Another important stereoelectronic effect operating in molecules of spiropyrans and spirooxazines **1** that affects the structural parameters of their spiro sites and their proneness to the isomerizations shown in Scheme 1 is caused by a specific orbital interaction resulting in partial donation of a lone electron pair at the heteroatom Z to a vacant antibonding σ^*-orbital of the C_{spiro}−O bond. Such orbital interactions (negative hyperconjugation) have been recognized as the main factor determining anomeric effects,[19] strong attractive closed-shell interactions,[20] and even the nature of hydrogen bonds.[21] The $n_Z \rightarrow \sigma^*_{CO}$ interaction shown in Scheme 11a manifests itself in length-

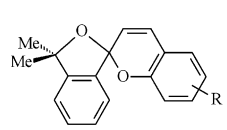
Scheme 11



(*a*) (*b*)

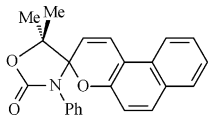
ening the C_{spiro}−O bonds in indolinospiropyrans (X = CH), spiroindolinonaphthoxazines (X = N, R′ = C_6H_4), and many other spiropyrans and spirooxazines **1**. The structural consequences of this effect are only partly compensated by the $n_O \rightarrow \sigma^*_{CN}$ orbital interaction (Scheme 11b), which is substantially weaker than that shown in Scheme 11a because of the poorer donating properties of the more electronegative oxygen center and, therefore, the larger energy gap between the interacting orbitals. As shown by X-ray structural determinations of a broad variety of indolinospiropyrans and spirooxazines (see refs 22a,b for a recent comprehensive review of structural studies of spiroheterocyclic compounds by X-ray diffraction), the C_{spiro}−O bond lengths in these compounds fall into the range of 1.452−1.501 Å and 1.45−1.478 Å, respectively, and are considerably longer than normal C_{sp^3}−O bonds (1.41−1.43 Å).

As was shown by quantum chemical modeling of reaction paths for the valence isomerization of spiropyrans[18] and spirooxazines,[23] the reaction coordinate at the early stage of the reaction (Scheme 1) in both ground and first singlet excited states corresponds well to stretching a C_{spiro}−O bond. It is not, therefore, surprising that the proneness of compounds **1** to the thermal and photoinitiated rearrangements shown in Scheme 1 correlates with degree of initial stretching of this bond in the ground state, determined by the efficacy of the $n_Z \rightarrow \sigma^*_{CO}$ orbital interaction. In 2-oxaindano spiropyrans **13a**, this interaction is relatively weak compared with that shown in Scheme 11a, which is due to the lower energy level of the lone electron pair orbital located at the oxygen in the five-membered ring. This is also true for spiropyrans **13b**,**c** because of the involvement of the n_N orbital at the nitrogen centers in π-conjugation with the adjacent carbonyl group. Both of these effects operate in spiropyrans of the 2-oxaindan-3-one series **13d**, in which case the lengths of the C_{spiro}−O bonds reach the minimal values currently known for spiropyrans.



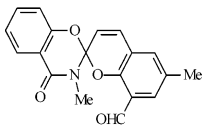
13a

l $C_{spiro-O}$ 1.444-465 Å (5 compounds)[24a]



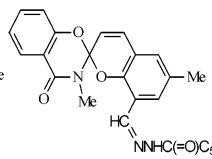
13b

l $C_{spiro-O}$ 1.440 Å[24b]



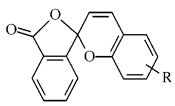
13c

l $C_{spiro-O}$ 1.439 Å[24c]



13d

l $C_{spiro-O}$ 1.415 Å[24d]



13d

l $C_{spiro-O}$ 1.399-1.418 (2 compounds)[24e]

Under continuous irradiation of their liquid or glassy solutions, all spiropyrans with C_{spiro}−O bonds longer than 1.42 Å can undergo the thermal and photochemical transformations described by Scheme 1. However, the spiropyrans **13d**, with shorter C_{spiro}−O bonds, exhibit neither thermochromic nor photochromic properties.

3. Spiropyrans and Spirooxazines

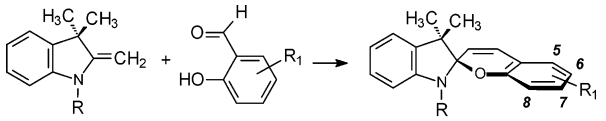
3.1. Synthesis

Several detailed reviews are available that deal with the synthesis of spiropyrans **1** and cover the literature and patents through 1997.[9a,b,d] In this section, we shall outline the principal approaches to the preparation of main groups of spiropyrans and give some illustrative examples.

The two most commonly used methods consist of the condensation of a heterocyclic quaternary salt with an alkyl group in a vicinal position with respect to the heteroatom or the corresponding methylene

base with 2-hydroxyarenealdehydes or their heterocyclic analogues. Due to the ready availability of 1,3,3-trimethyl-2-methyleneindoline (Fischer's base) and its derivatives, and due to the particularly valuable properties of spiropyrans containing their fragments, the reaction (Scheme 12) already em-

Scheme 12

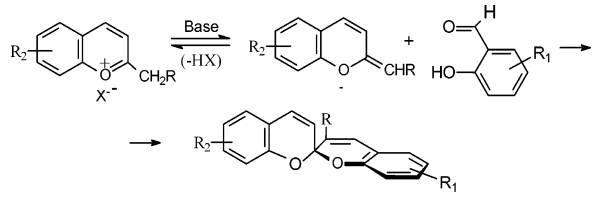


11

ployed for the preparation of many hundreds of 1,3-dihydrospiro(2*H*-1-benzopyran-2,2′-(2*H*)-indoles **11** may undoubtedly be regarded as the most important in the chemistry of spiropyrans. Generally, the reaction occurs smoothly upon refluxing ethanol solutions of equimolar amounts of the components to afford **11** in 70−98% yields.

The majority of heterocyclic methylene bases tends to dimerize instantly upon formation and cannot be used directly in the reaction shown in Scheme 12. For the synthesis of spiropyrans of benzoxazoline, benzothiazoliine, benzodithiole, benzopyran, and some other series, the corresponding alkylimmonium, thionium, and oxonium salts must be used as the precursors to the methylene bases, and the transformation illustrated by Scheme 13 is performed as a one-pot reaction in the presence of basic reagents.

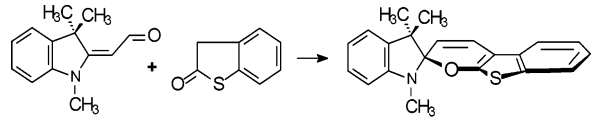
Scheme 13



14

By shifting a carbonyl group from one reagent to another in the reaction shown in Scheme 12, Bertelson[9a] developed its useful modification, allowing involvement into this transformation of heterocyclic hydroxyaldehydes that are generally stable in the ketomethylene tautomeric form (Scheme 14). The

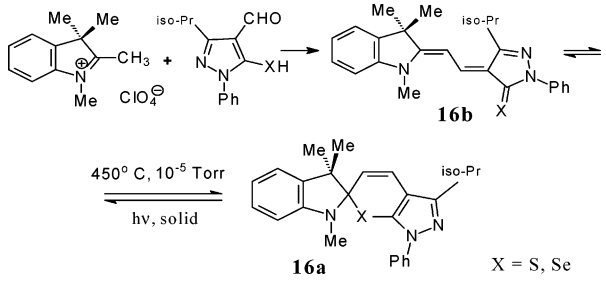
Scheme 14



15

spirocyclic isomers of spiropyrans with their "right" halves containing a heterocycle instead of a benzene ring are not infrequently less energy favorable than the merocyanine forms. In this case, reactions of methylene active compounds with various heterocyclic hydroxyaldehydes usually give rise to the thermodynamically or kinetically stable merocyanine forms **2**. Nevertheless, if ring-closed and ring-opened isomers are divided by a substantial energy barrier, the metastable spirocyclic isomer **1** can be isolated. As a method for preparation of kinetically stable spiropyrans that cannot be obtained with the use of the standard synthetic procedures, vacuum deposition of their merocyanine isomers has been suggested.[25a] Evaporation of the merocyanine **16b** in a vacuum followed by deposition on a quartz or potassium bromide substrate leads to the formation of the otherwise inaccessible spirocyclic isomer **16a**. By UV irradiation, the formed solid film of **16a** can be converted to **16b**. These transformations are shown in Scheme 15. In some cases, similar merocyanine-to-spiropyran

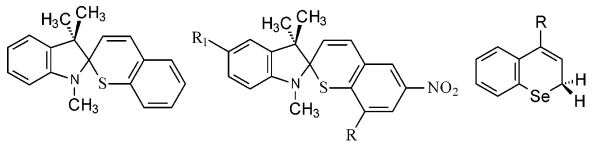
Scheme 15



X = S, Se

transformations can be performed under irradiation of a solution of a stable colored form.[25b,c]

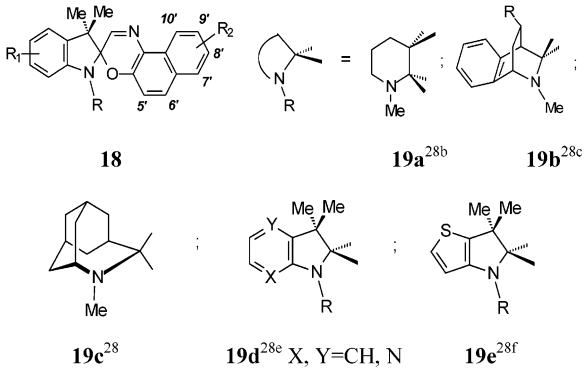
Condensation of Fischer's base with derivatives of thiosalicylic aldehydes leads to spirobenzothiopyrans **3**, the first representative of which, **17a**, was reported by Becker and Kolc.[26a] The colored opened form of this compound absorbs at about 100 nm longer wavelengths than the analogous spiropyran. The near-IR absorption is an advantageous property for applications of photochromic dyes in erasable disks driven by the standard diode lasers. Unfortunately, the colored form of **17a** is thermally unstable and rapidly bleached at room temperature. The stability of this form was substantially enhanced by introducing a 6-nitro group into the thiobenzopyran ring of **17a** through condensation of various Fischer bases with 5-nitrothiosalicylic aldehyde and its derivatives.[26b−e] By copolymerizing 6-nitrospirobenzothiopyrans **17b** with methyl methacrylate, a series of diode-laser-susceptible isotacting polymers anchoring these photochromic units were prepared, the colored cast films of which, induced by UV irradiation, retained the initial color for half a year.[26f] No selenopyrans have been reported to date. However, selenochromenes (2*H*-1-benzoselenapyrans) **17c** were synthesized and exhibited photochromic properties, with the colored form absorbing beyond 900 nm.[27]



17a **17b** R=H, OAlk, $CH_2O(C{=}O)C(=CH_2)Me$, R_1=H, OMe **17c** R =H, Ph

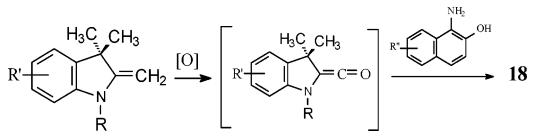
As was mentioned in the Introduction, spirooxazines **1** (X = N) possess particularly valuable photochromic properties, especially excellent resistance of

both of their isomeric forms to photodegradation, for applications in diverse devices, primarily eyewear. Recognition of this important advantage of spirooxazines drew much interest to investigation into the synthesis of these compounds (see refs 9f−h and 28a for reviews). The most widespread method for the synthesis of spirooxazines **1** (X = N) is closely related to the reaction depicted by Scheme 12, employed for the preparation of spiropyrans. *o*-Hydroxyarenealdehydes are replaced by their *o*-hydroxynitroso analogues, and solutions of the reactants in methanol, acetone, or trichloroethene are refluxed, preferably under an atmosphere of nitrogen, to give spirooxazines **1** (X = N) in 30−50% yields. By this method, the first spirooxazines—derivatives of 1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphth[2,1-*b*][1,4]oxazine] **18**—were obtained in 1970.[29] The scope of the method, as applied to spirooxazines, is more limited since oxygen- and sulfur-containing heterocyclic methylene bases or the corresponding quaternary salts do not react with *o*-hydroxynitroso compounds, which restricts variations in the "left" part of **1** (X = N) to only nitrogen-containing heterocycles such as **19**. In general, the *o*-hydroxynitroso component of the reaction must contain at least two fused benzene rings to produce stable ring-closed structures **1** (X = N). Only recently, a novel technique based on condensation of the indoleninium iodides with the Cu(II) complexes of *o*-hydroxyphenols provided a means for the preparation of a series of stable spiroindolinobenzoxazines.[30]



Another approach to the spirooxazines of type **18** consists of coupling Fischer's bases with aminonaphthols in the presence of mild oxidants, such as selenium dioxide or dimethyl sulfoxide.[31a] The advantages of this approach (Scheme 16) are in the ease of structural modification of aminonaphthols and the higher yields of the products, for which the method has recently gained much attention and has been successfully applied to the synthesis of a variety of less accessible spirooxazines.[31b−f]

Scheme 16



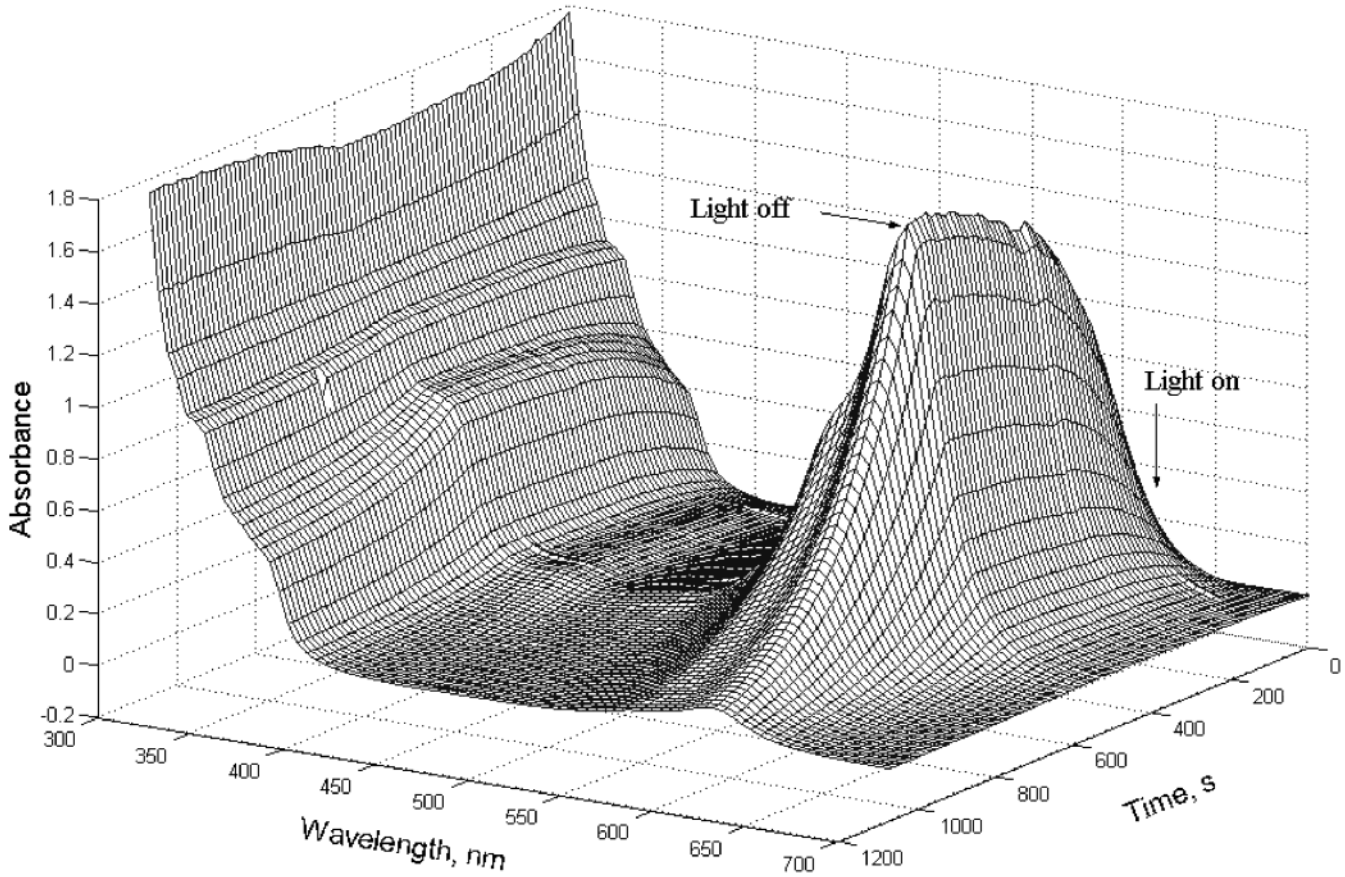
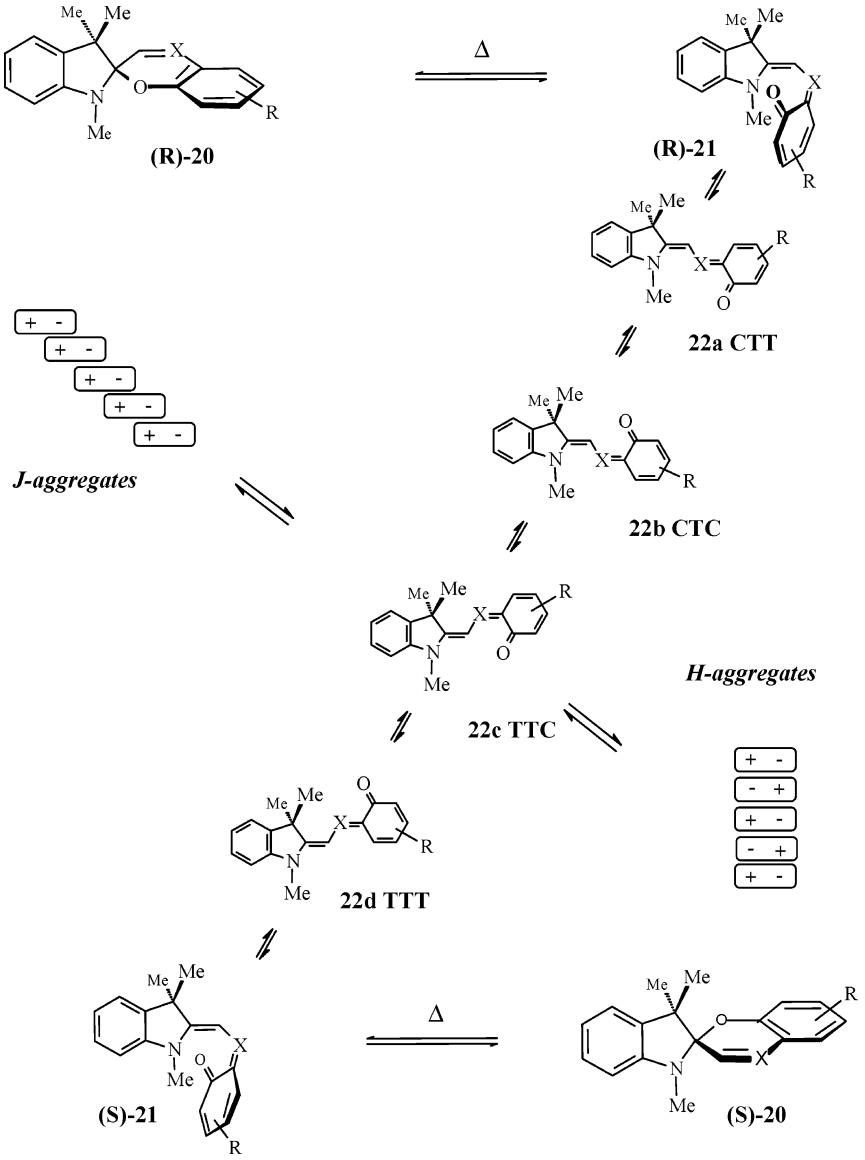


Figure 1. Evolution of the absorption spectrum of a toluene solution (1.2×10^{-4} mol L^{-1}, 293 K) of 8′-cyanospiroindoline-2,3′-naphtho[2,1-*b*][1,4]oxazine **18** (R = CH_3, R_1 = H, R_2 = 8′-CN) under irradiation with 365 nm light and after extinguishing irradiation.[9h]

Scheme 17



At the present time, several thousand spiropyrans and spirooxazines have been prepared. Tabulated information on the preparation, structural characteristics, and properties of many of these compounds can be found in monographs[9a,b,d,f,g] and a recent review paper.[9h] The first steps in work on the development of a comprehensive database comprising systematic data on all important classes of photochromic compounds have also been reported.[32]

3.2. Ground-State Ring-Opening/Ring-Closing Reactions

3.2.1. Thermal Equilibria

In solutions of nonpolar solvents, most spiropyrans and spirooxazines exist as ring-closed isomers **1**, but upon dissolving in polar solvents they can undergo thermal ring opening to the corresponding merocyanine forms **2**. The position of the established complex equilibrium depends on many factors, primarily solvent polarity, the nature of the substituents, and the concentration of the solution. Formation of the merocyanines can also be induced by irradiation of the solution in the near-UV, and equilibrium of the valence isomers is attained through the reverse dark ring-closing reaction. Such a relaxation of the photoinduced merocyanine form from the photostationary state is illustrated by the spectral behavior of a spirooxazine **18** (R = CH_3, R_1 = H, R_2 = 8′-CN), shown in Figure 1.

Thermal equilibrium established in solutions of spiropyrans and spirooxazines is depicted in Scheme 17, with indolinospirobenzopyrans **20** (X = CH) or indolinospirooxazines **20** (X = N) by way of example. The ring-opening reaction starts with cleavage of the C−O bonds in the stereoisomers **20** to give rise to sterically strained chiral intermediates **21**, which rapidly convert to nearly planar merocyanine isomers **22**, labeled according to the configurations of the molecular fragments relative to the two double bonds (cis, trans: **C** and **T**) and a partially double bond (*s-cis*, *s-trans*: **C**, **T**). Because *s-cis* conformers are significantly higher in energy than their *s-trans* isomers, Scheme 17 is restricted to the interconversions of the latter.

The presence of more than one merocyanine isomer in solutions of spiropyrans and spirooxazines has

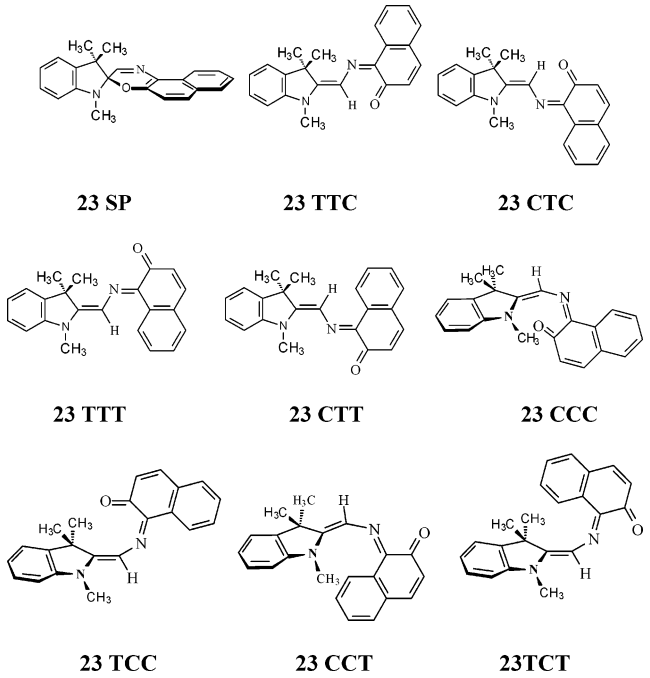
been shown in several studies using transient spectroscopy,[33,34] ^{1}H, ^{13}C, and ^{19}F NMR NOE,[35,36] and time-resolved resonance Raman spectroscopy[37] experiments. The structure of the most stable isomers was determined as **TTC** and **CTC** conformers. This finding is in accord with the conclusions made on the basis of theoretical modeling[23,35,36e,38] of the equilibria represented by Scheme 17. Table 1 contains some

Table 1. Calculated Relative Energies (kcal mol^{-1}) of the Merocyanine Conformers of 23 in the Gas Phase and in Ethanol Solution[a]

	B3LYP/6-31G*/ 3-21G[23b]		B3LYP/ 6-31G*[23a]		MP2/3-21G/ 3-21G[35]
species	gas phase	ethanol	gas phase	ethanol	gas phase
SP	0	−7.2	0	0	0
TTC	2.8	−1.4	3.1	0.7	6.7
CTC	4.1	−0.4	4.6	2.2	9.2
TTT	12.7	7.5	11.6	7.6	16.8
CTT	12.6	7.8	11.0	8.0	18.9
CCC	15.5	11.3	15.3	13.2	
TCC	21.7	17.2	25.7	20.1	
CCT	25.5	17.7			
TCT	28.8	21.2			

[a] The polarizable continuum solvation model (PCM)[39] was employed to account for solvation effects.

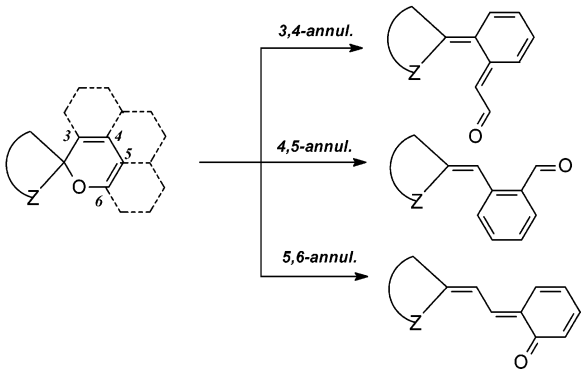
results of the most detailed DFT and ab initio calculations of the relative stability of all ring-opened conformers of the archetypical spirooxazine **23** (1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphth[2,1-*b*][1,4]-oxazine) = **20** (X = N, R = benzo).



The DFT calculations[23] afford reasonable estimates of the relative stability of the ring-closed and ring-opened forms of **23** in the gas phase (that may be correlated with experimental data on the equilibrium shown in Scheme 17 in nonpolar solvents) and in ethanol. Quite satisfactory agreement with the experimental results can be generally achieved also with the aid of semiempirical calculations, as exemplified by the data in Table 2.

The dependence of the relative stability of the ring-closed and ring-opened forms of spiropyrans **1** on the structure of their left half and the type of annulation of the 2*H*-pyran moiety with benzene ring(s) was studied in much detail. Whereas the structure of the heterocycle spiroannulated to the 2*H*-pyran ring does not have a pronounced effect on the position of the equilibrium (Scheme 1) in nonpolar media, it is considerably sensitive to the structure of the right half of molecules **1**. Electron-withdrawing substituents in 2*H*-chromene moieties of spirobenzopyrans favor the stabilization of the ring-opened forms. The maximal effect is attained when strong elcctron-accepting groups, such as nitro or arylazo groups, are placed in the *p*- or/and *o*-position relative to the phenolate oxygen of the merocyanine acquiring the zwitterionic character **2b**. Solutions of these compounds in polar solvents at room temperature contain measurable amounts of the minor ring-opened forms.[40,41] The monocyclic spiropyrans prefer the ring-opened isomeric form.[42] According to the results of the semiempirical calculations,[43] which are in general agreement with the available experimental data,[9a−d] 3,4- and 5,6-benzoannulation (Scheme 18) stabilizes the

Scheme 18



ring-closed form of spirobenzopyrans, whereas 4,5-benzoannulation leads to the opposite effect.

As illustrated by an example of a series of polycondensed 2-oxaindanospirans **24**,[24a] further benzoannullation and naphthoannulation also exert the opposite sign effects on the relative stability of the isomers of spiropyrans. The compounds **24b**−**e** exhibit thermochromic properties due to the narrowing energy gap between their uncolored spirocyclic and colored merocyanine forms compared with the parent compound **24a**. On the other hand, linear benzoannulation enlarges this gap and additionally stabilizes the spirocyclic form **24f**.

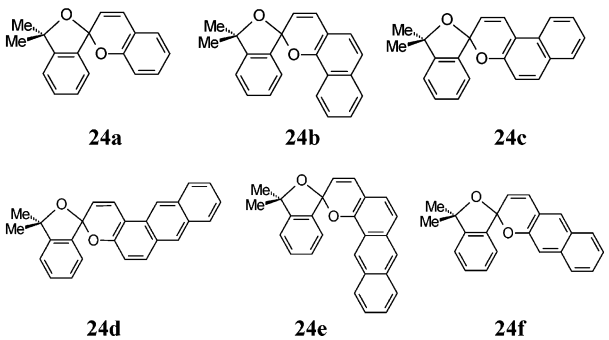


Table 2. MNDO/PM3 Modeling of the Equilibria Shown in Scheme 1[38a]

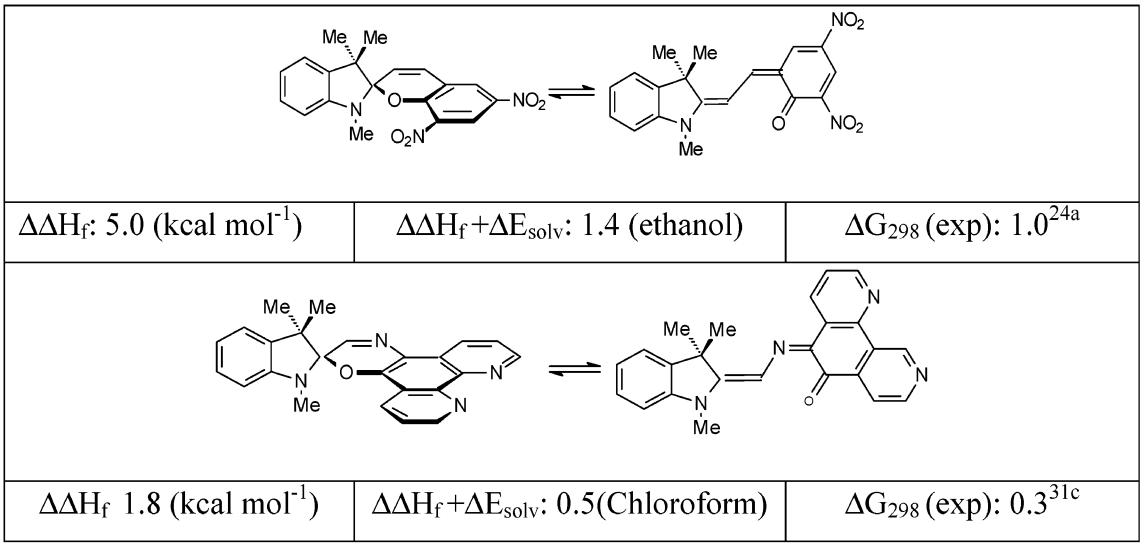
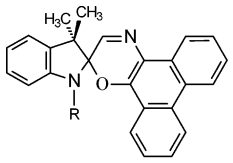


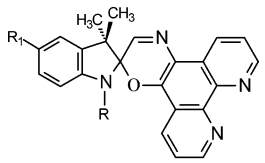
Table 3. Thermodynamical Parameters of the [2]/[1] Equilibria (Scheme 1) in Solutions of Spirooxazines 18 and 25

type	R	R_1	R_2	solvent	K_{25}	$\Delta H°$, kcal/mol	$\Delta S°$, e.u.	ΔG_{25}, kcal/mol	ref
18	CH_3	H	H	toluene	10^{-5}	5.2	−5.0	6.7	44a
				ethanol	10^{-4}	5.0	−1.3	5.4	
18	CH_3	H	6′–N	toluene	6×10^{-4}	4.3	−0.3	4.4	44a
				ethanol	6×10^{-3}	3.6	1.8	3.1	
18	CH_3	H	8′-$COOCH_3$	ethanol	4×10^{-4}	4.9	0.9	4.6	44b
18	CH_3	H	5′,6′-Benzo	toluene	5×10^{-3}	2.3	−2.8	3.1	44a
				ethanol	1×10^{-2}	2.6	−0.2	2.4	
25	CH_3	H	H	toluene	2×10^{-2}	2.9	1.6	3.8	45
				ethanol	8×10^{-2}	2.6	3.6	1.5	
25	CH_3	OC_9H_{19}	H	toluene	8×10^{-2}	2.0	1.6	1.5	45
				ethanol	3×10^{-1}	0.8	0.5	0.7	

In contrast with spiropyrans **1** (X = CH), the thermochromic behavior of which was studied mostly in a qualitatitive manner,[4] detailed information has been accumulated on the thermodynamics of the thermal equilibria determining the thermochromism of spirooxazines **1** (X = CH).[4,9h] An excerpt of these data for two types of spirooxazines is given in Table 3. Solutions of the parent spirooxazine **18** (R_1,R_2 = H) contain almost negligible amounts of the merocyanine isomers, and due to the negative entropic factor their equilibrium concentration decreases with increasing temperature. The content of the colored merocyanine forms increases appreciably in the compounds with phenanthrene (**18**, R_1 = H, R_2 = 5′,6′-benzo)[44c] or phenanthroline (**25**)[31d] rings fused to the oxazine moiety. A similar trend is observed in the compounds containing electron-releasing groups in the indoline part of the molecules.[4,9h,45]



18 (R_1=H, R_2 = 5',6'-C_6H_4)



25

As shown in Scheme 17, the polar merocyanine forms of spiropyrans and spirooxazines tend to associate into stack-like aggregates.[9e,46] This tendency is very strong, and rather stable associates are formed in very diluted solutions and even in polymeric films. Absorption spectra of J-aggregates, which have a parallel (head-to-head) arrangement of the molecular dipoles, are shifted to longer wavelengths relative to the spectra of the isolated merocyanine molecules. For H-aggregates having a head-to-tail arrangement of the molecular dipoles, the spectra are shifted to shorter wavelengths. An important property of the J-aggregates produced by irradiation of solutions of spiropyrans in nonpolar solvents is that their spectra consist of very narrow absorption bands (absorption peak widths are a few tens of nanometers), which is a necessary condition for design of wavelength-multiplexed memory systems.[47a,b] It has been shown that the formation of the spiropyran aggregates causes very large changes in refractive indices and, thus, provides a new approach toward the synthesis of tunable photonic gap materials.[47c]

3.2.2. Solvatochromism

The solvatochromic behavior of spiropyrans and spirooxazines, showing itself as pronounced changes in the position and intensity of their UV−vis absorption bands induced by variation in the polarity of a medium, may be governed by two different mecha-

nisms. The first one is related to the shift of the equilibrium (Scheme 1) when passing from one solvent to another. The manifestation of this mechanism is the redistribution of intensities of absorption bands in the spectrum of a solution containing an equilibrium mixture of the isomers or even an appearance of new bands if only one of the isomers was present in a solution of a certain solvent. Such behavior is shown by spirooxazines **18** and **25**, listed in Table 3, and many other spiropyrans and spirooxazines.[4,9,38] The second mechanism is inherent in the general phenomenon of solvatochromism and is related to differences in solute−solvent interactions in solvents of different polarity. Since solvent effects on absorption spectra are usually studied by measuring the longest-wavelength absorption band shifts, and since these bands in solutions of spiropyrans and spirooxazines belong to their ring-opened forms, determining the origin of these interactions requires an understanding of the structure and polarity of the merocyanines **2**.

Experimental data on dipole moments of spirooxazines **1** (X = N) are unavailable and are rather scarce for spiropyrans **1** (X = CH) and their merocyanine isomers **2**.[48] For two 6-nitro- and two 6,8-dinitro-substituted spiropyrans **11** (R = CH_3, CH_2CH_2COOH; R_1 = 6-NO_2 and 6,8-$(NO_2)_2$), the most accurate electrooptical absorption measurements[48b] gave the values 3.0−4.5 D (10−15 C·m) and 15−18 D (50−60 C·m) for the ground-state dipole moments of the spiro and the merocyanine forms, respectively. Although these high values are in large measure determined by the presence in the molecules of polar nitro groups, they indicate convincingly that the merocyanine isomers are much more polarized than the ring-closed forms. This conclusion is corroborated by quantum mechanical calculations at various levels of approximation.[4,22c,23,48b] According to the ab initio calculations,[23a] the most stable merocyanine isomers of the parent spironaphthoxazine **23 TTC** and **CTC** possess much larger dipole moments (3.6 and 4.3 D, respectively) than the ring-closed form **23 SP** (0.6 D). The same tendency is characteristic of all principal types of spirooxazines and spiropyrans. This explains the significant stabilization of the merocyanine isomers in polar media predicted by calculations and observed experimentally.[9a,b,d−g] This effect is generally discussed in terms of the balance between the quinoidal **2a** and zwitterionic **2b** resonance forms, which is estimated on the basis of the trends in solvatochromic behavior. Positive solvatochromism (i.e., bathochromic shift of the longest wavelength of the UV−vis spectrum with increase in the polarity of a solvent[5a]) observed for a limited set of spirooxazines led to the widely accepted conclusion on the predominantly quinoidal structure of merocyanines (X = N).[33b,36e,44a,49] It has been shown, however, that the electronic structure of the merocyanines—derivatives of **23**—is extremely sensitive to the influence of substituents in both indoline and naphthalene rings of these compounds. By varying the acceptor or donor properties and the position of the substituents, it is possible to polarize the π-system of the ring-opened form sufficiently to reach a zwitterionic-like structure **2b** and observe negative solvatochromism in the *push*−*pull*-type compounds containing electron-releasing groups in the indoline and electron-withdrawing ones in the naphthalene moieties of **18**.[31f,50] A good linear relationship was found between the wavenumber of the absorption maximum of the ring-opened forms of these compounds versus χ_B (blue shift), Brooker's solvatochromic parameter.[51] Negative solvatochromism, well correlated with Reichardt−Dimroth's $E_T(30)$ parameters,[5] was also observed for the open forms of indolinospiropyrans with a 6-nitro group in the 2*H*-chromene ring.[38b] These results imply that the ground-state merocyanine structures of the considered spirooxazines and spiropyrans are better solvated than their first electron excited states and the ground-state dipole moments are larger than those of the excited states. The latter conclusion has been confirmed by the electrooptical absorption measurements[48b] of the dipole moments of the merocyanine forms of spiropyrans **11** (R = CH_3, CH_2CH_2C OOH; R_1 = 6-NO_2 and 6,8-$(NO_2)_2$) in the first singlet excited state. It was found that, with the excitation, the dipole moments of the merocyanines decrease by about 3.3−6.6 D.

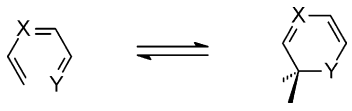
For the parent spirooxazine **23** = **18** (R_1,R_2 = H), the DFT-computed geometry[23b] is averaged between the quinoidal and zwitterionic formulas: the calculated C=C, C−N, and N=C bond lengths in the −C=C−N=C triad of **23CTC** (1.378, 1.372, and 1.262 Å, respectively) and the C=O bond length (1.262 Å) are of intermediate value between those for normal single and double bonds.

In the spiropyran series, crystals of several merocyanine isomers **2** (X = CH) have been preparatively isolated from ethanol solutions by recrystallization under UV irradiation, and their molecular structures have been determined by X-ray.[22a,b] As for indolinospirooxazines, the most stable isomeric form of the indolinospiropyran merocyanines is represented by the **TTC** conformation. The principal structural parameters of these compounds are listed in Table 4. The C_2-C_3 bond lengths in **MC1**−**MC5** are very close to the value characteristic of a standard double CC bond (1.34 Å), which points to a significant contribution of the zwitterionic form to the resonance hybrid, additionally enhanced by the presence of strongly electron-withdrawing substituents in the phenolate moiety of the merocyanines.

3.2.3. Kinetics and Mechanism

The principal reaction that governs the interconversion of valence isomers of spiropyrans and spirooxazines, shown in Scheme 1, is the archetypal reversible electrocyclization (Scheme 19), which is the basic

Scheme 19



rearrangement defining the mechanisms of thermochromic and photochromic behavior of fulgides and diarylethenes (X = CR, Y= CR_1R_2), spiropyrans (X = CR, Y = O), and spirooxazines (X = N, Y = O).

Because of this, the mechanism of the model rearrangement given by Scheme 19 was studied theoretically in much detail with the use of semiempirical[18a,b,52] and ab initio[18c] methods of quantum chemistry. The principal results of these calculations—a disrotatory-like reaction path at the rate-determining stage of cleavage of the C−O bond (X = O) and a two-step mechanism with the involvement of a cisoid ring-opened form (modeling by **21** in Scheme 17)—were in general reproduced by semiempirical calculations of the reaction paths for thermal rearrangements of indolinospiropyrans[38b,53] and spirooxazines.[4]

Recent DFT calculations[23] of the thermal ring-opening reactions of 1,3,3-trimethylspiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazine] **23** and its 2,2′-[2*H*]-naphtho[1,2-*b*] isomer elucidated details of the reaction path and energy profile of these transformations. The principal results are pictured in Figure 2. The reac-

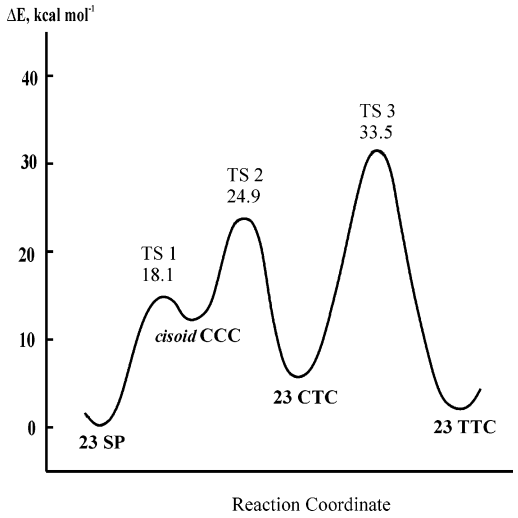
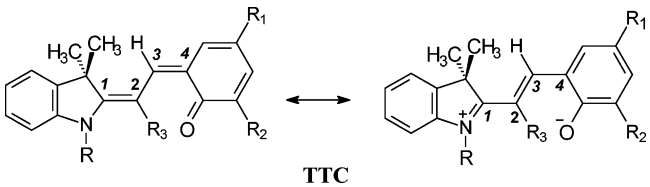


Figure 2. Ground-state adiabatic potential energy profile (gas phase) for the ring-opening/ring-closing reaction of spirooxazine **23** according to the results of B3LYP/6-31G** calculations.[23a]

tion starts with stretching and cleavage of the C−O spiro bond to give rise to the *cisoid* intermediate shown in Scheme 17 as **21** (R = 5,6-benzo). Subsequent rotation around the C−X (X = N) bond leads to the merocyanine isomer **23CTC** (**22b**, X = N, R = benzo in Scheme 17), which undergoes *Z*/*E* isomerization by rotation around the C=C bond with the formation of the most stable isomer **23TTC** (**22c**, X = N, R = 5,6-benzo in Scheme 17). Less energy favorable merocyanine isomers **23CTT** and **23TTT** (**22a** and **22d**, R = 5,6-benzo in Scheme 17) arising from inversion of the imine nitrogen of **21** and combination of the processes of nitrogen inversion and rotation about the C=C bond in **22b** (**23CTC**), correspondingly, lie outside the minimal energy reaction path for the ring-opening reaction. The kinetics of the back-ring-closing reaction of spiropyrans and spirooxazines is generally studied as the relaxation kinetics of merocyanine forms induced upon irradiation of a solution of the spirocyclic isomers.[33b,34,54] Under these conditions, the initial mixture of the formed merocyanine isomers contains minor ring-opened forms of the latter. For **23**, it was assumed that irradiation of its methylcyclohexane or toluene solutions gives rise to two merocyanine isomers corresponding to the **CTC** and **CTT** forms.[54b] The experimental activation energies of the first-order decay of these species, respectively 15.5 and 18.6 kcal mol^{-1} in methylcyclohexane and 14.8 and 16.5 kcal mol^{-1} in toluene, are in reasonable agreement with the computational results when account was taken for solvation energy.[23]

The kinetics of the ring-opening reactions of spiropyrans and spirooxazines has been studied using two principal approaches. The first one employs dynamic NMR spectroscopy and is applied to the compounds containing diastereotopic groups, as in the case of indolinospiropyrans **11** and spiropyrans **13a**,**b**. Another approach is based on the preparative separation or enrichment of the enantiomers of **1** and direct determination of the rate constants of thermal racemization. Resolution of spiropyrans of several types, **11**, **13a**, and **14**, as well as spirooxazines **20** (X = N), with the use of chiral-phase HPLC on microcrystalline triacetyl- and tribenzoylcellulose has been accomplished for the first time by Mannschreck and coworkers,[30,55] who measured energy barriers to the ring opening by polarimetry and off-line or on-line circular dichroism (CD). The most representative data on the energy barriers of ring-opening reactions obtained with the use of NMR and chiroptical methods are collected in Tables 5−7. In general, the

Table 4. Structural Parameters of the Merocyanine Isomers of Indolinospirobenzopyrans According to the X-ray Determinations[22a,b]



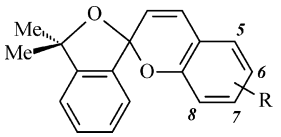
	merocyanine				
	MC1[a]	**MC2**	**MC3**	**MC4**[b]	**MC5**
R	CH_3	C_5H_{11}	$C_6H_4CH_3$-*p*	H	CH_2CH_2OH
R_1	NO_2	NO_2	NO_2	NO_2	NO_2
R_2	Br	Br	NO_2	NO_2	OCH_3
R_3	H	H	H	CH_3	H
C_1−C_2, Å	1.420	1.419	1.439	1.443	1.403
C_2−C_3, Å	1.345	1.357	1.375	1.353	1.366
C_3−C_2, Å	1.486	1.446	1.434	1.443	1.444
C=O, Å	1.258	1.228	1.282	1.269	1.253

[a] In the crystals isolated from ethanol, **MC1** molecules are 1:1 solvated with water molecules with the formation of HOH···O=C− hydrogen bonds. [b] **MC4** molecule adopts in crystal **CTC** conformation.

barrier of re-formation of the C−O spiro bond is lower than that of the rotation to more stable *trans* isomers of the ring-opened forms **22** (see Figure 2 as an example). Therefore, the $\Delta G^{\ddagger}$ values in Tables 5−7 correspond to the C−O bond-cleavage step **20** → **21** (Scheme 17).

Although not fully systematic, the data presented in Tables 5−7 provide for certain conclusions about relationships between the structure of the spiroheterocyclics **1** and their readiness to the valence

Table 5. Free Energy Barriers to the Thermal Ring-Opening Reaction of Derivatives of 3,3-Dimethylspiro[3*H*-benzopyran-3,1′-[2]oxaindan] 13a

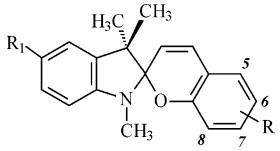


no.	R	method	solvent	$\Delta G_{25}^{\ddagger}$, kcal mol^{-1}	ref
1	5,6-benzo	NMR	C_4Cl_6[a]	19.7	18b
			$C_6H_5NO_2$	19.5	
2	7,8-benzo	NMR	C_4Cl_6[a]	20.2	18b
			$C_6H_5NO_2$	21.3	
3	5,6-benzo-8-OH	NMR	C_4Cl_6[a]	19.6	24
			C_6H_5CN	18.8	
4	5,6-benzo-6-Br	NMR	C_4Cl_6[a]	22.5	24
5	5,6-benzo-6-NO_2	NMR	C_4Cl_6[a]	21.3	24
6	H	polarimetry	diglyme	25.7[b]	55a
7	6-Cl	polarimetry	diglyme	28.0[b]	55a
8	6-OCH_3	polarimetry	diglyme	25.9[b]	55a

[a] Hexachlorobutadiene. [b] At 74 °C.

isomerization presented in Scheme 1. From comparison of spirobenzoxazines (nos. 6 and 7 in Table 7) with spirobenzopyrans (nos. 6 and 16 in Table 6) and spironaphthoxazine (no. 1 in Table 7) with the analogous spironaphthopyran (no. 1 in Table 6), it follows that the replacement of the methine group in **1** by an aza nitrogen increases $\Delta G^{\ddagger}$ by 3−5 kcal mol^{-1}. Whereas structural variation in the "left" half of **1** does not significantly affect energy barriers to the ring opening, benzoannulation in the "right" half substantially decreases the $\Delta G^{\ddagger}$ value (see Table 6 and compounds nos. 1 and 2 in Table 7). The maximal lowering of the energy barrier is achieved in compounds containing two strongly electron-withdrawing groups in the benzopyran ring of **1** (compounds nos. 8, 9, 12, and 13 in Table 6). The effect of solvent polarity on the rate of the ring-opening reaction was studied through thermal racemization of a series of 6-substituted indolinospirobenzopyrans **11**, resolved by chiral stationary-phase HPLC.[57] It was found that the rate of racemization of compounds with electron-withdrawing substituents in the benzopyran ring is much more sensitive to solvent polarity than that of spiropyrans with electron-donating groups. This remarkable contrast was explained as a consequence of operating two competing mechanisms of the reaction: a polar one involving heterolytic C−O bond cleavage with anchimeric assistance from the indoline nitrogen, and a nonpolar electrocyclic ring-opening mechanism. In the polar transition state, negative charge developing on the benzopyran oxygen is stabilized by *para*-positioned electron-withdrawing substituents and by polar solvents. Under these circumstances, the polar mechanism represents the major pathway for the ring-opening reaction. In contrast, nonpolar solvents and electron-donating substituents disfavor charge separation in the transition state, and the nonpolar electrocyclic mechanism appears to be predominant, as is the case with 6-dimethylamino-**11** (R = CH_3), the thermal racemization of which displays a very moderate dependence on solvent polarity.

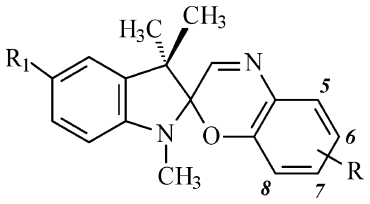
Table 6. Free Energy Barriers to the Thermal Ring-Opening Reaction of Derivatives of Spiro[2*H*-1-benzopyran-2,2′-indoline] 11



no.	R	R_1	method	solvent	$\Delta G_{25}^{\ddagger}$, kcal mol^{-1}	ref
1	5,6-benzo	H	NMR	CCl_4	20.1	56a
				C_6H_5CN	22.6	56b
				C_4Cl_6[a]	20.3	
				$C_6D_5NO_2$	19.5[b]	30
2	6-NO_2	H	NMR	$C_6D_5NO_2$	22.6	56c
				DMSO	21.9	40
				CCl_4	24.4	56a
3	8-NO_2	H	NMR	CCl_4	24.9	56a
4	6-CHO	H	NMR	DMSO	23.7	40
5	6-OCH_3	H	NMR	DMSO	23.9	40
			polarimetry	Hex/Prop[c]	24.4[d]	30
6	7-OCH_3	H	polarimetry	Hex/Prop[c]	22.1[d]	30
7	8-OCH_3	H	NMR	DMSO	23.5	40
				CCl_4	24.2	56a
			polarimetry	Hex/Prop[c]	24.1	30
8	6-NO_2, 8-NO_2	H	NMR	DMSO	<17	40
9	6-NO_2, 8-Br	H	NMR	DMSO	18.1	40
10	6-NO_2, 7-OCH_3	H	NMR	C_6H_5CN	27.6	56c
11	6-CH_3, 8-CHO	H	NMR	$C_6D_5NO_2$	26.8	56c
12	6-$COOCH_3$, 8-NO_2	H	NMR	DMSO	17.7	40
13	6-COOH, 8-NO_2	H	NMR	DMSO	<16	40
14	8-OCH_3	Cl	polarimetry	Hex/Prop[c]	24.5[d]	30
15	6-NO_2	Cl	polarimetry	Hex/Prop[c]	>26[d]	30
16	7-OCH_3	Cl	polarimetry	Hex/Prop[c]	22.4	30

[a] Hexachlorobutadiene. [b] At 108 °C. [c] Hexane/2-propanol, 9:1. [d] At 42.2 °C.

Table 7. Free Energy Barriers to Thermal Ring-Opening Reaction of Derivatives of Spiro[2*H*-1-benzo[1,4]-oxazine-2,3′-indolines] As Obtained from Circular Dichroism Determinations[30]



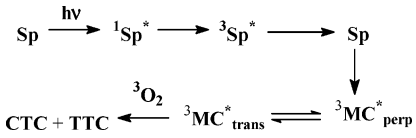
no.	R	R_1	solvent	*T*, °C	$\Delta G^{\ddagger}$, kcal mol^{-1}
1	5,6-benzo (**23**)	H	$C_6D_5NO_2$	108	22.3
2	H	H	EtOH/H_2O, 96:4	64.8	28.3
3	6-Cl	H	EtOH/H_2O, 96:4	66.2	27.7
4	6-CH_3	H	EtOH/H_2O, 96:4	66.1	28.6
5	7-CH_3	H	toluene	75.9	30.3
6	7-OCH_3	H	Hex/Prop[a]	42.0	26.8
7	7-OCH_3	Cl	Hex/Prop[a]	42.0	27.0
8	5,7-$(OCH_3)_2$	H	EtOH/H_2O, 96:4	64.7	24.8

[a] Hexane/2-propanol, 9:1.

3.3. Excited-State Ring-Opening Reaction

The primary step of the photochromic reaction (Scheme 1) of spiropyrans and spirooxazines is the dissociation of a C−O bond in an electronic excited state. The nature of the active excited state depends on substitution in the benzopyran and naphthoxazine rings of compounds **1**. The studies of the reaction dynamics with the use of time-resolved resonance Raman spectroscopy,[33c,58] laser flash photolysis,[59,60] and quenching experiments[61] have shown that, for spiropyrans with a nitro group, a triplet state plays a crucial role in the photochemical ring-opening reaction. The mechanism (Scheme 20) suggested for

Scheme 20



description of the photochemical behavior of a series of indolinobenzopyrans **11** with a nitro group in position 6 and with or without substituents in position 8 involves intersystem crossing to the short-lived triplet state of the ring-closed isomer ^{3}**Sp*** that could not be directly identified by nanosecond laser photolysis. It serves as the precursor to the triplet so-called "perpendicular" merocyanine form $^3\mathbf{MC}^*_{\mathbf{perp}}$ that may be correlated with structure **21** in Scheme 17. The $^3\mathbf{MC}^*_{\mathbf{perp}}$ conformation is in equilibrium with the triplet of the trans isomer, observed as a short-lived transient with absorption maxima at 420−440 and 560−590 nm and a lifetime <10 ms. The reaction ends with quenching the triplet with oxygen and establishing a thermal equilibrium between the most stable merocyanine isomers, presumably **CTC** and **TTC** (Scheme 17). This mechanism is evidenced by the extreme sensitivity of the dynamics to the presence of oxygen in solution and the identity of the quantum yields of population of the merocyanine triplet state and the overall process of a spiropyran-to-merocyanine photoconversion.[60,62a−d] The triplet states also take an active part in the photochemistry of nitro-substituted spirooxazines.[62e]

A nitro group in spiropyrans has a dual effect on their photochromic capacity. On one hand, it strongly enhances the quantum yield of the photocoloration (up to 0.7−0.9 in solvents of low polarity[60,62c]), and on the other hand, it also enhances the quantum yield of the intersystem crossing, which facilitates formation of singlet molecular oxygen $O_2(^1\Delta_g)$ from the triplet excited state ^{3}**MC*** and, thus, photodegradation of spiropyrans via oxidation by singlet oxygen. The adverse influence of the inclusion of highly reactive triplet states (both ^{3}**Sp*** and ^{3}**MC***) of spiropyrans into the mechanism of the ring opening on their fatigue resistance properties has been recognized by many authors.[9b,61,63,64] It was found that the quantum yields of irreversible photodegradation of various spiropyrans are virtually independent of the nature of their "left-half" heterocyclic moiety and are directly correlated with the lifetime of the triplet-state intermediate formed upon excitation.[63]

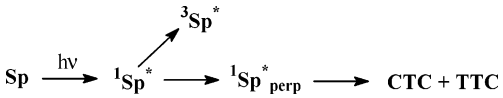
For spiropyrans without nitro groups in the benzopyran rings, the quantum yields of the phocoloration are essentially independent of solvent polarity and are substantially (on average, by half[32,60,62,65]) lower than those for spiropyrans with nitro groups (Table 8). In contrast to the latter, spiropyrans

Table 8. Quantum Yields of Photocoloration of Indolinospiropyrans 11[62d]

no.	R_1	toluene	acetonitrile	ethanol
1	H	0.16	0.12	0.18
2	8-OCH_3	0.06	0.06	0.07
3	6-OCH_3	0.08	0.07	
4	6-Br	0.10	0.06	0.06
5	6,8-Br_2	0.07	0.08	0.07
6	5,6-benzo	0.22	0.25	0.25

without nitro groups display photochromism only in the excited singlet manifold. The mechanism of the photochemical process is represented relatively simply in Scheme 21,[62d] where the structure of the singlet

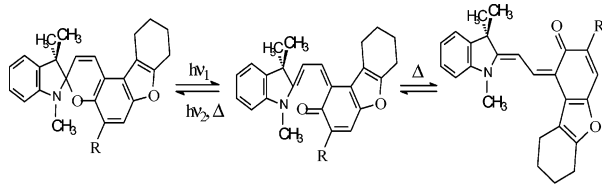
Scheme 21



excited-state intermediate $^1\mathbf{Sp}^*_{\mathbf{perp}}$ corresponds to that formed upon immediate cleavage of the C_{spiro}−O bond and is, therefore, close to **21** in Scheme 17. According to the CASSCF modeling of this process,[18e] the structure similar to $^1\mathbf{Sp}^*_{\mathbf{perp}}$ in Scheme 21 does not conform to a real intermediate but rather a crossing point, i.e., a conical intersection between the lowest singlet excited-state and ground-state energy surfaces. At this point, two reaction valleys are generated, one of which leads to ring closing to the initial spirocyclic form and the other one to the formation of the *cis*-cisoid (**CCC**) ring-opened form, to be compared with **21**. The existence of this intermediate, usually called the X-form, was first proposed[7c] on the basis of the studies of the photochemistry of spiropyrans in low-temperature matrices.

Recently, the formation of a long-lived *cis*-cisoid isomer was observed in the course of the study of the photochromic behavior of spiropyrans **26a** (Scheme 22).[66a] In contrast with the spectral behavior of the

Scheme 22



26a **26** **26b**

R = H, Br, NO_2, *t*-Bu

compounds **26a** (R = H, Br, NO_2; Figure 3a), similar to that of the majority of spiropyrans **11**, UV irradiation (365 nm) of an isopentane/2-propanol solution of **26a** (R = *t*-Bu) at 77 K leads to a spectral pattern characterized by a longest-wavelength absorption band at 471 nm (Figure 3b). Heating the solution to 178 K or prolonged irradiation at 77 K transforms the spectrum to that shown in Figure 3c, with the

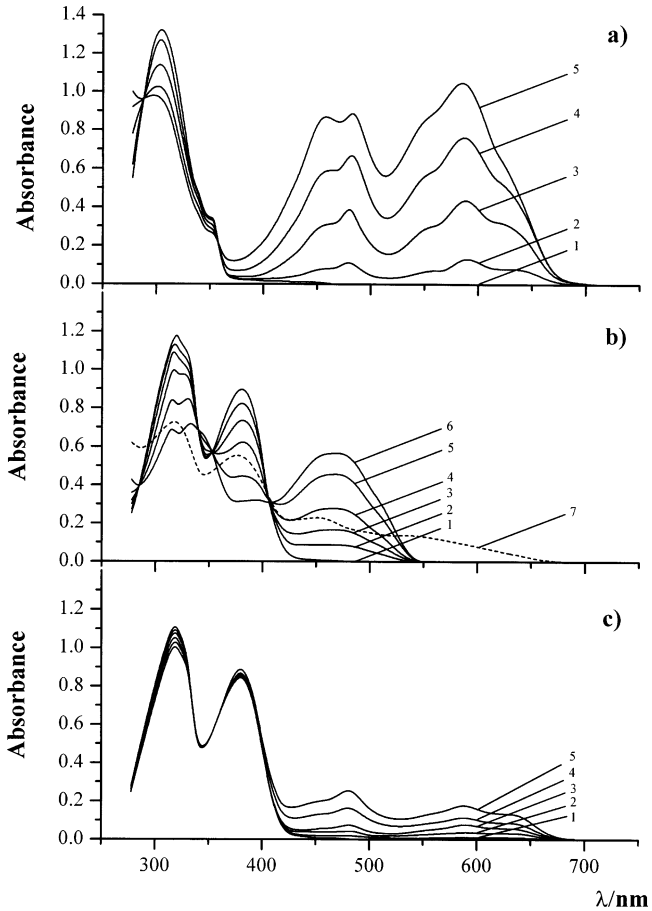


Figure 3. UV−vis spectra of isopentane/2-propanol (4:1) solutions of (a) spiropyran **26a** (R = Br) at 77 K [before (1) and after irradiation with the light (313 nm) of a mercury lamp for 60 (2), 180 (3), 360 (4), and 630 (5) min], (b) spiropyran **26a** (R = *t*-Bu) at 77 K [before (1) and after irradiation with the light (365 nm) of a mercury lamp for 3 (2), 8 (3), 18 (4), 80 (5), and 160 (6) min and (7) subsequent irradiation with the nonfiltered light for 30 min], and (c) spiropyran **26a** (R = *t*-Bu) at 178 K [before (1) and after irradiation with the light (365 nm) of a mercury lamp for 10(2), 25(3), 45 (4), and 80 (5) min].[66a]

585−625 nm longest-wavelength absorption bands typical of *trans*-merocyanines **2**. It was concluded that, in spiropyrans **26a** (R = *t*-Bu), a bulky *tert*-butyl group significantly hinders the **26** → **26b** conformational rearrangement in viscous media. The relaxation time of **26** in ethanol solution reaches 66 s at room temperature.

Low-temperature absorption spectroscopy has been also used in the studies[66b] of a nonplanar intermediate photoproduct **X** formed on UV irradiation of polystyrene films of spironaphthoxazine **18** (R = CH_3, R_1 = R_2 = H). At the temperatures higher than 25 K, **X** was found to undergo both the thermal bleaching reaction to the ring-closed form and the thermal transformation to give not less than three merocyanine isomers.

The solution dynamics of the photochromic reaction of a series of indolinospirobenzopyrans and indolinospironaphthopyrans were studied with picosecond and femtosecond transient electronic absorption spectroscopy.[53,59d−h,67] The first work in this series,[59a] performed at picosecond time resolution, demonstrated that the colored ring-opened photoisomers of spiropyrans arose as soon as 15 ps after an exciting pulse. Of three characteristic times revealed in the kinetics of absorption formation and disappearance for indolinospironaphthoxazines **11** under excitation at 370 nm (150 fs), those in the ranges of 50−100 ps and 1.3−1.7 ns were assigned to the relaxation of the *cis*-cisoid isomers to various possible merocyanine forms.[69] The initial step of this reaction, associated with fission of the C_{spiro}−O bond, is even faster. For the 6-hydroxy derivative of indolinospirobenzopyran **11** (R = CH_3, R_1 = 6-OH), it takes less than 100 fs after excitation at 300 nm to form a metastable species **X**,[67] for which an acoplanar *cis*-cisoid structure, corresponding to **21** (X = CH, R = 6-OH) in Scheme 17, was assigned in accordance with the assumptions based on nano- and picosecond spectroscopic data.[59a,e,68] A minor fraction of **X** re-establishes the broken bond on the time scale of 200 fs, whereas the rest of the formed metastable species vibrationally relaxes in a few picoseconds and after this vibrational cooling converts to a mixture of merocyanine conformers with a decay time constant of about 100 ps. The principal scheme of the photochemical reaction described above is illustrated by Figure 4.

A similar mechanism was found to operate in the photochemical ring-opening reaction of spirooxazines. As shown by transient absorption spectroscopy experiments carried out at picosecond[33a,69] and femtosecond[33b,70] temporal resolution, the formation of the colored merocyanine isomers of spiroindolinonaphthoxazines **18** occurs entirely from the excited singlet state. This observation is also true for other spirooxazines **19**, and the uninvolvement of the triplet states of spirooxazines in the principal photochemical reaction well explains the high fatigue resistance of compounds of this class. The rate constants for C−O bond cleavage and subsequent relaxation to a metastable merocyanine in 1-butanol solution were estimated to be approximately 700 and 470 fs, respectively.[70a] The final relaxation to the stable merocyanine, presumably **23TTC**, is completed in a few

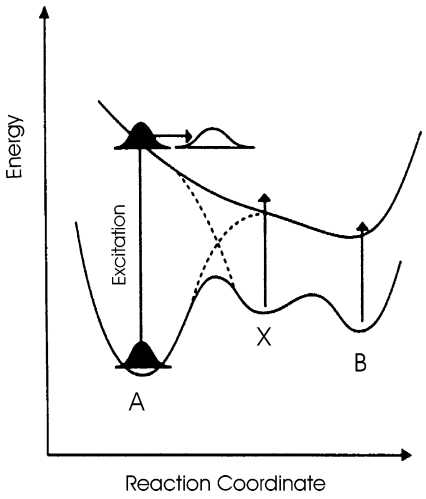


Figure 4. Schematic illustration of the photochemical reaction (Scheme 1) of a spiropyran in a wave packet picture according to the data.[67] The adiabatic surfaces are represented by the solid curves, and the dashed lines indicate the diabatic surfaces. **A** and **B** correspond to ring-closed and ring-opened (*trans*-merocyanine) isomeric forms, and **X** refers to the initial (presumably *cis*-cisoid) product formed after the C−O bond is broken. The reaction coordinate is considered as a combination of C−O stretching and rotation around a C−C bond of the molecule.

hundred picoseconds. No agreement is achieved as to the nature of the transient absorption with a peak around 490 nm that appears just after excitation (in less than 2 ps), ascribed to either the nonplanar *cis*-cisoid photoproduct **X**[33c,69] (to be compared with **21** (X = N, R = 5,6-benzo) in Scheme 17) or the $S_n \leftarrow S_1$ absorption spectrum of **23Sp**.[70]

The fast kinetics of the ring-opening reaction of spirooxazines favors the efficiency of their photocoloration, which is one of the most important requirements imposed upon the photochromic compounds with a potential for application to the photonic devices. Among other important parameters of the photochromic process are sufficiently high quantum yields of the photoreaction, which are generally in the range of 0.2−0.8,[9f,g,h,34,71] and thermal stability of the photocolored form, as assessed by the energy barrier to the back dark reaction. Whereas the photochemistry and mechanism of the ring-opening reactions of spiropyrans and spirooxazines are now amply studied and relatively well understood, the reverse photoinitiated ring-closing reaction of the colored merocyanine isomeric forms of these compounds has not yet been adequately explored. The ultrafast ring-closure kinetics of the merocyanines formed from two 6,8-dinitrosubstituted spiropyrans **11** (R = CH_3, CH_2CH_2COOH) has been studied in acetonitrile solution under photoexcitation with 390 nm light.[25c] It was concluded that the first singlet excited state of the merocyanines, formed from the higher-energy states for about 500 fs, partitioned between the recovery of the ground state and the formation of the corresponding spiro isomers via intermediates *cis* or twisted about the central CC bond and, thus, similar to **21** (X=CH) in Scheme 21). The singlet manifold was found to be predominant, and no evidence for triplet-state transients was presented.

In practice, it is not always easy to get all the necessary parameters of a photochromic system through direct experimental determination at uniform conditions. Micheau and co-workers[72] developed a useful photokinetic method for investigation into thermal and photochemical processes that is based on monitoring the absorbance vs time kinetic curves recorded under continuous monochromatic irradiation, followed by analysis within the framework of an appropriate mathematical model of a system of differential equations. The model includes consideration of all photochemical and thermal direct and back reactions involved in the photochromic transformation (eq 1). A solution of the differential equation system enables one to obtain the direct and reverse quantum yields of photocoloration and photobleaching and the spectral, kinetic, and thermodynamic parameters of a photochromic reaction. The reliability of the photokinetic method was tested against direct experimental determinations of these parameters on a number of diverse photochromic systems. Some of the results of application of the photokinetic method for calculating activation energies and quantum yields for two groups of spirooxazines, **18** and **25**, are given in Table 9. As can be seen

Table 9. Quantum Yields of Photocoloration (Φ_{AB}) and Photobleaching (Φ_{BA}) and Activation Energies (E^a_{25}) of the Thermal Back Reaction of Spirooxazines 18 (R = CH_3, R_1 = H) and 25, Determined with the Use of the Photokinetic Method[45,50a]

no.	spirooxazine	solvent	Φ_{AB}	Φ_{BA}	E^a_{25}, kcal mol^{-1}
1	**18**, R_2 = 5′-NO_2	toluene	0.616	0.016	19.1
		methanol			16.0[a]
2	**18**, R_2 = 5′-OCH_3,	toluene	0.106	0.016	22.8
	6′-CN	methanol	0.054	0.024	23.0
3	**18**, R_2 = 5′-OCH_3,	toluene	0.584	0.014	22.3
	8′-NO_2	methanol	0.347	0.037	23.2
4	**18**, R_2 = 6′-NC_5H_{10}	toluene	0.477	0.004	18.3
		methanol			22.1
5	**18**, R_2 = 6′-CN	toluene	0.171	0.011	23.2
		methanol	0.110	0.027	20.6
6	**18**, R_2 = 8′-NO_2	toluene	0.584	0.014	22.3
		methanol	0.347	0.037	23.2
7	**18**, R_2 = 9′-OCH_3	toluene	0.356	0.012	16.5
		methanol	0.345	0.013	20.4
8	**25**, R = CH_3,	toluene	0.26	0.005	
	R_1 = H	methanol	0.24	0.022	18.5[b]
9	**25**, R = $C_{16}H_{33}$,	toluene	0.25	0.002	
	R_1 = H	methanol	0.24	0.015	18.8[b]
10	**25**, R = CH_3,	toluene	0.18	0.002	16.8[b]
	R_1 = 5-$OC_{16}H_{33}$	methanol	0.09	0.030	27.2[b]

[a] In acetonitrile. [b] At 23 °C.

from the data presented, the quantum yields Φ_{AB} of the direct photoreaction are substantially larger than those (Φ_{BA}) of the reverse photochemical process. However, the occurrence of the latter cannot be ignored, and photochromic systems should be considered in photostationary states. Quantum yields of the photocoloration reaction (Φ_{AB}) decrease when the naphthoxazine fragment of **18** contains electron-withdrawing substituents in the 6′-position. The same tendency is observed when going from compounds **18** to **25**. The dependences of the quantum yields of the direct (Φ_{AB}) and back (Φ_{BA}) photoreaction on the nature of the solvent are opposite in

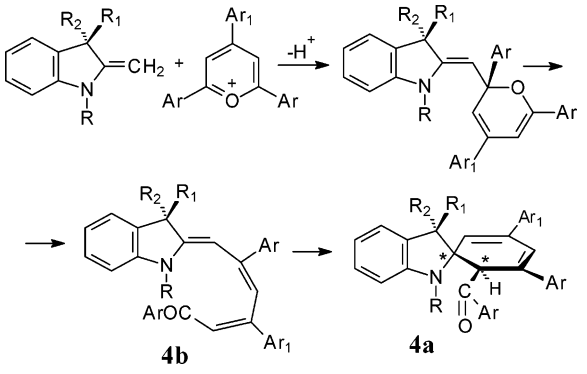
character: the former values are lower in polar solvents, whereas the latter ones become higher in polar solvents and alcohols.[45,50a]

For many applications related to the phenomenon of photochromism, it is important to have compounds that show photochromic properties in the solid state or in crystals, which helps to increase the lifetime of the photogenerated merocyanine isomeric form by retarding the dark back reaction and hindering the photodegradation pathways. Reversible photochromism was observed in amorphous and microcrystalline vacuum-deposited thin solid films of a number of indolinospiropyrans **11** containing electron-withdrawing groups (NO_2, CHO, $COOCH_3$) in positions 6 and/or 8 of the benzopyran moieties[73] and *N*-methylated spiroquinoxazine **18** (in which the $^+$-NMe group stands for CH in position 7′).[74] Another way to enhance the stability of the colored merocyanine isomers involves the inclusion of spiropyrans and spirooxazines into host polymer matrices,[9a,e,f,g] sol−gels,[75] clays,[76] zeolites,[77] complexes with cyclodextrins,[78] and self-assembled monolayers.[79] Significant increases in the lifetimes of the merocyanines may also be achieved through complexation of the photo- or thermally induced polar merocyanine forms with metal cations.[80] The complexation reactions of photochromic spiropyrans and spirooxazines have been successfully employed in the development of a new family of photodynamic chemosensors for metals ions.[81,82]

4. Spiro(cyclohexadiene-indolines)

A novel class of photochromic spiroindolines, the 6-aroyl-3,5-diarylspiro(cyclohexa-2,4-diene-1,2′-indolines) **4**,[10,83] were synthesized by the condensation of 2,4,6-triarylpyrilium salts with 2-methyleneindolines generated in situ from the corresponding 3*H*-indolium salts. The intermediately formed 2*H*-pyrans undergo the ring-opening reaction to their valence isomers **4b**, which recyclize to give spiro(cyclohexadieneindolines) **4a**. The reaction shown in Scheme 23

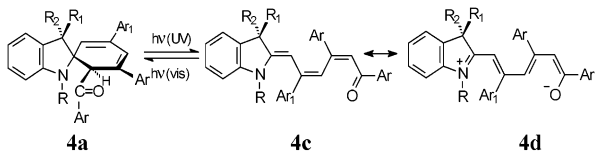
Scheme 23



proceeds smoothly when refluxing ethanol or 1-butanol solutions of the components for about 2 h. An interesting feature of this transformation is its high diastereoselectivity. Although two asymmetric carbon atoms (marked in the scheme by asterisks) are created in the course of the reaction with 1,3,3-trimethyl-2-methyleneindoline ($R_1 = R_2 = CH_3$), and hence two diastereomers of **4a** may be formed, only the isomers with trans configuration of the bulkier substituents (ArCO and CMe_2) at the C_1 (spirocarbon) and C_6 stereocenters were obtained.[83a] The stereochemistry of the transformation products is not affected by the substituents in the aryl ring Ar_1 of **4**.

The photochromism of spiro(cyclohexadieneindolines) **4a** was studied using UV and visible stationary photolysis and laser flash photolysis.[10b,84] Under UV irradiation, the light yellow ($\lambda_{max} \approx 410$ nm) solutions of **4a** convert to red color ($\lambda_{max} \approx 500$ nm) due to formation of the merocyanines **4c** ↔ **4d**, which are vinylogues of the merocyanines **2**. The important feature of the photochromic system shown in Scheme 24 is the very high thermal stability of the colored

Scheme 24



merocyanine form. The thermal back reaction is a very slow process, taking several days at room temperature, and is observed only in a polyethylene matrix. The back recyclization is induced photochemically by irradiating the merocyanines with visible light. The quantum yields of the photorearrangement and the absorption spectra are dependent on solvent polarity. In nonpolar solvents, the photoisomerization (Scheme 24) proceeds via the first excited singlet states of the spiro compounds and merocyanines, respectively. In the polar acetonitrile, a triplet state of the spiroindoline **4a** ($R = R_1 = R_2 = CH_3$, $Ar = Ar_1 = Ph$) was observed, while photocoloration occurs with substantially lower quantum yields than in nonpolar cyclohexane.

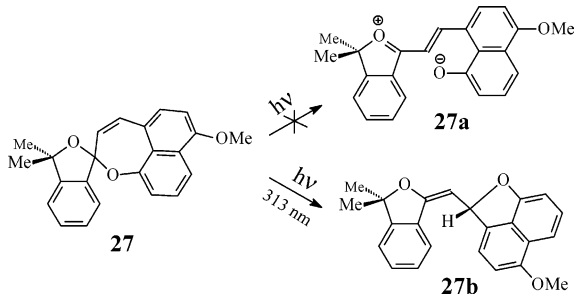
Both the ring-closed and ring-opened forms of the spiro(cyclohexadieneindolines) display fluorescence, which is very important for application of photochromic compounds in optical switching and memory devices.[1d,e,85] However, relatively low quantum yields for the forward (0.02−0.15) and the back (0.02−0.2) photoreactions and the occurrence of fast decomposition reactions competing with the recyclization (in liquid solutions, not more than three switching cycles can be detected) restrict the technical utility of this photochromic system.

5. Spirooxepines and Spirooxocines

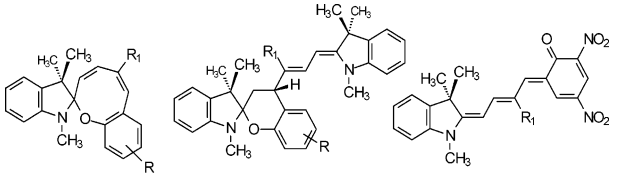
In the search for spiropyrans whose open forms absorb in the near-infrared spectral region that makes possible adoption of the commercially available diode lasers (GaAlAs, InP) for optical recording and retrieval, attempts were undertaken to prepare larger size spirocyclics potentially capable of valence isomerization similar to that shown in Scheme 1. Although the expectations that the compounds of this type may show photo- or thermochromic behavior and possess the desired spectral properties have not been justified, it seems appropriate to consider briefly some efforts in this direction.

A significant long-wavelength absorption was predicted by CNDO/S and PPP calculations for the ring-opened isomers of spirooxepines, seven-membered ring analogues of spiropyrans.[9c,43] The first representative of these compounds, 3,3′-dimethyl-7-methoxyspiro[2*H*-naphtho[1,8-*bc*]oxepin-2,1′-(2)-oxaindan] **27**, was synthesized by the condensation of 1,3,3-trimethylbenzofurylium perchlorate with 4-methoxy-8-hydroxy-1-naphthaldehyde and its photoinduced rearrangement investigated.[86] It was found that, under conditions of steady-state UV illumination, photocleavage of the C−O bond in **27** affords not the betaine **27a** (calculated $\lambda_{max} \approx 1500$ nm) but the yellowish naphtho[1,8-*bc*]furan isomer **27b** (Scheme 25).

Scheme 25



In attempts to obtain spiro-2*H*-oxocines **28**, Fischer's base was allowed to react with 2-hydroxycinnamaldehyde, but the reaction resulted in the products (**28a**) of condensation of two molecules of the methylene base with a molecule of the aldehyde.[87] With 3,5-dinitrocinnamaldehyde, the black crystalline open form **28b** was formed in a moderate yield, but it could not be rearranged to the corresponding spirocyclic isomer **28**.



28 **28a** **28b**

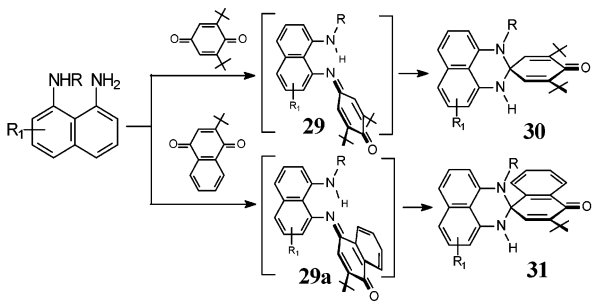
R = 5-Br, 5-NO_2, 3,5-Br_2, 3-Br, 5-NO_2, 3,5-$(NO_2)_2$; R_1 = H, C_2H_5

6. Perimidinespirocyclohexadienones

This new group of photo-, thermo-, and electrochromic compounds was first described in 1988.[88a]

While no heterocyclization occurs in the reaction of *o*-phenylenediamines and *o*-aminophenols with *p*-quinones, which stops at the stage of formation of quinoneimines, with 1,8-naphthylenediamines the reaction leads to derivatives of the spirocyclic system **5** (Y = CH).[11,88] With 2,6-di-*tert*-butyl-1,4-benzoquinone, the reaction proceeds smoothly under noncatalytic conditions when refluxing 1-propanol or toluene solutions of the components to give 2,3-dihydro-2-spiro-4′-[2′,6′-di-*tert*-butylcyclohexadien-2′,5′-one]perimidines **30** in 40−70% yield. By contrast, catalysis with strong proton acids is necessary when 2,6-di-*tert*-butyl-1,4-benzoquinone is replaced

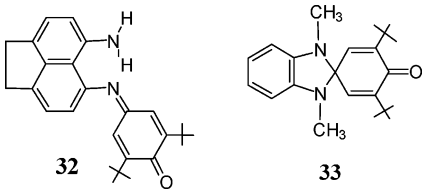
Scheme 26



R = H, Alk; R_1 = H, 4-CH_3, 4,5-(-CH_2 CH_2-), 5-Br, 7-Br, 2,5,7-Br_3

in this reaction by 2-*tert*-butyl-1,4-naphthoquinone (Scheme 26).

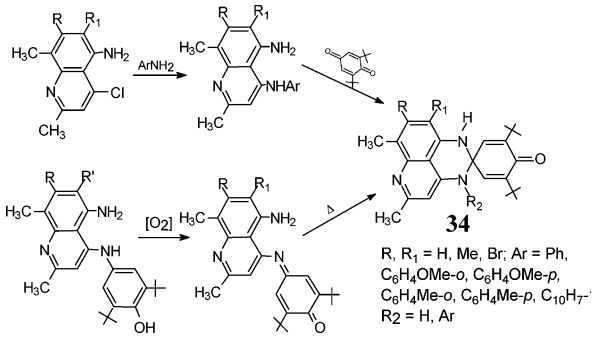
The different courses of the reactions of *o*-phenylenediamines and 1,8-diaminonaphthalenes with *p*-quinones cannot be assigned to different terms for the thermodynamic control. As shown by semiempirical MNDO/PM3 calculations,[11] the spirocyclic isomers are energy-preferable forms for the products of the condensation of various vicinal diamines with *p*-quinones. The cyclization step is definitely kinetically controlled. Even tiny structural variations strongly affect the result of the condensation reaction. Thus, when 5,6-diaminoacenaphthene was coupled with 2,6-di-*tert*-butyl-1,4-benzoquinone under the same conditions at which 1,8-diaminonaphthalenes afford spirans **30**, the only product of the reaction was the ring-opened tautomer **32**.[89] At the same time, condensation of this quinone with *N*,*N*′-dimethylphenylenediamine gives rise to the spiran **33**, which is photochemically inert.



32 **33**

Two methods have been developed for the preparation of derivatives of 2,3-dihydro-2-spiro-4′-(2,6-di-*tert*-butylcyclohexa-2′,5′-dien-1′-one)pyrido[4,3,2-*d*,*e*]-quinazoline **34**—another heterocyclic system congeneric to **30**. Both the approaches shown in Scheme 27[90] employ as the starting material 4-chloro-5-

Scheme 27



aminoquinolines that are susceptible to ready nucleophilic substitution of the chlorine atom by an arylamino group.

When UV-irradiated, an octane solution of **30** (R = H, Alk) changes its color from yellowish to deep blue due to the appearance of a long-wavelength absorption band ($\lambda_{max} \cong 600$ nm) assigned to the ring-opened isomer **29 (**Figure 5). Upon extinguishing UV

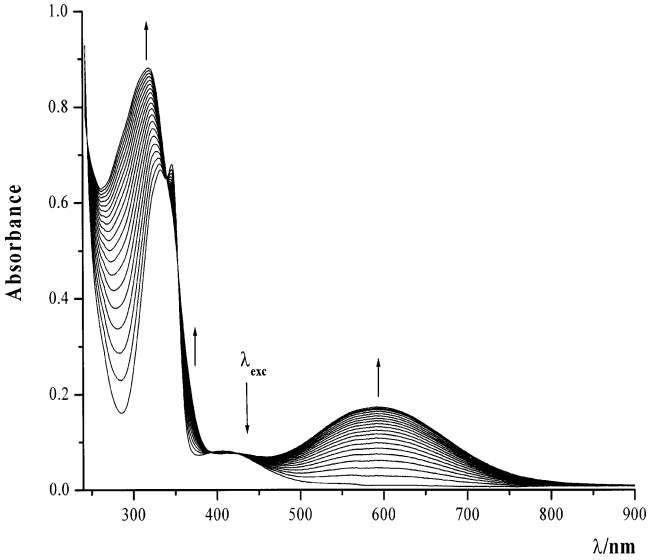
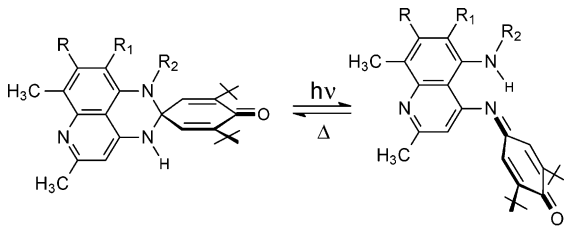


Figure 5. Changes in the UV−vis absorption spectrum of a perimidinespirocyclohexadienone **30** (R = CH_2Ph, R_1 = H) on irradiation of its acetonitrile solution (25 °C, c = 5.15 × 10^{-5} M) at the longest-wavelength band of the spirocyclic form (436 nm) with a time interval of 20 s. Data from refs 11a and 88a.

irradiation, the decoloration process that restores the initial spectrum occurs very slowly at room temperature (the effective lifetime of the colored form at room temperature is about 10^4 s). Photochromic perimidinespirocyclohexadienones **30** possess high fatigue resistance properties. The photocoloration−thermal decoloration cycles can be repeated several dozen times without noticeable loss in intensity of the longest-wavelength absorption of the spirocyclic isomer. Similar photochromic transformations are also characteristic of the heteroanalogues **34** (Scheme 28) as well as of perimidinespiro-4*H*-naphthalenone **31**.

Scheme 28

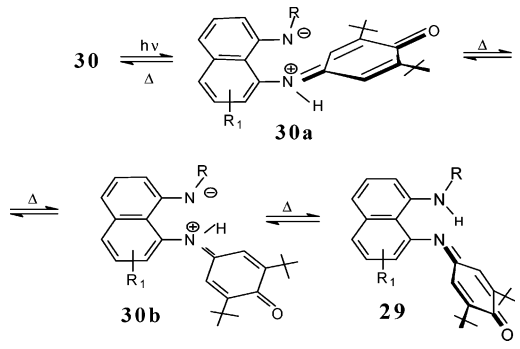


34 **35**

No concentration dependence of the rate of the dark reaction was observed, which points to the intramolecular nature of the reaction. Figure 5 shows the evolution of the absorption spectrum of a perimidinespirocyclohexadienone **30** (R = Me) during UV irradiation of its hexane solution. As shown by X-ray determinations,[89] the two spiroannelated halves of perimidinespirocyclohexadienones **30** are mutually orthogonal, and their absorption spectra may, to a first approximation, be considered as the superposition of the spectra of these fragments. The nonadditivity pointed to appreciable charge transfer between the spiroconjugated heterocyclic and cyclohexadienone moieties of **30** in the first singlet excited state, which manifests itself in the appearance of a low-intensity ($\epsilon \approx 1500-2000$ l·M^{-1}·cm^{-1}), long-wavelength absorption band in the region of 390−440 nm that is nonexistent in the spectra of any of their orthogonal fragments.

The mechanism of the photochromic reaction (Scheme 29) involves cleavage of a C−N bond in the

Scheme 29



first singlet excited state of **30**, followed by conformational rearrangement of the thus formed zwitterionic intermediate **30a** that undergoes conformational rearrangement to its trans isomer **30b**, which precedes the final step of the intramolecular proton transfer. Despite the complex character of the reaction, the initial spiro form **30** (R = CH_3, R_1 = H) is fully transformed into the final quinoneimine photoproduct for about 40 ps.[88c] For spiroperimidinecyclohexadienones **30** (R = Alk, CH_2Ph), the quantum yields of the photoreaction measured in octane solution were found in the range 0.24−0.42 and are close to those typical of spiropyrans.[9b,d] In polar solvents (acetonitrile), the quantum efficiency of the photocoloration reaction is substantially lower (Φ = 0.05−0.06 mol·einstein^{-1}). Triplet quenchers do not inhibit the photocoloration, which indicates that the main channel of the light-initiated ring-opening reaction relates to the first excited singlet state of the spirocyclic structure **30**.

The nature of the colored isomers of photochromic perimidinespirocyclohexadienones has been unambiguously proven through comparison of their UV−vis absorption spectra with those of *N*-acetyl (**29**, R_1 = H, R = $COCH_3$) and *N*-tosyl (**29**, R_1 = H, R = $SO_2C_6H_4CH_3$-*p*) derivatives of **30**. These compounds were obtained in the stable ring-opened forms, and their structure was determined by X-ray.[89] An additional confirmation stems also from the close similarity of the absorption spectra of photoinduced isomers of **30** with the spectrum of the acenaphthylene derivative possessing the quinoneimine structure **29** (R = CH_3, R_1 = 4,5-$(CH_2)_2$).[91] Table 10 contains data on positions and intensities of the longest-wavelength absorption bands of the ring-opened photoisomers of perimidinespirocyclohexadienones **30** and spirocyclohexadienonepyridoquinazolines **34**. Although the absorption maxima of these bands lie in

Table 10. Position and Extinction Coefficients of the Longest-Wavelength Absorption Bands of Photoisomers of Perimidinespirocyclohexadienones 29 and Spirocyclohexadienonepyridoquinazolines 34 35[88a,89,90,93]

compound	λ_{max}, nm	ϵ, $l \cdot M^{-1} \cdot cm^{-1}$	solvent
29 (R = H)	584	5300	octane
29 (R = Me)	620	4700	octane
	602	3900	acetonitrile
29 (R = Et)	626	4400	octane
	602	3700	acetonitrile
29 (R = Pr)	630	4600	octane
	607	4200	acetonitrile
29 (R = *i*-Bu)	630	4200	octane
29 (R = CH_2Ph)	611	4300	octane
	595	3900	acetonitrile
29 (R=H, R_1 = 4,5-$(CH_2)_2$	614	4700	octane
29a (R, R_1 = H)	571	4400	octane
29a (R = H, R_1 = 4,5-$(CH_2)_2$	616	4600	octane
29 (R = H, R_1 = 7-Br)	584	4600	octane
29 (R = H, R_1 = 5-Br)	569	3400	octane
29 (R = H, R_1 = 2,5,7-Br_3)	557	2100	octane
35 (R, R_1, R_2 = H)	552	4300	octane
35 (R, R_2 = H, R_1 = Me)	597	1700	benzene
35(R = Me, R_1, R_2 = H)	560	6700	benzene
35 (R, R_1 = H, R_2 = $C_{10}H_7$)	556	6700	toluene
35 (R, R_1 = H, R_2 = C_6H_4Me-*o*)	535	3100	ethanol
	559	6500	octane
35 (R, R_1 = H, R_2 = C_6H_4Me-*p*)	560	7000	octane

the range of 560−630 nm, the tails of the bands usually extend to 800−900 nm, i.e., to the near-IR spectral region. An analogous spectral pattern is also characteristic of indoaniline dyes[92] whose structure and, therefore, the nature of the relevant electronic transitions are similar to those of quinoneimines **29**.

In the solid state, most of the perimidinespirocyclohexadienones and their derivatives are stable in the ring-closed form **30**. Upon dissolution in nonpolar solvents (e.g., hydrocarbons or tetrachloromethane), an equilibrium is gradually established between **30** and its deeply colored **29** quinoneimine isomeric form, the appearance of which is detected by the characteristic long-wavelength absorption band in the region of 560−630 nm (Table 10). Some of the perimidinespirocyclohexadienones that exist in a solid as purely spirocyclic compounds, such as **30** (R, R_1 = 4,5-$(CH_2)_2$, **34**), fully convert to the quinoneimine form when dissolved in octane.[11a,90,93] The position of the **30** ⇌ **29** equilibrium depends strongly on the solvent in use and the temperature of the solution, which defines respectively solvato- and thermochromic properties of perimidinespirocyclohexadienones. In proton donors and polar solvents (alcohols, acetonitrile, dimethylformamide), the equilibrium is shifted to the spirocyclic form, spirocyclic isomers of compounds **30** (R = Alk, R_1 = H, 5-Br) being the only isomers present in such solutions.[88a,89]

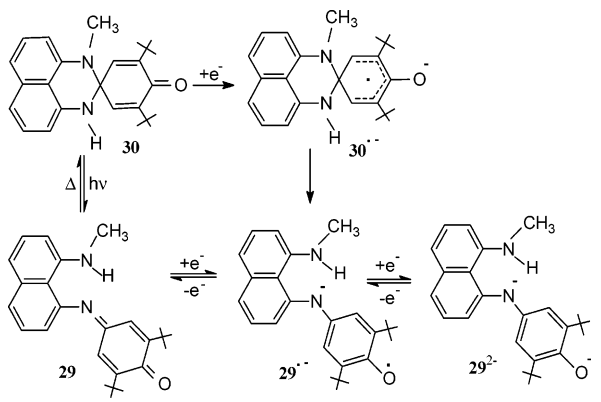
Thermodynamic parameters of the thermal equilibria of a number of perimidinespirocyclohexadienones **30** and spirocyclohexadienonepyridoquinazolines **34** were determined by use of dynamic ^{1}H NMR spectroscopy techniques. The acoplanarity of the quinoneimines **29** and **35** provides for the diastereotopicity of the tertiary butyl groups in these compounds, appearing in the ^{1}H NMR spectra as two distinct signals. By contrast, in the spirocyclic isomers **30** and **35** possessing symmetry planes, the *tert*-butyl groups form a common 18-proton signal. By measuring the redistribution of the intensities of these signals with changing temperature of solution, thermodynamic parameters of the spiran−quinoneimine equilibrium were determined. The time during which the thermal equilibrium between the interconverting isomers is established is particularly long for the type **34** compounds. The thermodynamic and activation parameters for some of these equilibra are listed in Table 11.

Table 11. Thermodynamic and Activation Parameters of the Equilibrium 34 ⇌ 35 in Nitrobenzene-d_5 solution[90b]

compound	K_{293} = [**35**]/[**34**]	$\Delta G_{293}^{\ddagger}$, kcal mol^{-1}
R = R_1 = R_2 = H	0.37	22.5 (423 K)
R = CH_3, R_1 = R_2 = H	0.64	24.0 (453 K)
R_1 = CH_3, R = R_2 = H	0.06	

The photoinitiated rearrangement of **30** to **29** causes drastic changes in the electrochemical properties of the interconverting isomers. This makes possible light-triggered switching of redox and electronic conduction properties of solutions of perimidinespirocyclohexadienones. The initial spirocyclic isomer **30** requires a very high negative potential (E_p^r = −2150 mV vs ferrocene) for its irreversible two-electron reduction to the dianion. The reduction proceeds as a multistep process consisting of electrochemical and chemical substeps. The latter process is due to the valence isomerization occurring at the radical anion stage, **30**$^{\bullet-}$ → **29**$^{\bullet-}$. The acceptor capability of the compound is raised to the extent that the redox potential for dianion formation of the quinoneimine form becomes more positive than E_p^r, so that **29**$^{\bullet-}$ is immediately reduced further to **29**$^{2-}$ at the existing electrode potential.[94] After the potential scan is reversed, two distinctly separated voltammetric signals appeared which correspond to the oxidation of **29**$^{2-}$ via **29**$^{\bullet-}$ to **29**. With the use of a UV−vis−near-IR spectroelectrochemistry technique,[95] the thermal back reaction of the electrochemically formed quinoneimine **29** to its spirocyclic isomeric form **30** was observed. The overall process **30** → **29** → **29**$^{\bullet-}$ → **29**$^{2-}$ induced by reduction/oxidation is summarized in Scheme 30.

Scheme 30



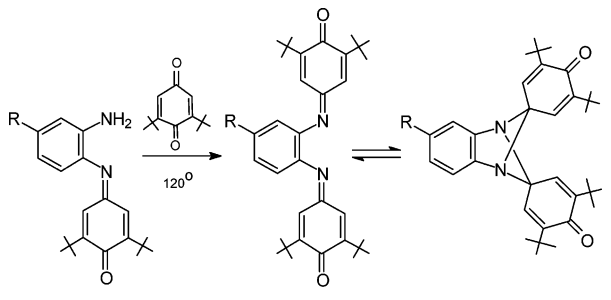
The much less negative reduction potential of the conjugated quinoneimine isomer **29** compared with that of its spirocyclic counterpart **30** allows for potential application of this photochromic system as a light-to-electron conversion molecular device. By generating **29** through irradiation of a solution of **30** in a spectroelectrochemical thin-layer cell under potentiostatic conditions and applying a potential at which **29** is reduced to $\mathbf{29}^{\bullet-}$, a cathodic current is repeatedly observed as a signal, which decays after extinguishing the light. These experiments[94] reveal the potential of perimidinespirocyclohexadienones for the design of multiswitchable electrochromic devices.

7. 1,3-Di(spirocyclohexadien-4-one)diazacyclobutanes

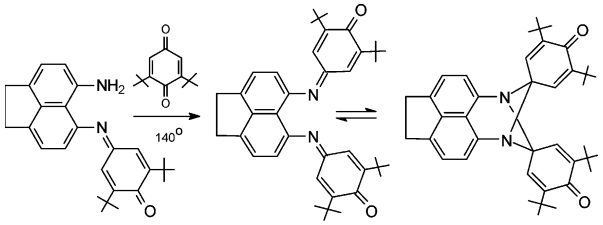
As stated in section 6, the reaction between equimolar amounts of 2,6-di-*tert*-butyl-1,4-benzoquinone and *o*-phenylenediamine and acenaphthylene-5,6-diamine stops at the stage of quinoneimines, respectively **36** and **32**. By heating these compounds with an excess amount of 2,6-di-*tert*-butyl-1,4-benzoquinone or by melting together the diamines with the quinone taken in a molar ratio of 1:2 at 110−160 °C for 4−7 h, condensation on the second amino group occurs, giving rise to the formation of both ring-opened and bis-spirocyclic isomers of bis-quinoneimines. The isomers can be chromatographically separated and isolated in the pure state. When allowed to stand in solution at room temperature, bis-quinoneimines derived from *o*-phenylenediamine(2,4,10,12-tetra-*tert*-butyl-7,14-*o*-benzeno-7,14-diazaspiro [5.1.5.1]tetradeca-1,4,9,12-tetraene-3,11-dione) **37b** slowly converts and that derived from acenaphthylene-5,6-diamine (2,4,10,12-tetra-*tert*-butyl-7,14-*peri*-acenaphthene-7,14-diazaspiro[5.1.5.1]tetradeca-1,4,9,12-tetraene-3,11-dione) **38b** rapidly converts to their bis-spirocyclic isomeric forms, **37a** and **38a**, respectively.[96] These transformations are illustrated by Schemes 31 and 32.

Upon irradiation of solutions of **37a** and **38a** with the light in their λ_{max}, reversible isomerizations occur to form the photoisomers **37b** and **38b**, respectively. The back reactions cannot be thermally driven and proceed only on irradiation of the solutions of photogenerated colored isomers with the light in their absorption maxima. Quantum yields for the interconversion of the photoisomers of compounds **37**and **38** are rather low ($\sim 10^{-3}$). It was found that much

Scheme 31

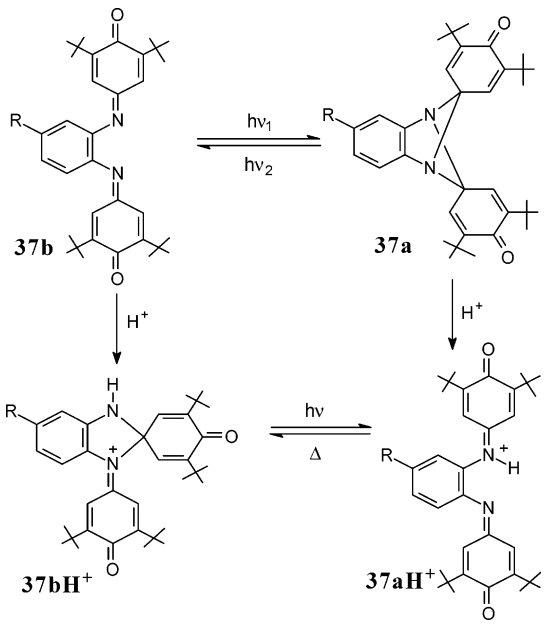


Scheme 32



greater quantum efficiencies are characteristic of the photochromic reactions of their cations formed by protonation of **37a** and **38a**. On activation by UV light, the cations $\mathbf{37aH}^+$ and $\mathbf{38aH}^+$ undergo rearrangements, with the formation of deeply colored protonated diaminoquinones $\mathbf{37bH}^+$ and $\mathbf{38bH}^+$, respectively. In contrast to the rearrangements of their conjugated bases triggerred only by light, the back reactions of $\mathbf{37bH}^+$ and $\mathbf{38bH}^+$ readily occur as a thermal relaxation process. The photochromic rearrangements of compounds **37** and their protonated forms are depicted in Scheme 33.

Scheme 33



The long-wavelength absorption bands of $\mathbf{37bH}^+$ and $\mathbf{38bH}^+$ are shifted bathochromically with respect to those of **37b** and **38b**. Table 12 contains some data on spectral and photochemical parameters of the photochromic systems described in this section. Their photochromic behavior is exemplified by the spectral pattern shown in Figure 6.

8. Dipolar Spiro-σ-complexes

In nonpolar solvents and in the solid state, *O*-(2,4,6-trinitrophenyl) derivatives of *o*-hydroxyarenealdehydes exist in the colorless benzenoid form **39a**. When passing to polar solvents (acetone, DMSO), an equilibrium is established between **39a** and the isomeric dipolar spirocyclic form **39b**,[97] as manifested by the appearance of intense bands in the regions of 400 and 500 nm of the electronic absorption spectra

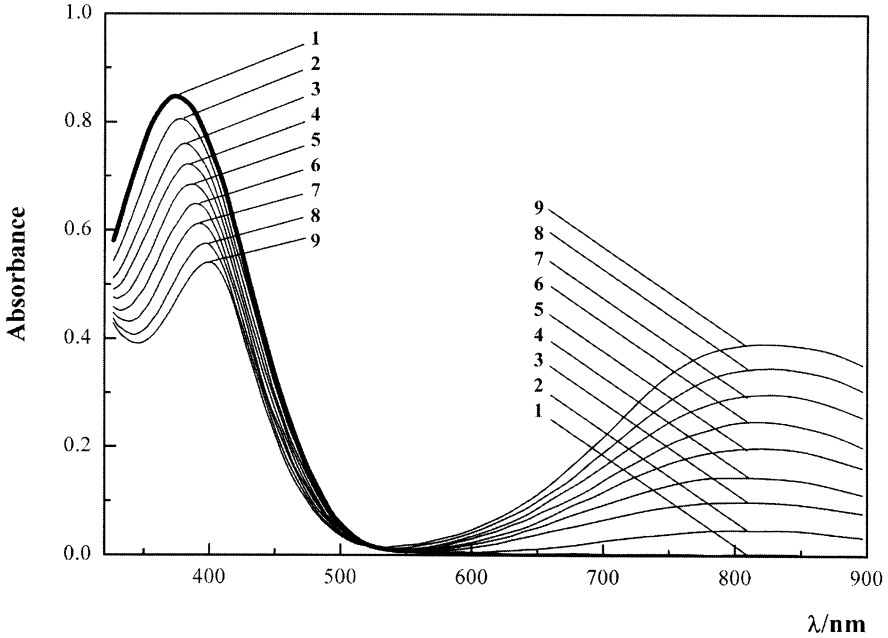


Figure 6. Changes in the absorption spectrum of the cation **37aH**$^+$ under irradiation of its toluene solution ($c = 9 \times 10^{-5}$ M; 16 μL of CF_3COOH added to 1 mL of the solution) at 365 nm: (1) before and (2−9) after irradiation for 30, 60, 120, 240, 480, and 960 s with the light of a mercury lamp.[96]

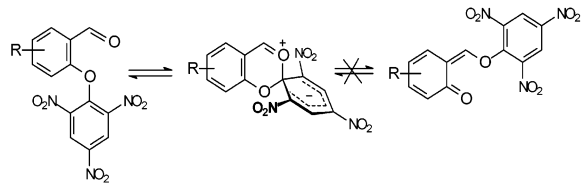
Table 12. Spectral Parameters of the Photochromic Bis-spirocyclic Compounds 37 and 38 (Toluene, 24 °C) and Their Protonated[a] Forms, Lifetimes of the Photocolored Isomers (τ), and Quantum Yields of the Photochromic Reaction (Scheme 33)[96]

compound	λ_{max} ($\epsilon \times 10^{-3}$)	τ_{24}, s	Φ
37a (R = H)	474 (8.8)	*b*	*c*
37b (R = H)	593 (8.0)		
37a (R = CH_3)	484 (8.5)	*b*	*c*
37b (R = CH_3)	602 (7.8)		
37a (R = OCH_3)	502 (12.0)	*b*	*c*
37b (R = OCH_3)	597 (12.0)		
38a	535 (9.2)	*b*	*c*
38b	665 (19.6)		
37aH$^+$ (R = H)	375 (20.0)	900	0.17
37bH$^+$ (R = H)	803 (7.0)		
37aH$^+$ (R = CH_3)	384 (21.1)	2400	0.14
37bH$^+$ (R = CH_3)	810 (7.3)		
37aH$^+$ (R = OCH_3)	377 (23.4)	1800	0.16
37bH$^+$ (R = OCH_3)	766 (9.9)		
38aH$^+$	504 (12.0)	<1	0.15
38bH$^+$	833 (11.3)		

[a] By addition of trifluoroacetic acid. [b] Stable. [c] $\Phi_{b \to a} \cong 0.001$.

and upfield shifts of the ^{1}H NMR resonances of the picryl moiety characteristic of Meisenheimer complexes (see ref 98). Inclusion of the quinonoid isomer **39c** into the equilibrium shown in Scheme 34 was

Scheme 34



39a **39b** **39c**

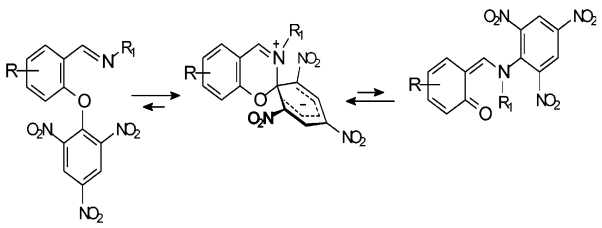
R = H, 5-Br, 5-NO_2, 5,6-Benzo

not detected by these methods. For the derivatives of salicylic aldehyde (R = H), the equilibrium constants K_{25} = [**39b**]/[**39a**] were found to be 0.075 (dioxane) and 4.0 (DMSO). The compounds **39a** are susceptible to the reversible photochromic rearrangent **39a** → **39b** occurring in a frozen isopentane solution under prolonged irradiation with the light of a mercury lamp. The dark back reaction proceeds rapidly on defrosting the solution.

In the case of *N*-alkylimines **40**, the equilibrium between the benzenoid (**40a**) and the dipolar spirocyclic (**40b**) isomers is shifted to the latter, even in nonpolar solvents. The compounds **40** exhibit a pronounced negative thernochromism: the ratio of the colored ($\lambda_{max} \approx 540$ nm) form **40b** to the almost colorless open form **40a** gradually decreases with increasing temperature of the solution. In diglyme, the content of the spirocyclic form was determined to 52% at 60 °C, 75% at 20 °C, and 100% at −30 °C for **40b** (R = H, R_1 = *i*-Pr) and 60% at 60 °C, 86% at 20 °C, and 100% at −30 °C for **40b** (R = 5,6-benzo, R_1 = *i*-Pr). Another distinctive property of the compounds **40** is the presence of detectable amounts of the quinonoid isomers **40c** in the equilibria established in their solutions (Scheme 35). In the solid state, all the compounds **40** are stable in the dipolar spirocyclic form. The molecular and crystal structures of **40b** (R = 5,6-benzo, R_1 = *i*-Pr) and its trifluorosulfo analogue **41** were determined by X-ray.[12c,97,99]

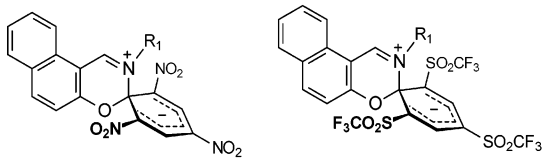
It is worth mentioning that compounds **40b** and **41** are the quaternary salts of the elusive spiro[1,3]-oxazine system which remains a synthetic target in the search for close analogues of photochromic spiropyrans and spiro[1,4]oxazines.[9a,b] The only reported compounds of this type, spiro[1,3]oxazines **42** prepared by the condensation of 2-imino-3-methylbenzothiazoline with *o*-hydroxyarenealdehydes, were described in a patent.[100] The attempts to reproduce the synthesis of **42** failed, and the reaction of 2-imino-3,5-dimethylthiazolidine with *o*-hydroxyarenealde-

Scheme 35



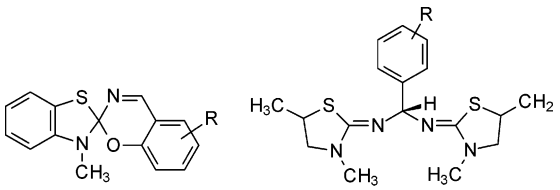
40a **40b** **40c**

R = H, 5-Br, 5-NO_2, 5,6-Benzo; R_1 = CH_3, $CH(CH_3)_2$, CH_2Ph



40b (R = 5,6-benzo, R_1 = *i*-Pr) **41**

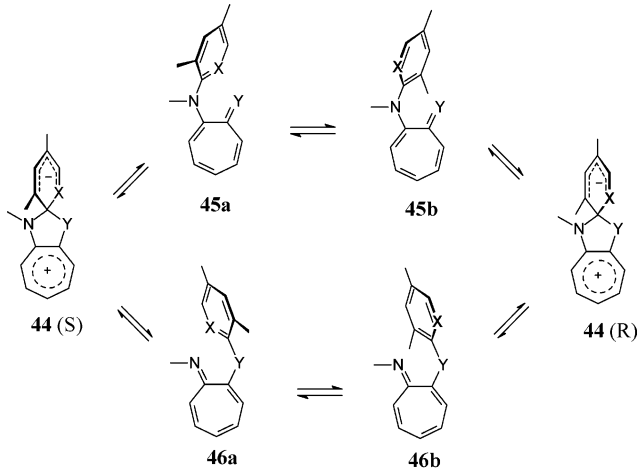
hydes led not to derivatives of the spiro[1,3]oxazine system but to the dimeric products **43**.[101]



42 **43**

The most amply studied class of dipolar spiro-*σ*-complexes **44** is represented by derivatives of tropolone, aminotropone, aminothiotropone, and aminotroponeimine, formed on coupling these compounds with highly electrophilic aromatic and heterocyclic substrates.[12,102] In general, compounds of type **44** serve as intermediates in nucleophilic rearrangements caused by fast **45**(**46**) ⇌ **44** ⇌ **45**(**46**) migration of aryl and heterocyclic groups, activated by strong electron-withdrawing substituents or electronegative heteroatoms in the ring (Scheme 36).

Scheme 36

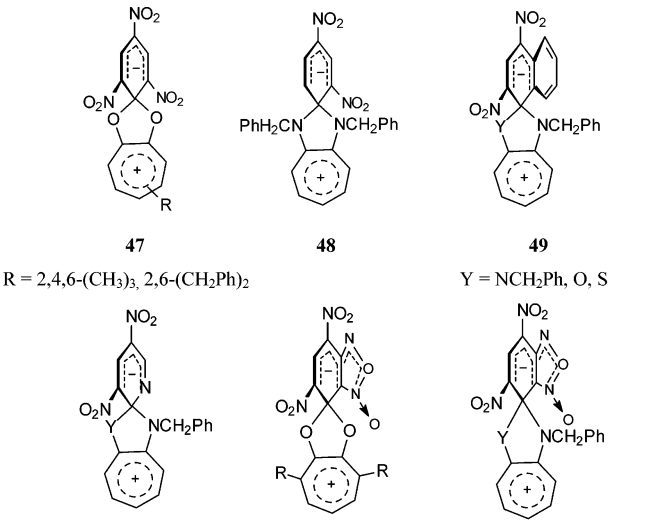


44 (S) **45a** **45b** **44** (R)

46a **46b**

Y = O, S, NR

When three such activating units are present in the migrant (two units are sufficient in the case of the amino derivatives), spiro-*σ*-complexes appear to be thermodynamically more stable species than ring-opened forms and can be readily isolated as deeply colored crystalline compounds. Compounds **47**−**52** exemplify stable spiro-*σ*-complexes, the structure of which was proven by X-ray studies.



47 **48** **49**

R = 2,4,6-$(CH_3)_3$, 2,6-$(CH_2Ph)_2$ Y = NCH_2Ph, O, S

50 Y = NCH_2Ph, S **51** R = CH_3, CH_2OCH_3 **52** Y = NCH_2Ph, O, S

Molecules of spiro-*σ*-complexes possessing no symmetry plane contain a stereogenic spiro-carbon center and are, therefore, chiral. On heating of their solutions, some of these undergo thermal rearrangements (Scheme 36), resulting in inversion of stereochemical configuration at the tetrahedral spiro-carbon atom **44**(*R*) ⇌ **44**(*S*). The energy barrier to the configurational inversion is the sum of the free energy differences between the spirocyclic and ring-opened isomers (**44** and **45** or **46**, respectively) and the free activation energy of internal rotation about the C_{aryl}−N bond in **45** or C_{aryl}−O, C_{aryl}−S in **46**. It was shown that the energy-favored mechanism of the rearrangement involves cleavage of the C−O and C−S bonds, and the C−N internal rotation **45a** ⇌ **45b** represents the principal energy component of the total barrier to the stereoisomerization of the derivatives of 2-aminotropone and 2-aminothiotropone (**49**, **50**, and **52**).

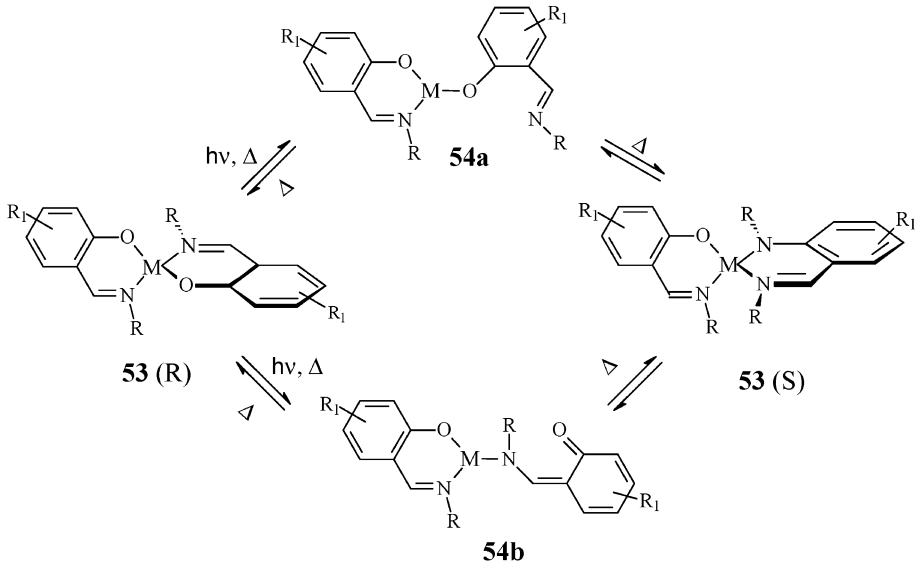
The kinetics of the rearrangements was studied using dynamic ^{1}H NMR technique.[102d,e,g] Rate constants and energy barriers to the racemization reaction are summarized in Table 13. It may be seen that

Table 13. Kinetics of the Thermal Enantiomerization of Spiro-*σ*-complexes 49−52[102d,e]

compound	solvent	k_{25}, s^{-1}	$\Delta G^{\ddagger}_{25}$, kcal mol^{-1}
49, Y = NCH_2Ph	nitrobenzene-d_5	$<10^{-9}$	>27
49, Y = S	nitrobenzene-d_5	3.4×10^{1}	15.3
49, Y = O	$CDCl_3$	1.2×10^{3}	13.2
50, Y = NCH_2Ph	nitrobenzene-d_5	2.0×10^{-2}	19.8
50, Y = S	nitrobenzene-d_5	3.0×10^{2}	14.1
51	brombenzene-d_5	1.7×10^{-2}	19.8
52, Y = NCH_2Ph	DMSO-d_6	$<10^{-9}$	>27
52, Y = O	DMSO-d_6	5.0×10^{-5}	23.3
52, Y = S	DMSO-d_6	$<10^{-9}$	>27

the enantiomerization reaction is a rather fast process, the lifetimes of the ring-opened isomers **45** are

Scheme 37



M = Be, Zn, Cu Co; R=Alk, Aryl; R_1=Benzo, Hetaryl

very short, and their equilibrium amounts are too low to cause noticeable changes in the UV−vis absorption spectra of the spiro-σ-complexes.

9. Concluding Remarks

A property common to various spiroheterocyclic compounds considered in this review is the readiness of their spiro carbon sites to break the C_{spiro}−X (X = C, N, O, S, Se) bonds, leading to the inclusion of that carbon atom in an extended π-conjugated system of the formed ring-opened isomer. This property is at the root of all thermally, photochemically, and electrochemically induced rearrangements of the spiroheterocyclic systems containing a C_{spiro}−X fragment in diverse structural environments, as shown in Schemes 1, 15, 17, 22−24, 26, 28−36. The general character of this property of spirocyclic systems and the versatility of the dynamical transformations inherent in the compounds, in which two conjugated fragments are linked by a spiro site, is additionally illustrated by low-energy-barrier thermal[103] and recently discovered photoinitiated[104] rearrangements (Scheme 37) of a broad series of the tetrahedral metal chelate complexes **53**, the structure of which closely resembles that of spiropyrans and spirooxazines. The short-lived isomers **54**, formed upon fission of the M_{spiro}−N (thermal reaction) or M_{spiro}−O (photochemical process) bonds, were detected using millisecond and nanosecond flash photolysis techniques and found to absorb at 600−900 nm.

No rearrangements of this type resulting in photochromic or thermochromic behavior have yet been documented for the spirocyclic compounds in which C_{spiro} and M_{spiro} atoms are exchanged for other isoelectronic or isolobal centers. However, the area of spiroheterocyclic compounds continues to be a subject of intense investigation, and it may be assumed that novel spiroconjugated scaffolds will soon be presented to further extend the potential of this important group of bistable systems for various technical applications.

10. Acknowledgments

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