

Thermal and Photodegradation of Photochromic Spiroindolenaphthooxazines and -pyrans: Reaction with Nucleophiles. Trapping of the Merocyanine Zwitterionic Form

Vincenzo Malatesta,^{*,†} Carlo Neri,[†] Maria Lucia Wis,[†] Luciano Montanari,[‡] and Roberto Millini[‡]

Contribution from the Great Lakes Chemical Italia s. r. l., Via Maritano 26, 20097 S. Donato (MI), Italy, and Eniricerche s. p. a., Via Maritano 26, 20097 S. Donato (MI), Italy

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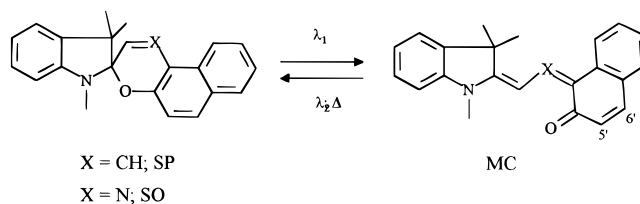
Abstract: Adducts of the zwitterionic (ZW) form of merocyanine (MC) of five photochromic spirooxazines (SO) and spiropyran (SP) have, for the first time, been prepared photochemically or thermally through a trapping reaction of metastable MC with trimethylsilyl cyanide (TMSCN) in dichloromethane. The adducts (ZWAs) form easily and are obtained in almost quantitative yields. X-ray diffraction analysis of ZWA of spirooxazine **2** shows that in the adduct the planes of the indolyl and naphthyl moieties form a ca. 29° angle. The adduct crystallizes in the monoclinic space group $P2_1/n$ with $a = 22.663(4)$ Å, $b = 8.234(1)$ Å, $c = 14.455(2)$ Å, $\beta = 104.72(1)^\circ$, $V = 2637.4(7)$ Å³, and $D_{\text{calcd}} = 1.1476$ Mg/m³ for $Z = 4$. Least-squares refinement of the model based on 1986 reflections ($F > 4\sigma(F)$) converged to a final $R = 0.066$ and $R_w = 0.068$. ZWAs form through an unprecedented, clean, and regioselective Michael-type 1,6-addition of TMSCN to either a strongly polarized quinoidal MC form or its charge-separated zwitterionic limit structure. No evidence for the more common 1,2- and/or 1,4-addition has been found. The observed high reactivity of SOs and SPs with nucleophiles may contribute to the reported limited durability of these classes of photochromes.

Introduction

Spiroindolenaphthooxazines (SO)¹ and spiroindolenaphthopyrans (SP)^{2,3} are photochromic materials that have been extensively studied due to their potential applications in several important areas, including high-density optical storage, optical switchings, image processing, and displays. Exposure of SOs and SPs in solution or in a polymer matrix to UV-A or sunlight results in a color change due to the formation of a deeply colored merocyanine (MC) form that tends to revert back to the closed spiro form either thermally⁴ or photochemically⁵ (Scheme 1), with kinetics that depend, in a given solvent, on the substitution pattern of the spiro compound.⁴

The photochromic reaction features the dissociation of the C_{spiro}–O bond producing a distribution of MC isomers.^{6–10} Several models have been proposed to explain the properties

Scheme 1



and photochromic reaction mechanisms of these molecules based on both frequency domain^{11–14} and time domain^{6–10,15,16} spectroscopic studies. The rate constants of the excited-state spiro C–O bond cleavage have been estimated to be approximately 700 fs⁻¹ for spirooxazines¹¹ and less than 100 fs⁻¹ in the case of a spiropyran.¹⁷ These excited states relax first to vibrationally hot ground-state MC forms that subsequently yield ground-state MCs whose lifetime values depend on the solvent and structure and may vary from microseconds to several hundreds seconds.⁴ It has been proposed by several authors^{1–3}

* To whom correspondence should be addressed.

[†] Great Lakes Chemical Italia.

[‡] Eniricerche.

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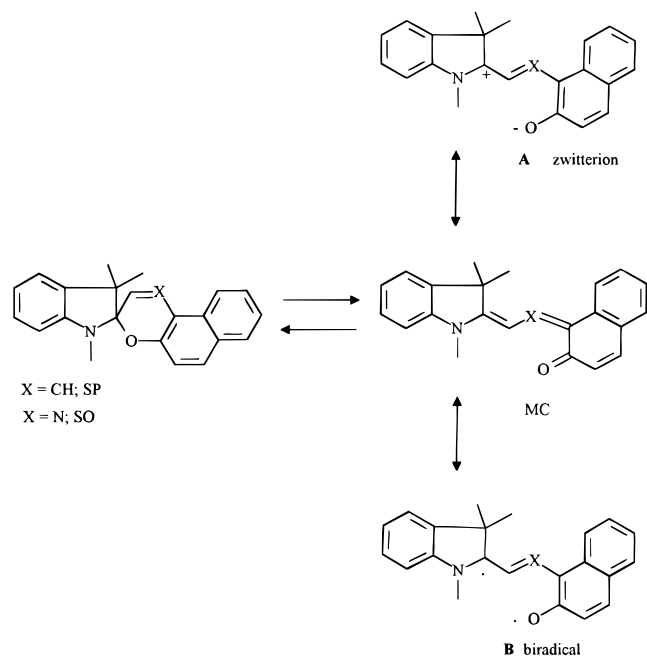
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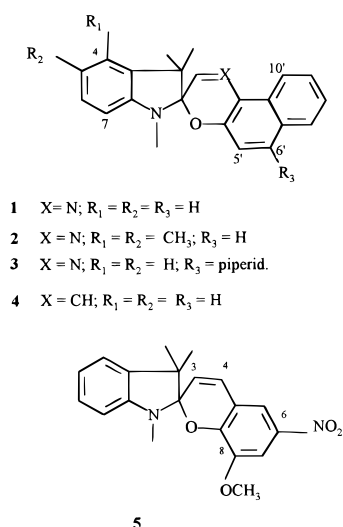
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Scheme 2



Scheme 3



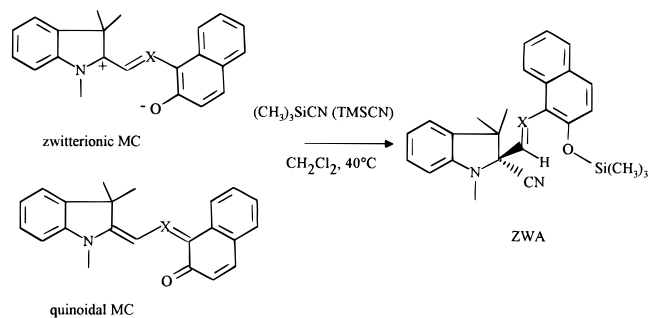
that the light-induced opening of the pyran or oxazine ring is essentially a heterolytic process, yielding a short-lived transient that rearranges in less than 100 ps to give the merocyanine(s), having a quinoidal ground-state form¹⁰ MC and a polar zwitterionic excited state, as indicated by the red shifting that the absorption maximum undergoes in solvents of increasing polarity (positive solvatochromism).⁴ The spectroscopic evidences so far produced point to a relatively nonpolar quinoidal-type merocyanine form MC. On the other hand the reported substituent effects on photodegradation³ seem to indicate that the ground state MC has a strong zwitterionic character (Scheme 2, A).

The possibility of a homolytic process has also been considered and indirect evidence of a biradical transient formation has been provided by spin-trapping experiments¹⁸ although, because of its extremely low concentration, the biradical is most likely not on the main reaction pathway originating photochromism.

We have tried, without success, to trap the biradicaloid resonance form (B, Scheme 2) of MC by photolyzing SOs in a

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Scheme 4



solution containing a radical source such as e.g. azobisisobutyronitrile. Instead we could isolate only the diamagnetic adduct(s) of the isopropylcyano radical C(CH₃)₂CN to the C5′=C6′ double bond α to the quinone carbonyl group of MC.^{19a}

As part of our continuing effort to elucidate the degradation mechanism(s) of SOs¹⁹ we have sought a direct evidence for the presence in solution of the zwitterionic form (A) and have, for the first time, succeeded in isolating its derivative (ZWA) formed by chemical trapping of the MC zwitterion of 1–5 (Scheme 3) with trimethylsilyl cyanide (CH₃)₃SiCN (TMSCN) (Scheme 4).

The adducts form in almost quantitative yields through an unprecedented, clean, and regioselective 1,6-addition to a doubly unsaturated carbonyl group.

Results and Discussion

A. Synthesis and Characterization. UV-A light irradiation of 1,3,3,4,5-pentamethylspiro[indoline-2,3′-[3H]naphtho[2,1-*b*]-[1,4]oxazine] (**2**, 1.9×10^{-2} M) in the presence of TMSCN (5 equiv) in dry CH₂Cl₂ at room temperature, produced, in quantitative yields, a crystalline adduct ZWA arising from the interception of the zwitterionic form of MC. Product structures were assigned on the basis of ¹H and ¹³C NMR data. 2D nuclear Overhauser and exchange spectroscopy (NOESY) NMR experiments have shown that the azomethine H2′ (δ = 8.16 ppm) correlates with NCH₃ (δ = 2.93 ppm) and one of the *gem*-CH₃ (δ = 1.40 ppm), whereas the CH₃ groups on Si correlate only with H5′. On the basis of the NMR data we infer that the indoline and naphthyl moieties of the ZWA molecule are not co-planar. ZWA has an electronic absorption spectrum with a maximum at 340 nm (log ε = 3.69) that very closely resembles that of the corresponding spirooxazine. This is further evidence that the two π-electron systems do not interact because of their off-plane mutual orientation. ZWA is also formed in high yield through a “clean” thermal process by heating a solution of TMSCN and photochrome in CH₂Cl₂ at 40 °C. As TMSCN quenches the zwitterionic form of MC, the occurrence of the thermal reaction strongly indicates that the quinoidal form, invoked by many authors as representing the MC ground state (GS), must be strongly polarized. It remains however the fact that the excited state is more polarized than GS because all of the compounds included in this study show a positive solvatochromism.⁴ The reaction is rather fast and solvent dependent. In principle the TMSCN–MC adduct formation results from a Michael-type reaction of CN[−] to the double bond in γ–δ position to the quinone carbonyl group followed by quenching of the phenolate by (CH₃)₃Si⁺.

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In this context it is worth noting that such a 1,6-addition to unsaturated carbonyl groups is, to the best of our knowledge, unprecedented. Indeed for the cyanosilylation of unsaturated carbonyls only the 1,2-addition product, i.e. α -silyloxy nitrile, is reported to form.²⁰ In no case was ever the 1,4-adduct isolated except when strong acids were present in the reaction medium.²⁰ In the case of our photochromes the NMR data are not consistent with a 1,2-addition. Such an adduct would have two equivalent CH₃ groups at C3; the observed significant difference in the chemical shifts ($\delta = 1.4$ and 1.9 ppm, respectively) indicates both the presence at C2 of two substituents of rather different electronegativity, viz. CN and $-\text{CH}=\text{N}-$, and a nonplanar geometry at the former C_{spiro} atom. In a planar geometry C_{spiro}=CH-N= the azomethine H2' would resonate at a lower field ($\delta > 9$ ppm) as found in MC ($\delta = 10.22$ ppm)^{10c} and for the free-radical adducts ($\delta = 9.2$ ppm) previously reported.^{19a}

In the case of the spiropyran **5** the ZWA adduct has also an orthogonal geometry resembling that of the starting closed form SP, but the CH=CH bridge has now the two Hs in a *trans* conformation. Indeed in the closed spiro form $J_{\text{H,H}} = 8.9$ Hz whereas in the adduct $J_{\text{H,H}} = 16$ Hz. In this structure the CH ($\delta = 7.52$ ppm) β to the C_{spiro} is pointing toward the indolyl group and correlates with NCH₃ ($\delta = 2.91$ ppm) and one of the *gem*-CH₃s ($\delta = 1.25$ ppm). The other olefinic proton ($\delta = 6.34$ ppm) correlates with H10' ($\delta = 8.13$ ppm).

As mentioned above the formation of 1,6-adducts to the doubly conjugated carbonyl system of MC is quite unusual and must reflect the strongly polarized nature of these systems even in their ground state. The polarity will be enhanced in the excited state as required by the positive solvatochromism exhibited by these photochromes. The facile nucleophilic attack at the former C_{spiro} might be contributing to the thermal and light-induced degradation of SOs and SPs with formation of products that so far have not been reported and that have eluded detection by conventional spectrophotometric analytical methods perhaps because of the close resemblance of their absorption spectra to those of the starting spiro compounds. The reactivity of **5** deserves some comments. Its blue CH₂Cl₂ solution turned yellow by addition of TMSCN and the HPLC analysis revealed that the adduct was formed instantaneously. The reaction was carried out to completion by a brief (5 min) exposure to UV light. The TMSCN adduct lost, by prolonged (15 min) UV photolysis, the (CH₃)₃Si-group with formation of the phenolic OH group. The reaction is most likely homolytic and takes place easily because of the low bond energy of the (CH₃)₃Si-O bond having an electron-withdrawing group NO₂ *para* and an electron donor CH₃O group *ortho*. We note that the removal of (CH₃)₃Si causes an upfield shift of the CH=CH aromatic hydrogens, whereas the indoline and methyl H-atoms resonances remain practically unaltered. The geometry about CH=CH is still *trans* ($J_{\text{H,H}} = 16$ Hz).

B. Reactivity of MC toward TMSCN. The reaction between MC and TMSCN follows a second-order kinetics, and its rate will depend on the concentration and reactivity of the reacting species. If we assume that the polarity of the C=C-N=C-C=O group in the various merocyanines is not very different (as indicated by the size of the solvatochromic effect) then the reactivity will depend mostly on the MC concentration and therefore on the yield of photocoloration Φ_c . We have recently measured²¹ Φ_c s for **1–3** and found that in a polar solvent, namely C₂H₅OH, they vary in the order **2** > **3** > **1**. When we carried out competitive experiments by irradiating CH₂Cl₂ solutions of **1–3** and TMSCN we found that the

Table 1. Experimental X-ray Data of 2/TMSCN Adduct

formula	C ₂₈ H ₃₃ N ₃ O ₅ i
FW	455.67
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>a</i> (Å)	22.663(4)
<i>b</i> (Å)	8.324(1)
<i>c</i> (Å)	14.455(2)
β (deg)	104.72(1)
<i>V</i> (Å ³)	2637.4(7)
<i>Z</i>	4
<i>T</i> (K)	293
<i>D</i> _{calcd} (Mg/m ³)	1.1476
diffractometer radiation (λ (Å))	Mo K α (0.710 69)
<i>F</i> (000)	976
μ (cm ⁻¹)	1.076
abs correction	no
data collected	$\theta/2\theta$
θ max (deg)	25
std ref	311 (no decay)
no. of refl collected	4924
no. of unique refl	4385
<i>R</i> _{int}	0.022
no. of refl obsd with (<i>F</i> > 4 σ (<i>F</i>))	1986
<i>R</i>	0.066
<i>R</i> _w	0.068
<i>S</i> (goodness of fit)	1.834

Table 2. Selected Bond Lengths (Å) and Angles (deg)

N1–C2	1.414(6)	N1–C9	1.462(4)
N1–C22	1.454(5)	C7–C8	1.533(6)
C8–C9	1.558(6)	C9–C27	1.498(5)
C10–N11	1.237(4)	N11–C12	1.427(6)
C13–O29	1.377(5)	C27–N28	1.140(4)
O29–Si30	1.651(3)	Si30–C31	1.771(9)
Si30–C32	1.763(9)	Si30–C33	1.787(8)
C9–N1–C22	117.4(3)	C2–N1–C22	118.7(3)
C2–N1–C9	106.2(3)	N1–C2–C7	110.6(4)
N1–C2–C3	127.6(4)	C6–C7–C8	131.4(4)
C2–C7–C8	108.1(4)	C7–C8–C9	99.9(3)
N1–C9–C8	103.4(3)	C8–C9–C27	109.7(3)
C8–C9–C10	114.5(3)	N1–C9–C27	108.3(3)
N1–C9–C10	111.5(3)	C10–C9–C27	109.2(3)
C9–C10–N11	122.1(4)	C10–N11–C12	118.4(3)
N11–C12–C21	119.2(4)	N11–C12–C13	120.2(4)
C12–C13–O29	119.1(4)	C14–C13–O29	119.9(4)
C9–C27–N28	173.9(4)	C13–O29–Si30	127.5(2)
O29–Si30–C33	109.1(3)	O29–Si30–C32	111.3(3)
O29–Si30–C31	107.2(3)	C32–Si30–C33	109.6(4)
C31–Si30–C33	108.0(4)	C31–Si30–C32	111.4(4)

^a Estimated standard deviations are in parentheses.

photochrome relative reactivity followed the predicted order. Admittedly we have not considered the thermal contribution to the MC formation (thermochromism). For most of the spirooxazines included in this study we have calculated^{4c} the rate constants for the ring opening (SO \rightarrow MC) k_f and closure (MC \rightarrow SO) k_r and the equilibrium constants $K_{298} = k_f/k_r$ for the SO \rightleftharpoons MC thermal process. K_{298} are 5.8×10^{-3} and 1.2×10^{-4} for **3** and **1**, respectively,^{4c} i.e. **3** is more thermochromic than **1**, besides having a larger photocoloration quantum yield Φ_c . This explains the observed higher reactivity of **3** toward TMSCN. Furthermore comparison of thermal and photochemically induced reactivities, together with the observed high reaction yields, support the strongly polarization of the MC ground state.

C. X-ray Structure of 2/TMSCN Adduct. The main crystallographic data are reported in Table 1; selected bond lengths and angles in Table 2. The molecule is formed by an indoline and a naphthalene moiety linked, in a *trans* configuration, through a C=N group. Addition of TMSCN occurs on C(9) (the former C_{spiro}) and on O(29) (Figure 1). The mean

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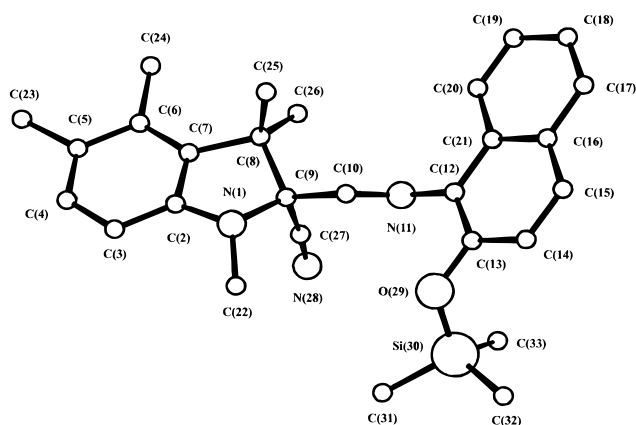


Figure 1. Atomic numbering and X-ray structure of the 2/TMSCN adduct.

planes of the indoline and naphthalene moieties form an angle of 29.1° and the $-\text{Si}(\text{CH}_3)_3$ group points away from the indoline system toward the $\text{C}5'-\text{H}$ bond. This is verified also in solution as indicated by the NMR results that show a cross-peak NOESY between CH_3 on Si and $\text{H}5'$.

Conclusion

The present study was undertaken in the context of the investigation of the mechanisms leading to oxidative degradation of photochromic spiro-indolinenaphthoxazines and -pyrans. The smooth reaction of these compounds with trimethylsilyl cyanide under UV irradiation or mild heating, which leads to a nearly quantitative formation of an unusual 1,6-adduct, indicates that a zwitterionic form of the merocyanine indeed exists, and its reactivity toward nucleophiles contributes, in a so far unsuspected manner, to the degradation of these two classes of photochromes.

Experimental Section

General Methods. Infrared and electronic absorption spectra were recorded on a Digilab FTS-15E and a HP 8452A spectrophotometer respectively. ^1H and ^{13}C NMR spectra were measured using a Bruker-300 AMX spectrometer. The assignments of the ^1H resonances were made by 2D nuclear Overhauser and exchange spectroscopy (NOESY), whereas DEPT and 2D heteronuclear correlation techniques were used for the mapping of the ^{13}C chemical shifts. All the chemical shifts reported are in parts per million (δ) relative to internal tetramethylsilane. Mass spectra were obtained on a Finnigan Incos 50 mass spectrometer. The photochromes were synthesized according to literature methods.^{1,2} Methylene chloride, ethanol, hexane, and ethyl acetate were Aldrich products and were dried over SE-40 molecular sieves.

Preparation of the Adduct(s). In a typical preparation, 5 equiv of TMSCN was added at room temperature to a solution of photochrome **2** (1.9×10^{-2} M) placed in a quartz cuvette equipped with a teflon screw stopper. The solution was then photolyzed in a photochemical reactor (Applied Photophysics, UK) equipped with six fluorescent lamps (12 W) peaking at 320 nm. After 20 min the solution was analyzed by HPLC on a silica column (Microbore, 10 cm \times 3.1 mm) eluted with hexane/ethyl acetate 95:5 v/v. The adduct could also be prepared thermally by keeping the solution at 40°C in the dark for up to 24 h. In all cases only one product was formed. The solvent was evaporated and the sample kept for 12 h under vacuum on a rotary pump. An off-white foamy solid was obtained; that by treatment with hexane/ethyl acetate (95:5, v/v) gave light-yellow crystals (85% isolated yield): mp 163.4°C ; UV/vis (ACN) λ_{max} (log ϵ) 298 (3.86), 340 (3.69); ^1H NMR (300.13 MHz, CDCl_3) δ = 8.16 (azomethine H), 7.00 (H6), 6.43 (H7), 7.16 (H5'), 7.59 (H6'), 7.78 (H7'), 7.40 (H8'), 7.50 (H9'), 8.11 (H10'), 2.93 (NCH₃), 1.92 (CH₃ at C3), 1.40 (CH₃ at C3), 0.34 (CH₃ on Si); ^{13}C NMR (75.47 MHz, CDCl_3) δ = 134.60 (C4a), 127.53 (C6), 106.43 (C7), 147.25 (C7a), 140.79 (C4'a), 121.04 (C5'), 129.58

(C6'), 132.33 (C4), 126.51 (C7'), 123.18 (C8'), 126.28 (C9'), 124.46 (C10'), 133.11 (C10'a), 129.32 (C11'), 163.5 (CH=N), 116.25 (CN), 32.97 (NCH₃), 82.45 (C2), 50.81 (C3), 24.67 (CH₃ at C3), 22.71 (CH₃ at C3), 14.79 (CH₃ at C4), 19.66 (CH₃ at C5), 0.78 (CH₃ on Si); FT-IR (Digilab FTS-15E spectrophotometer) no CN band was observed (this is in keeping with what reported in the literature²² for nitrile groups bonded to carbon atoms carrying an electronegative group, e.g. for acetone cyanohydrin the intensity of CN stretching is extremely weak); MS *m/e* (relative intensity) 455 (M^+ , 6), 440 ($\text{M}^+ - \text{CH}_3$, 2), 306 ($\text{M}^+ - \text{OSi}(\text{CH}_3)_3$, 6), 73 ($\text{Si}(\text{CH}_3)_3^+$, 85). Anal. Calcd for $\text{C}_{28}\text{H}_{33}\text{N}_3\text{OSi}$: C, 73.80; H, 7.24; N, 9.22; O, 3.51; Si, 6.17. Found: C, 73.82; H, 7.20; N, 9.25; O, 3.54; Si, 6.19. MW = 455.6.

1/TMSCN adduct: off-white waxy compound; UV/vis (ACN) λ_{max} (log ϵ) 292 (3.80), 340 (3.68); MS *m/e* (relative intensity) 427 (M^+ , 5), 412 ($\text{M}^+ - \text{CH}_3$, 2), 338 ($\text{M}^+ - \text{OSi}(\text{CH}_3)_3$, 5), 73 ($\text{Si}(\text{CH}_3)_3^+$, 100). Anal. Calcd for $\text{C}_{26}\text{H}_{29}\text{N}_3\text{OSi}$: C, 73.05; H, 6.79; O, 3.75; N, 9.83; Si, 6.26. Found: C, 73.08; H, 6.75; O, 3.78; N, 9.81; Si, 6.61. MW = 427.6.

3/TMSCN Adduct. It was prepared following the same procedure described for **2**. Off-white crystals were obtained from hexane (95% isolated yield): mp 179°C ; UV/vis (ACN) λ_{max} (log ϵ) 296 (3.86), 360 (3.79); ^1H NMR (300.13 MHz, CDCl_3) δ = 7.09 (H4), 6.89 (H5), 7.21 (H6), 6.64 (H7), 6.72 (H5'), 8.33 (H2'), 8.1 (H7'), 7.40 (H8'), 7.52 (H9'), 8.29 (H10'), 2.97 (NCH₃), 1.75 (CH₃ at C3), 1.34 (CH₃ at C3), 0.34 (CH₃ on Si); piperidinyl group hydrogens 3.03 (H in α to N), 1.86 (H in β to N), 1.68 (H in γ to N); ^{13}C NMR (75.47 MHz, CDCl_3) δ = 82.37 (C2), 160.45 (C2'), 49.73 (C3), 136.52 (C4a), 121.68 (C4), 120.46 (C5), 128.47 (C6), 108.84 (C7), 148.65 (C7a), 141.74 (C4'a), 109.96 (C5'), 150.37 (C6'), 124.95 (C6'a), 123.39 (C7'), 123.83 (C8'), 126.67 (C9'), 123.99 (C10'), 136.52 (C10'a), 131.67 (C11'), 116.32 (CN), 24.54 (CH₃ at C3), 23.86 (CH₃ at C3), 32.50 (NCH₃), 0.86 (CH₃ on Si); piperidinyl group carbons 54.68 (C in α to N), 26.55 (C in β to N), 24.84 (C in γ to N); MS *m/e* (relative intensity) 510 (M^+ , 5), 495 ($\text{M}^+ - \text{CH}_3$, 2), 421 ($\text{M}^+ - \text{OSi}(\text{CH}_3)_3$, 2), 73 ($\text{Si}(\text{CH}_3)_3^+$, 100). Anal. Calcd for $\text{C}_{31}\text{H}_{38}\text{N}_4\text{OSi}$: C, 72.93; H, 7.45; O, 3.14; N, 10.98; Si, 5.51. Found: C, 72.96; H, 7.42; O, 3.18; N, 10.97; Si, 5.48. MW = 510.1.

4/TMSCN adduct was prepared as described above: whitish crystals; mp 160°C ; UV/vis (ACN) λ_{max} (log ϵ) 296 (4.12), 332 (3.78); ^1H NMR (300.13 MHz, CDCl_3) δ = 7.1 (H4), 6.88 (H5), 7.2 (H6), 6.63 (H7), 7.13 (H5'), 7.73 (H6'), 7.81 (H7'), 7.39 (H8'), 7.52 (H9'), 8.13 (H10'), 7.56 (H2', $J_{\text{H,H}} = 16$ Hz), 6.34 (H3'), 1.25 (CH₃ at C3), 1.65 (CH₃ at C3), 2.91 (NCH₃), 0.36 (CH₃ on Si); MS *m/e* (relative intensity) 426 (M^+ , 10), 411 ($\text{M}^+ - \text{CH}_3$, 56), 73 ($\text{Si}(\text{CH}_3)_3^+$, 100). Anal. Calcd for $\text{C}_{27}\text{H}_{30}\text{N}_2\text{OSi}$: C, 76.06; H, 7.04; O, 3.75; Si, 6.59. Found: C, 76.10; H, 7.06; O, 3.77; N, 6.55; Si, 6.52. MW = 426.6.

The NMR data of the starting spiroindolinenaphthopyran **4** are reported: ^1H NMR (300.13 MHz, CDCl_3) δ = 7.14 (H4), 6.9 (H5), 7.23 (H6), 6.57 (H7), 7.03 (H5'), 7.64 (H6'), 7.75 (H7'), 7.36 (H8'), 7.53 (H9'), 8.06 (H10'), 5.82 (H2', $J_{\text{H,H}} = 10$ Hz), 7.64 (H3'), 1.26 (CH₃ at C3), 1.38 (CH₃ at C3), 2.77 (NCH₃).

5/TMSCN Adduct. The first adduct that was isolated has the following physicochemical data: UV/vis (ACN) λ_{max} (log ϵ) 336 (3.58); ^1H NMR (300.13 MHz, CDCl_3) δ = 7.4 (H2'), 6.31 (H3'), 7.06 (H4), 6.87 (H5), 7.19 (H7), 7.71 (H6'), 8.06 (H8'), 1.54 (CH₃ at C3), 1.21 (CH₃ at C3), 2.79 (NCH₃), 3.92 (OCH₃), 0.31 (CH₃ on Si); MS *m/e* (relative intensity) 451 (M^+ , 3), 436 ($\text{M}^+ - \text{CH}_3$, 6), 342 ($\text{M}^+ - \text{OSi}(\text{CH}_3)_3$, 3), 73 ($\text{Si}(\text{CH}_3)_3^+$, 100). Anal. Calcd for $\text{C}_{24}\text{H}_{29}\text{N}_3\text{O}_2\text{Si}$: C, 63.84; H, 6.43; O, 14.18; N, 9.31; Si, 6.26. Found: C, 63.86; H, 6.45; O, 14.16; N, 9.28; Si, 6.31. MW = 451.6.

By prolonged photolysis the $(\text{CH}_3)_3\text{Si}$ group was lost and for the desilylated compound we have: ^1H NMR (300.13 MHz, CDCl_3) δ = 7.32 (H2'), 6.48 (H3'), 7.06 (H4), 6.87 (H5), 7.19 (H7), 7.71 (H6'), 8.06 (H8'), 1.55 (CH₃ at C3), 1.21 (CH₃ at C3), 2.79 (NCH₃), 4.01 (OCH₃); ^{13}C NMR (75.47 MHz, CDCl_3) δ = 80.56 (C2), 128.82 (C2'), 49.32 (C3), 136.44 (C4a), 128.37 (C4), 120.45 (C5), 128.37 (C6), 105.34 (C7), 148.52 (C7a), 140.78 (C4'a), 146.58 (C5'), 108.96 (C6'), 149.29 (C7'), 116.5 (C8'), 121.50 (C8'a), 117.13 (CN), 23.04 (CH₃ at C3), 24.64 (CH₃ at C3), 31.79 (NCH₃), 56.79 (CH₃O).

Crystal Structure Analysis of 2/TMSCN Adduct. The X-ray diffraction data were collected on a Siemens AED automated diffrac-

tometer with Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$, $\theta/2\theta$ scan, $\theta_{\max} = 25^\circ$). The structure was solved by direct methods by using the SIR-92²³ program system and refined by the block-matrix least-squares method that uses the SHELX-76²⁴ software package. The function minimized was $\sum w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F)$. The final cycles of refinement included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms, with the exception of atoms C(31), C(32), and C(33) refined isotropically (283 parameters). These atoms, in fact, were not well localized, probably because of a limited rotation of the $-\text{Si}(\text{CH}_3)$ moiety around the O(29)–Si(30) bond. The positions of the H atoms were calculated on geometrical grounds and maintained fixed during the refinement, with $U_{\text{iso}} = 0.06 \text{ \AA}^2$ also being fixed. The refinement converged to $R = 0.066$, $R_w = 0.068$, $S = 1.834$ for the observed 1986 reflections with $F > 4\sigma(F)$. The low number of observed reflections (reflections/parameter ca. 7) and the disorder phenomena observed for the SiCH_3 group were probably responsible for the relatively high R and R_w values obtained in the final refinement.

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The difference Fourier map was featureless. The analysis of the molecular geometry has been carried out using the PARST program.²⁵ Crystallographic data are given in Table 1, selected bond lengths and angles in Table 2. The atomic numbering scheme is shown in Figure 1.

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Supporting Information Available: Tables listing fractional atomic coordinates, isotropic equivalent thermal parameters, anisotropic thermal parameters, calculated fractional coordinates for H atoms, bond lengths and angles and mean plane equations (6 pages). See any current masthead page for ordering and Internet access instructions.

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