Photochromic Spiropyrans. II. Emission Spectra, Intramolecular Energy Transfer, and Photochemistry

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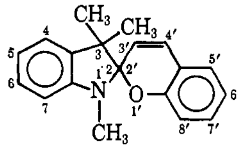
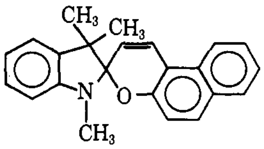
Abstract: The emission and excitation spectra of the colorless forms of a series of indolinobenzospiropyrans at 77°K are given. Spectral data for some chromenes, an indoline, and a substituted aniline, which are used as models for the appropriate halves of the benzospiropyrans, are also presented. Comparison of the spectral data of the model compounds with that of the benzospiropyrans indicates that the emissions are localized or originate from a particular half of the molecule. With the exception of the 5,6′-dinitro derivative, the emissions of the benzospirans considered are shown to originate from the chromene portion of the molecule. Assignments of the nature of the emissions, *i.e.*, whether fluorescence of phosphorescence and of n,π^* or π,π^* character, are made for a number of the molecules considered. Calculations of the relative quantum yields of emission as a function of exciting wavelength are shown for the 6′-nitrobenzospiropyran and β-naphthospiropyran. Intramolecular energy transfer between the indoline and chromene halves of the molecule is shown to occur. In addition, for the β-naphthospiropyran and the two mononitrobenzospiropyrans, a vibronic effect in photochemistry as shown by Becker, *et al.*,[2] for the chromenes is found and the ratio of k_{IC}/k_{PC} for two vibrations of the β-naphthospiropyran is given.

In part I[3] of this series of papers, the π orthogonality of 1,3,3-trimethylindolinobenzospiropyran (I), four of its derivatives (5-chloro, 6′-nitro, 5-chloro-6′-nitro, and 5,6′-dinitro), and β-naphthospiropyran (II) was evaluated. The absorption transitions of the colorless forms of these molecules were shown to be localized on a particular half of the molecule, thus showing that the two halves of the molecule are essentially orthogonal, both relative to the topological symmetry and to the π-electron wave functions. In addition, assignment of the nature of the absorption transitions was made.

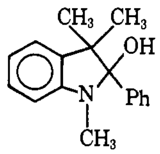


I

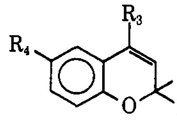


II

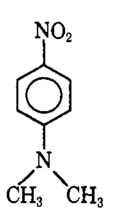
This part concerns the emissions and excitation spectra of the same molecules. Models of the constituent halves are again used in order to determine the nature of the emission transitions, *i.e.*, whether localized on a particular half of the molecule or "total molecule" in character. Evaluation of the data presented in part I along with these data allows further insight into the photochromic mechanism. The model compounds used are 1,3,3-trimethyl-2-hydroxy-2-phenylindoline (III), 2,2-diethyl-2H-chromene (IV), 4-phenyl-6-nitro-2H-chromene (V), p-nitro-N,N-dimethylaniline (VI), and 2,2-dimethyl-5,6-benzo-2H-chromene (VII).



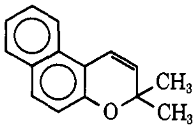
III



IV, $R_1 = R_2 = C_2H_5$; $R_2 = R_4 = H$
V, $R_1 = R_2 = H$; $R_3 = Ph$; $R_4 = NO_2$



VI



VII

Becker, *et al.*,[2] have shown a vibronic effect in photochemistry for the chromenes; *i.e.*, the relative quantum yield of fluorescence (ϕ_F) depends not only on the energy of the electronic state excited but, more importantly, also on the particular vibrational level excited within a given vibrational manifold of the excited electronic state. Further, they have developed a method to determine k_{IC}/k_{PC} (the ratio of the rate constant of internal conversion to that of photochemistry) for a particular vibrational sequence in an excited electronic state and have shown that this ratio is dependent (1) on the particular vibration involved and (2) on the excited electronic singlet state involved. One of the molecules considered here, the β-naphthospiropyran (II) shows sufficient structure to allow evaluation of k_{IC}/k_{PC} ratios. In addition, the emission of β-naphthospiropyran is a fluorescence whereas the nitro-substituted molecules show only phosphorescence. The parent benzospiropyran (I) also shows a fluorescence but it is so weak that it is impossible to determine an excitation spectrum for it. Relative quantum yields of phosphorescence were calculated for the 6′-nitro and the 5-chloro-6′-nitro derivatives but no evaluation of k_{IC}/k_{PC} ratios was possible due to the lack of structure in the absorption transitions.

Experimental Section

Emission spectra were taken at 77°K in rigid media using the same cell and dewar combination as used for the absorption and per cent transmission spectra. The emission apparatus consists of a Hanovia 1-kw Xenon DC lamp or 150-W Tungsten lamp as a source of exciting radiation. Aminco 0.25-m grating mono-

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[1] Taken in part from a dissertation to be submitted in partial fulfillment of the requirements for the Ph.D. degree.

[2] R. S. Becker, E. Dolan, and D. E. Balke, *J. Chem. Phys.*, **50**, 239 (1969)

[3] N. W. Tyer, Jr., and R. S. Becker, *J. Amer. Chem. Soc.*, **92**, 1289 (1970).

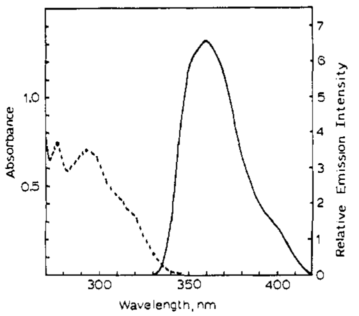

Figure 1. Absorption spectrum (- - -), ~1.7 × 10^{-4} *M*, and emission spectrum (——), ~9.8 × 10^{-3} *M*, of 1,3,3-trimethylindolinobenzospiropyran (I) in 3-methylpentane at 77°K.

chromators were used as exciting[4] and analyzing monochromators. An EMI 9558B phototube was utilized as a detector. A Jarrell-Ash combination amplifier and power supply was used to provide voltage to the phototube and to amplify the signal, which was recorded on a Houston Instrument X-Y recorder as intensity *vs.* wavelength. This system is geometrically arranged such that the exciting light is directed normal to the flat surface of the sample cell and the resultant emission monitored at an angle of 22–30°. This front surface arrangement minimizes errors due to reabsorption and allows monitoring of the entire emitting region. The emission and excitation spectra for the 5,6′-dinitro derivative were taken utilizing a 90° arrangement and a 10-mm square emission cell.

Excitation spectra (with the exception of the 5,6′-dinitro derivative) were taken on the same front surface apparatus. Several emission wavelengths were monitored in order to provide assurance that the emission was truly intrinsic to the spiropyran of concern. Wavelength accuracy was ensured by calibration with a mercury line spectrum directly on the chart paper so that true comparison could be made with the absorption spectrum. Relative quantum yields were calculated by utilizing the equation[5]

$$\phi(\lambda) = \frac{F(\lambda)}{I(\lambda)A(\lambda)}$$

where $\phi(\lambda)$ is the relative quantum yield of luminescence as a function of exciting wavelength, $F(\lambda)$ is the intensity of emission, $A(\lambda)$ is the light absorbed, and $I(\lambda)$ is the intensity of the exciting lamp–monochromator system. Unless otherwise indicated, the shape of all emission and excitation spectra may be assumed to be uncorrected.

The solvents used were primarily 3-methylpentane and EPA (ethyl ether, isopentane, ethyl alcohol, 5:5:2 by volume). The EPA was obtained from American Instrument Co. and carefully deoxygenated by a vacuum technique. Pure 3-methylpentane (>99 mole %) was obtained from Phillips Petroleum Co., fractionally distilled over sodium, and run through a silica gel column to ensure both purity and dryness. Deoxygenation was accomplished by at least two cycles of heating to boiling under a nitrogen atmosphere and bubbling with nitrogen gas while cooling to room temperature. This degassed solvent was then used to prepare solutions. Both deoxygenation methods gave clear glasses with no apparent cloudiness and showed no emission.

Sensitization experiments were performed by irradiating samples with and without sensitizer for equivalent periods of time with suitable wavelengths. Concentrations were on the order of 10^{-2} *M* for both acceptor and donor. Temperatures varied from 77°K to −100°. I, II, and 5-chloro-I showed coloration with benzophenone or thioxanthone as donors in fluid solution but not in rigid solution at 77°K.

Lifetimes were determined by using a phosphoroscope, a photomultiplier detector, and oscilloscope–camera system. The lifetime was then determined graphically. The lifetimes shown have a precision of ±5%.

All compounds were purified by fractional crystallization and/or solid–liquid partition chromatography. We wish to thank Dr. E. Fischer, Weizman Institute and National Cash Registor Co., for samples of some of the benzospiropyrans used in this study.

Results and Discussion

Table I compares the spectral properties of all the benzospiropyrans and model systems investigated.

Table I. Emission Properties of Benzospiropyrans and Model Compounds

Compound	Fluorescence wavelength (max), nm	Phosphorescence wavelength (max), nm	Lifetime, sec
Indolinobenzospiropyran	~360[a]	None obsd[a]	
6′-Nitro-	Absent	472[b]	0.079
5-Chloro-6′-nitro-	Absent	471[b]	0.056
5,6′-Dinitro-	Absent	534[c]	0.25
β-Naphthospiropyran	391	None obsd	
Indoline (III)	336	401	1.35
Diethylchromene (IV)	349	None obsd	
Nitrochromene (V)	Absent	510	0.25
p-Nitro-N,N-dimethylaniline (VI)	455	518	0.36
Benzochromene (VII)	392	None obsd	

[a] $\phi_F \simeq 0.001$ and ϕ_P estimated to be 0.0001 or less. [b] This is also the first band origin. [c] First band origin at 502 nm.

Indolinobenzospiropyran Parent (I). Becker and Roy[6] previously reported a phosphorescence for the parent benzospiropyran (I), maximizing at ~410 nm with a lifetime of 0.4 sec. In light of this further work on a highly purified sample, this phosphorescence reported earlier appears to be a spurious one arising from an impurity. We have recently observed a very weak emission, maximizing ~360 nm, Figure 1 and Table I, for the parent benzospiropyran (I). On the basis of the overlap with the absorption, this emission is assigned as a fluorescence. No phosphorescence was observed. The quantum yields determined are relative to 9,10-diphenylanthracene,[7] which has a quantum yield of 1.0.[8] Comparison of quantum yields determined in this manner with the accepted values show very good agreement. For example, the quantum yield of phosphorescence of benzophenone determined by this method is 0.74[7] which compares very well with an absolute quantum yield value of 0.75.[9] Thus, quantum yields determined by this method may also be considered to be absolute quantum yields. The quantum yield of fluorescence for the parent benzospiropyran (I) is, by this method, approximately 0.001 in 3-methylpentane at 77°K. Because of the extreme weakness of the signal, the error may be as large as ±0.0005. On the basis of the signal-to-noise ratio, the quantum yield of phosphorescence is expected to be 0.0001 or less. Thus, photochemistry and internal conversion must account for nearly 100 per cent of the excitation energy.

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(4) In some cases, a Bausch and Lomb 0.25-m grating monochromator was used. In this case, manual scanning of excitation spectra was possible by means of a pair of gears adapted to the wavelength drum which drove a potentiometer circuit supplying a sweep voltage to the *x* axis of the X-Y recorder.

(5) A more detailed explanation may be found in the following papers: R. S. Becker and A. Santiago, *J. Amer. Chem. Soc.*, **90**, 3654 (1968); and R. S. Becker, E. Dolan, and D. E. Balke, *J. Chem. Phys.*, **50**, 239 (1969), and references therein.

(6) R. S. Becker and J. K. Roy, *J. Phys. Chem.*, **69**, 1435 (1965).

(7) R. S. Becker and J. King, *J. Chem. Phys.*, in press.

(8) (a) E. Lim, J. Laposa, and J. Yu, *J. Mol. Spectrosc.*, **19**, 412 (1966). (b) E. J. Bowen and J. Sahu, *J. Phys. Chem.*, **63**, 4 (1959). (c) W. H. Melhuish, *J. Opt. Soc. Amer.*, **54**, 183 (1964).

(9) E. Gilmore, G. Gibson, and D. McClure, *J. Chem. Phys.*, **20**, 829 (1952); **23**, 399 (1955).

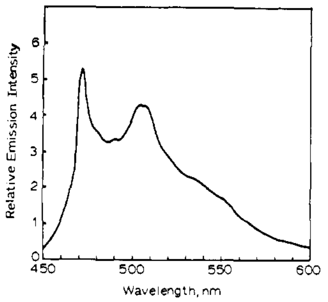

Figure 2. Emission spectrum, ~1.3 × 10^{-4} *M*, of the 6′-nitro derivative in 3-methylpentane at 77 °K.

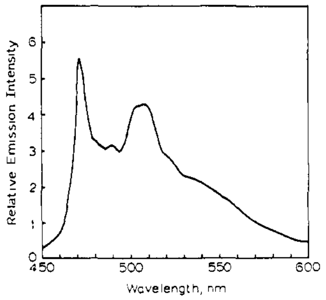

Figure 3. Emission spectrum, ~6.8 × 10^{-5} *M*, of the 5-chloro-6′-nitro derivative in 3-methylpentane at 77 °K.

Fischer, *et al.*,[10] have recently shown quantum yields in fluid solutions of both color formation and color erasure of a series of indolinobenzospiropyrans in 1-propanol–2-propanol solvent at various temperatures. They give a quantum yield of color formation of 0.055 and a quantum yield of color erasure of 0.01 for the parent benzospiropyran (I) at −120° in 1-propanol–2-propanol solutions with 313 nm wavelength irradiation. However, the quantum yield of color formation must be distinguished from the primary photochemical quantum yield in that it does not take into account the spontaneous thermal back-reaction; *i.e.*, unless the molecule remains in the open or colored modification after bond cleavage, it is not "counted" by the quantum yield of color formation. The difference can be more explicitly stated by the scheme

$$\begin{tikzcd} A \arrow[r, shift left, "h\nu"] & A^* \arrow[l, shift left] \arrow[r] & X \arrow[r] \arrow[ll, bend left] & B \end{tikzcd}$$

where A is the colorless form, B is a thermally stable colored form, and X is a thermally unstable intermediate which can either give B or regenerate A. The quantum yield of color formation applies only when the X → B reaction occurs, but the primary photochemical quantum yield would apply for all A → X reactions. Thus, the quantum yield of photochemistry may be expected to be larger than that of color formation, particularly in rigid media. In addition, the quantum yield of color formation in fluid solution may be different from that in rigid media.

On the basis of the above results and discussion and due to the lack of photochemical quantum yields in rigid media, it is impossible to determine whether the rate of internal conversion is greater than the rate of photochemistry or *vice versa*. Also, due to the weakness of the fluorescence observed for the parent benzospiropyran (I), it is impossible to assign unequivocally the exact nature of the transition, *i.e.*, whether it originates from the chromene or indoline half of the molecule. However, based on the facts that (1) a strong (approximately three times the fluorescence) phosphorescence intensity is seen for the indoline (III) and only a fluorescence is seen for diethylchromene (IV), Table I, and (2) the maxima of the fluorescence emissions of the diethylchromene[2] and benzospiropyran parent (I) are approximately the same, Table I, we believe that this weak fluorescence originates from the chromene portion of the molecule. The fluorescence of the parent benzospiropyran (I) is very poorly resolved due to the large slit widths that must be used to observe very weak emissions. Based on the nature of the fluorescence of diethylchromene and the overlap with the absorption transition,[2] the fluorescence of the diethylchromene is assigned as originating from a S_{π,π^*} state. Based on the foregoing, the fluorescence of the parent benzospiropyran (I) is assigned as originating from a S_{π,π^*} state localized on the chromene portion of the molecule. Although a detailed examination of the 5-chloro derivative has not been made, its spectral characteristics are expected to be similar to the parent due to the lack of any easily observable emission and to the mild perturbation due to the chloro substitution.[3]

6′-Nitro- and 5-Chloro-6′-nitrobenzospiropyrans. The spectral location and shape of the emission spectra of the 5-chloro-6′-nitro derivative and the 6′-nitro derivative are almost identical in 3-methylpentane as shown in Figures 2 and 3 and Table I. In addition, the emissions show no change with variation in the exciting wavelength. Both are quite strong emissions having very sharp onsets and strong maxima lying at 471 and 472 nm, respectively. In addition to the two strong bands seen, both emission spectra show weak structure, Figures 2 and 3. The similarity in these two emissions is quite a clear indication that the chloro substitution on the indoline half has no effect on the nature or shape of the emission and thus establishes the fact that the emission has a localized origin on the chromene half. This is in agreement with expectation based on the assignments made earlier (see part I).[3] Further, both emissions are displaced to lower energy from the onset of the absorptions and have nearly the same lifetimes. The lifetime of the 6′-nitro derivative is 0.079 sec and that of the 5-chloro-6′-nitro is 0.056 sec; thus, both emissions are assigned as phosphorescences. In 2-methyltetrahydrofuran the emission of the 6′-nitro derivative shows a sharp origin at 474 nm with a short but sharp vibrational progression of 1450 cm^{-1}. In EPA the origin blue shifts to 467 nm with a vibrational progression of 1530 cm^{-1}. On comparison with the vibrational frequencies observed for aromatic nitro compounds, the spacings correspond closely to NO stretching frequencies. The ground-state asymmetric stretching frequency is 1527 ± 16, 1518, 1523, and 1527 ± 16 cm^{-1} and the symmetric frequency is 1360, 1348 ± 11, 1349, and 1344 cm^{-1}, depending on the compounds used and the investigators.[11] On the basis of the emis-

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(10) T. Bercovici, R. Heiligman-Rim, and E. Fischer, *Mol. Photochem.*, 1, (1), 23 (1969).

(11) C. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958, p 300.

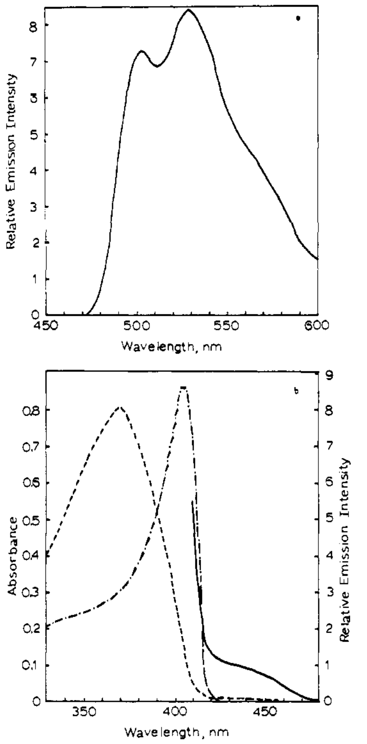

Figure 4. (a) Emission spectrum, ~7 × 10^{-4} *M*, of the 5,6′-dinitro derivative in EPA at 77°K; (b) absorption and excitation spectra of the 5,6′-dinitro derivative at 77°K in EPA. Absorption: ——, ~1.1 × 10^{-3} *M;* ---, ~1.3 × 10^{-4} *M.* Excitation: -·-, ~7 × 10^{-4} *M*, wavelength monitored, 534 nm, also see text relative to dashed portion.

sion data, it is difficult to assign the precise character of the vibration because of errors, particularly in determining the exact maximum of the broader second peak. Careful analysis, however, indicates that the second band in emission (~505 nm) is sufficiently structured in 3-methylpentane that actually two bands are discernible for both the 6′-nitro and 5-chloro-6′-nitro derivatives. In fact a vibrational analysis, at least through the broad second peak, is possible and is shown in Table II for both derivatives. Agreement between the two derivatives is excellent, further supporting assignment of the emission as localized on the chromene half of the molecule. The 1350- and 1360-cm^{-1} vibrations for the 5-chloro-6′-nitro and 6′-nitro derivatives, respectively, can be assigned as the symmetric O–N–O stretching frequency. The 1510- and 1480-cm^{-1} vibrations could be either an asymmetric O–N–O stretching frequency or a combination band (0 + 1350 + 355 and 0 + 1360 + 350 cm^{-1}, respectively). However, since the values determined are precise to ±50 cm^{-1} or less, the combination band possibility is unlikely. Thus, the respective 1510- and 1480-cm^{-1} vibrations appear to represent an asymmetric O–N–O stretching frequency.

Table II. Vibrational Analysis for Emission Spectra of the 5-Chloro-6′-nitro and 6′-Nitro Derivatives

Wavelength, nm	Energy, cm^{-1}	ΔE, cm^{-1}	Assignment
5-Chloro-6′-nitrobenzospiropyran			
471.0 (max)	21,226	0	0
479.0	20,871	355	0 + 355
488.5	20,465	761	0 + 2(355) or 0 + 760
503.0	19,875	1,351	0 + 1350
507.0	19,718	1,508	0 + 1510
6′-Nitrobenzospiropyran			
472.5 (max)	21,158	0	0
480.5	20,806	352	0 + 350
490.0	20,402	756	0 + 2(350) or 0 + 760
505.0	19,796	1,362	0 + 1360
508.0	19,679	1,479	0 + 1480

The emissions of both the 6′-nitro and 5-chloro-6′-nitro derivatives are assigned as a phosphorescence originating in a n,π* triplet state localized in the nitrochromene portion of the molecule based on the following data.

(1) There is a comparatively small separation of the phosphorescences from the absorptions that contain assigned $\pi^* \leftarrow n$ transitions in the long wavelength tails. A small energy separation is characteristic of $S_{n,\pi^*} - T_{n,\pi^*}$ states.

(2) There are sharp vibrational progressions corresponding to N–O stretching frequencies.

(3) There are relatively short lifetimes for the phosphorescences. The assignment of one of the phosphorescences as originating from a T_{n,π^*} is in agreement with an earlier assignment by Becker and Roy[6] for the 6′-nitro derivative.

5,6′-Dinitrobenzospiropyran. The 5,6′-dinitro compound, even after extensive purification, exhibited three emissions consisting of two phosphorescences and one fluorescence in EPA. The existence or intensity of these emissions was exciting wavelength dependent. This might ordinarily be an obvious indication of contamination but considering that the two halves are essentially orthogonal, an ultimate complexity of two phosphorescences and two fluorescence is theoretically possible if intramolecular energy transfer does not occur or is slow. Thus, it was necessary to resolve the source of the multiple emissions. Careful examination of the excitation spectra of one fluorescence (maximum near 495 nm) and one phosphorescence (maximum near 550 nm) indicated the emission intensities maximized outside the region of the onset of absorption of the first transition. Also, high concentrations (~1.1 × 10^{-3} *M*) of the dinitrobenzospiropyran at low temperatures indicate a very weak shoulder in the region of maximization of the foregoing emission intensities.

The other phosphorescence, maximum at 534 nm, Figure 4a, although having an excitation maximum at longer wavelength than the maximum of absorption, was within the region of absorption, Figure 4b. Therefore, although it is possible that the very weak absorption at very high concentration and the one fluorescence and other phosphorescence (maxima at 495 and 550 nm, respectively) are intrinsic to one or the other of the halves, we believe them to originate from impurities. This is based, in a large part, on the foregoing considerations. In addition, intramolecular energy transfer processes should be fast enough to quench the emissions; see later discussion. On the basis of the foregoing, we assign the phosphorescence with a maximum at 534 nm, Figure 4a, and a lifetime of 0.25 sec as the only intrinsic emission. The vibrational spacing is approximately 1000 cm^{-1} which is considerably lower than for the other nitro derivatives discussed earlier,

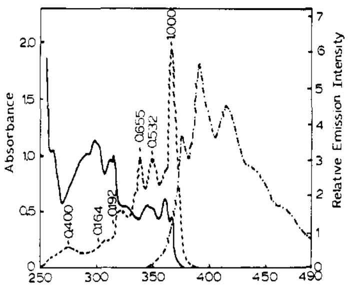

Figure 5. Absorption (——), emission (-·-), and excitation (- - -) spectra of ~4 × 10^{-4} *M* β-naphthospiropyran (II) in 3-methylpentane at 77 °K.

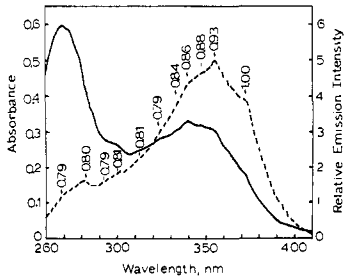

Figure 6. Absorption spectrum (——), ~7.3 × 10^{-5} *M* and excitation spectrum (- - -), ~1.3 × 10^{-4} *M*, of the 6′-nitro derivative in 3-methylpentane at 77 °K.

but the lifetime is also four to five times longer. It is difficult to make an unequivocal assignment of this emission, but we believe the following discussion and assignment to be valid.

The first absorption band maximum at room temperature (351 nm) red shifts some 20 nm (~550 cm^{-1}) at 77 °K (~370 nm), see Figure 5, part I,[3] with little change in structure. The very broad, more intense first band is indicative of a mixture of two transitions. It is very likely that because of a relatively larger red shift of the indoline transition upon nitro substitution compared to the chromene transition, the first band is composed of two electronic transitions, as was discussed in part I.[3] Further, based on the longer wavelength, longer lifetime, and different vibrational spacing of the emission of the dinitro case compared with the two mononitro cases, the emission is assigned as originating from a T_{π,π^*} state. Furthermore, in EPA the intrinsic phosphorescence of the 5,6′-dinitro derivative (τ 0.25 sec) has a first band origin at ~502 nm (maximum 534 nm). The 4-phenyl-6-nitrochromene (V) also has a phosphorescence with a first band origin at 510 nm, which is also the maximum, with a vibrational spacing of 1350 cm^{-1} in 2-methyltetrahydrofuran. The lifetime of the phosphorescence of the chromene is 0.25 sec. Another model which was considered for the nitroindoline half of the 5,6′-dinitro derivative was *p*-nitrodimethylaniline (VI). In EPA at 77 °K, this compound shows both fluorescence and phosphorescence. The phosphorescence has approximately the same splitting as for the 5,6′-dinitro derivative (~1000 cm^{-1}) with a first band origin at ~518 nm which is also the maximum. The phosphorescence lifetime is 0.36 sec. The presence of both a fluorescence and phosphorescence as well as the relatively long lifetime of the phosphorescence indicate that the phosphorescence originates in a T_{π,π^*} state. It is impossible to assign unequivocally the emission of the dinitrobenzospiropyran to one-half of the molecule or the other. However, based on the data from the model systems and since the properties of the intrinsic emission for the 5,6′-dinitro case is different from that for the mononitro cases based on the red shift of the origin by 1300 cm^{-1}, the lifetime, and the vibrational spacing, we feel that the *phosphorescence originates from a* T_{π,π^*} *state localized on the nitroindoline half of the molecule.* This assignment is also consistent with the large red shift of the absorption spectrum of this molecule, associated with the nitroindoline half, when compared to that of the 6′-nitro or 5-chloro-6′-nitro derivatives.[3]

β-Naphthospiropyran. Difficulty was encountered in determining the intrinsic emission of the β-naphthospiropyran (II), again because of the presence of impurities. The overlap of the intrinsic and impurity emissions is such that it is impossible to separate them completely. However, comparison of spectra before and after extensive purification indicates that the impurity emission overlaps only the long wavelength portion of the β-naphthospiropyran emission, and thus would not interfere with the excitation spectrum (see later discussion). The intrinsic emission is a fluorescence. This emission should be similar to that of dimethylbenzochromene[2] since irradiation was into bands assigned only to the chromene half of the molecule. The β-naphthospiropyran emission spectrum, shown in Figure 5, has bands at 375, 391, and 415 nm which compares well with the bands at 372, 392, and 415 nm for the dimethylbenzochromene.[2] The spectrum also is remarkably similar in shape and structure to that of the dimethylbenzochromene. Consequently, the emission is assigned as a fluorescence originating in the benzochromene portion of the β-naphthospiropyran (II).

Based on the characteristics of the dimethylbenzochromene emission, including overlap with the absorption and the mirror image relationship, the fluorescence of the dimethylbenzochromene is assigned as originating from a S_{π,π^*} state. Similarly, based on the above assignment, the similarity of the nature of the absorption and emission compared with the chromene and the overlap of the absorption and emisssion in the benzospiropyran, the fluorescence of the β-naphthospiropyran (I) is assigned as originating from a S_{π,π^*} state localized on the benzochromene half of the benzospiropyran.

Photochemistry and Vibronic Effects. Owing to the extreme weakness of the fluorescence of the benzospiropyran parent (I), it was impossible to obtain an excitation spectrum. For the same reason, no excitation spectrum was obtained for the 5-chloro derivative. The excitation and absorption spectra for the 6′-nitro derivative are shown in Figure 6. As expected, the excitation spectra for the 6′-nitro and 5-chloro-6′-nitro derivatives are strikingly similar although that for the 5-chloro-6′-nitro derivative is slightly better resolved. The nature of the individual excitation spectrum was independent of the wavelength monitored. Wavelength calibration of the excitation spectra was obtained by recording mercury lines on the chart immediately after recording the excitation spectrum. Both curves onset relatively sharply and the first shoulder in both cases corresponds to the longest wavelength shoulder in the

77°K absorption spectra of the two compounds. Both curves show the same following peculiarities.

(1) The emission intensity is highest in the region of onset of absorption.

(2) The emission intensity is weaker where the maximum of absorption occurs.

(3) The emission intensity continues to fall with excitation at shorter wavelengths than the maximum although there is little decrease in the degree of absorption.

Calculations of the relative quantum yields of phosphorescence (see Experimental Section), taking the long wavelength shoulder as 1.00 (372.5 nm and 370 nm in the 6′-nitro and 5-chloro-6′-nitro derivatives, respectively), show a decrease with decreasing wavelength of excitation in both cases. For the 6′-nitro derivative the decrease is not as drastic as in some of the chromenes and, in fact, after falling off initially, levels off at approximately 0.80. The relative quantum yields of emission at chosen wavelengths for the 6′-nitro derivative are shown in Table III and Figure 6. The standard deviations were determined for these relative quantum yields and are well within the limits observed for 9,10-dihydronaphthalene by Becker, *et al.*,[2] *i.e.*, within ±0.05.

Table III. Relative ϕ_P for the 6′-Nitrobenzospiropyran Derivative in 3-Methylpentane at 77°K

Wavelength, nm	ϕ_P
372.5	1.00
355.0	0.93
347.5	0.88
339.5	0.86
333.5	0.84
323.0	0.79
312.5	0.81
300.0	0.81
292.5	0.79
284.5	0.80
282.5	0.80
278.0	0.78
272.5	0.79
269.0	0.79

In order to interpret these results for the 6′-nitro case *i.e.*, the initial drop and then leveling off observed for the relative quantum yields of phosphorescence, several factors must be considered: (1) the possibility of intramolecular energy transfer between the indoline and chromene halves of the molecule and (2) the possibility that photochemistry may occur in either the singlet manifold or triplet manifold, or both.

First of all, the equation for calculating the relative quantum yields, $(\phi)\lambda = F(\lambda)/I(\lambda)A(\lambda)$ (see Experimental Section), contains the per cent absorption of the molecule as the $A(\lambda)$ term in the denominator. The absorption transitions of these molecules (see part I)[8] have been shown to be essentially localized on a particular half of the molecule; consequently, the $A(\lambda)$ term should be a sum of the per cent absorption due to the indoline and nitrochromene; *i.e.*, $A(\lambda)_{\text{total}} = A(\lambda)_{\text{indoline}} + A(\lambda)_{\text{chromene}}$. Further, the $F(\lambda)$ term represents the emission intensity; however, only one emission occurs and it is assigned as originating from the nitrochromene half of the molecule. Therefore, unless intramolecular energy transfer between the indoline portion of the molecule and the nitrochromene portion occurs, the $A(\lambda)$ term in the above equation should be equal only to the $A(\lambda)_{\text{chromene}}$ term in calculating $\phi(\lambda)$. Calculations replacing $A(\lambda)_{\text{total}}$ by $A(\lambda)_{\text{chromene}}$ in a region of strong absorption by the indoline portion (~290 nm) give $\phi(\lambda)$ values nearly twice those calculated using $A(\lambda)_{\text{total}}$; *i.e.*, using $A(\lambda)_{\text{total}}$, $\phi(\lambda) \simeq 0.80$ and using $A(\lambda)$ chromene, $\phi(\lambda) \simeq 1.4$. This indicates that either (1) *photochemistry* (which occurs in the chromene portion of the molecule) actually *decreases* as higher vibronic levels and electronic excited states are excited or (2) intramolecular energy transfer between the indoline moiety and the chromene moiety occurs. The very strong phosphorescence observed for the indoline model (III) is not observed and the energy of the indoline triplet (emission origin and maximum at ~402 nm) relative to that of the chromene triplet (emission origin and maximum at ~472 nm for the 6′-nitro derivative) is favorable for energy transfer.

We feel that relative quantum yield results as discussed above are best explained on the basis of intramolecular energy transfer between the indoline portion and the chromene portion of the 6′-nitro and 5-chloro-6′-nitro derivatives, in agreement with the work of Balny, *et al.*,[12] for the 6′-nitro derivative. Several authors[13] have shown the occurrence of both singlet–singlet and triplet–triplet intramolecular energy transfer with varying degrees of efficiency in systems with nonconjugated chromophores, including a system separated by a spiro carbon. Hammond, *et al.*,[13a] showed that the rate of singlet energy tranfer with $k \sim 10^7$–10^8 sec^{-1} was slower than triplet energy transfer and that triplet energy transfer was 100% efficient. We did not attempt to determine specifically whether the transfer was by singlet–singlet or triplet–triplet mechanisms but only that it did occur. Second, the emission monitored is a phosphorescence while absorption is into a singlet manifold. Sensitization of photocoloration with triplet sensitizers was accomplished by us only under conditions favorable to intermolecular energy transfer by a collisional mechanism. Sensitization attempts in rigid media at liquid nitrogen temperatures failed. This indicates that photochemistry can occur in the triplet state but does not show that it actually does occur utilizing direct excitation. Fischer, *et al.*,[10] observed the triplet as an intermediate decaying at a rate equal to the rate of color formation during flash photolytic coloration of some benzospiropyrans. This indicates participation of the triplet in photochemistry by direct excitation, at least in fluid solutions. However, since intersystem crossing is normally expected to occur only from the 0, 0 level of the lowest singlet excited state to some degenerate vibrational level of an excited triplet, the relative quantum yields of phosphorescence would be insensitive to variation in exciting wavelength into the singlet states if photochemistry occurs only in the triplet. If, however, photochemistry occurs in the singlet manifold *via* a vibronic effect,[2] the relative quantum yields of emission would *decrease* with decreasing wavelength of excitation. Since the relative quantum

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[12] C. Balny, A. Boukhors, C. Cailly, and R. Gautron, *Compt. Rend., Ser. C*, 263, 360 (1966), and references therein.

[13] (a) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Amer. Chem. Soc.*, 87, (11), 2322 (1965); (b) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *ibid.*, 85 (17), 2670 (1963); (c) D. E. Breen and R. A. Keller, *ibid.*, 90 (8), 1935 (1968); (d) R. A. Keller, *ibid.*, 90 (8), 1940 (1968).

yields of emissions for both the 6'-nitro (Table III) and 5-chloro-6'-nitro derivatives do *decrease*, it is evident that photochemistry occurs in the singlet manifold *via* vibronic effects for these derivatives in nonpolar rigid media. Fischer, *et al.*,[10] have recently shown that photochemistry in fluid solution can occur in the singlet manifold. However, whether the photochemistry was a function of the properties of the excited state or vibronic effects was not a part of the study and, therefore, was not determined by them.[10]

The leveling off of the relative quantum yields occurs in the region where the indoline chromophore begins to absorb. The emission of the 6'-nitro derivative arises from (1) direct excitation into the nitrochromene singlet manifold followed by intersystem crossing to the triplet and (2) direct excitation into the indoline singlet manifold and intersystem crossing to the indoline triplet and followed by intramolecular energy transfer to the nitrochromene singlet or triplet from either the indoline singlet or triplet. Based on the foregoing discussion, the relative quantum yields of phosphorescence would be expected to decrease with excitation into higher vibronic levels and excited singlet states of the nitrochromene. Intramolecular energy transfer would occur from the 0, 0 levels of the lowest excited singlet or triplet of the donor (indoline) to acceptor (nitrochromene) excited states, either singlet or triplet, where because of the absence of vibronic effects, the photochemistry is less competitive with emission. This would result in an increase in the relative quantum yields of phosphorescene when irradiating into areas of strong indoline absorption. A combination of the decrease in relative quantum yields due to excitation into upper vibrational levels of the nitrochromene and the increase in relative quantum yield because of excitation into indoline levels could easily account for the leveling off of the relative quantum yields observed. Similar considerations would apply for the 5-chloro-6'-nitro derivative. Unfortunately, the resolution is so poor for both the absorption and emission that a detailed attempt at a vibronic interpretation, as performed for the chromenes,[2] is impossible.

The excitation spectrum for the 5,6'-dinitro case is shown in Figure 4b. The dashed portion at the onset occurs because this has to be estimated since impurity fluorescence contributes in this region. This excitation spectrum maximizes at approximately 403 nm near the onset of the intrinsic absorption and falls off with decreasing wavelength to a greater extent than can be accounted for by the decrease in lamp intensity in the same region. Further, the emission (phosphorescence) monitored has been previously assigned as originating from T_{π,π^*} state localized on the indoline portion of the molecule.

In part I, the lowest absorption transition of the 5,6'-dinitro derivative was shown to consist of a superposition of a nitrochromene transition and a nitroindoline transition. In addition, in this case, we believe that the nitroindoline absorption transition is lowest. It is difficult to make any exact interpretation due to the lack of resolution. However, the characteristic nitrochromene phosphorescence observed for the 5-chloro-6'-nitro and 6'-nitro derivatives is not observed for the 5,6'-dinitro derivative. Further, the possibility of intramolecular energy transfer between the chromene (donor) and indoline (acceptor) portion of the molecule cannot be ruled out. The competition of intramolecular energy transfer with photochemistry cannot be evaluated due to lack of sufficient data. Although actual relative quantum yields of phosphorescence cannot be calculated in this case, reference to Figure 4b shows a drastic decrease in phosphorescence intensity at the absorption maximum (∼370 nm) compared to the onset of absorption (∼404 nm) which corresponds to the maximum of the excitation spectrum. Considering that the absorption at 370 nm is approximately three times that a 404 nm and the emission intensity at 370 nm is approximately one-third that at 404 nm, it is clear that the relative quantum yields of phosphorescence should drop rapidly. Correction for the dropoff in lamp intensity, etc., cannot account for a ninefold change.

The β-naphthospiropyran (II) excitation spectrum, Figure 5, is quite similar to that for dimethylbenzochromene,[2] showing excellent structure compared to the other benzospiropyrans considered. The relative quantum yields and the corresponding wavelengths are shown in Table IV and Figure 5. In the case of the β-naphthospiropyran there is a drastic decrease in emission intensity when the first vibrational level (0 + 450) of the first chromene transition is excited. When the second (0 + 1290) level is excited, the decrease is smaller but still quite large compared to dimethylbenzochromene.[2]

Table IV. Vibrational Analysis and Relative ϕ_F Values for β-Naphthospiropyran in 3-Methylpentane

Wavelength, nm	Energy, cm^{-1}	ΔE, cm^{-1}	Assignment	ϕ_F
366.5	27,277	0	0, 0	1.000
360.5	27,731	454	0 + 450	0.405
350.0	28,563	1,286	0 + 1,290	0.532
344.5	29,019	1,742	0 + 1,290 + 450	0.409
338.5	29,534	2,257	0 + 1,290 + 2(450)[a]	0.655
334.0	29,931	2,654	0 + 2(1,290)[a]	0.465
326.5	30,619	3,342	0 + 2(1,290) + 450 or 0 + 2(1,290) + 2(450)	0.315
321.0	31,144	3,867	0 + 3 (1,290)[a]	0.386
315.0	31,737	0	0, 0	0.192
312.0	32,042	305	0 + 305	0.180
302.0	33,103	1,366	0 + 1,370	0.164
299.0	33,435	1,690	0 + 1,370 + 305	0.166
291.0	34,354	2,617	0 + 2(1,370)	0.157
275.4				0.400
259.0				0.422

[a] This vibrational assignment was made from the excitation spectrum.

In general, however, for the β-naphthospiropyran the relative quantum yield of fluorescence drops from a value of 1.000 at 366.5 nm (0, 0 of the first chromene transition) to 0.192 at 315.0 nm (0, 0 of the second chromene transition) and then rises to 0.400 in a region where the indoline absorbs strongly (∼275 nm). The relative quantum yields of fluorescence for dimethylbenzochromene[2] drop smoothly from 1.0 at 364.0 nm (0, 0 of the first transition) to 0.54 at 315.0 nm (0, 0 of the second transition) and continue to drop to 0.09 at 260.0 nm. This difference probably results from the possibility of intramolecular energy transfer between the indoline (donor) and the benzochromene (acceptor) portions of the molecule and the different geometry of the excited states of the β-naphthospiropyran compared to the dimethylbenzochromene as shown by the difference in their absorption spectra, particularly the 0, 0 band of the first transition (part I).[3] In this case, analysis of the second chromene transition of the spiropyran is more difficult for several reasons. Primarily, the intensity of the second transition is extremely low, compared to that of the first and the structure is virtually unresolved. Second, mixing between the first indoline transition and the second chromene transition occurs.

Becker, *et al.*,[2] have shown that competition between photochemistry and internal conversion occurs at each level of a particular vibration and further that the ratio k_{IC}/k_{PC} can be determined for a particular sequence by consideration of the equation $\log \phi_F(n) = \{\log[k_{IC}/(k_{IC} + k_{PC})]\}n$ where $\phi_F(n)$ is the relative quantum yield of fluorescence, n = vibrational quantum number of a given sequence of a particular vibrational transition, k_{PC} = rate constant for photochemistry, k_{IC} = rate constant for internal conversion, and $n = 0, 1, 2, 3\ldots$ Thus, $\log [k_{IC}/(k_{IC} + k_{PC})]$ is the slope of a plot of $\log \phi_F$ *vs.* n, which should be a straight line. From the $\log [k_{IC}/(k_{IC} + k_{PC})]$ term, $k_{IC}/(k_{IC} + k_{PC})$ and k_{IC}/k_{PC} can be determined. Unfortunately, in the case of the spiropyrans considered here, only the absorption of β-napthospiropyran is sufficiently structured to allow determination of this ratio. Further, only one vibrational sequence of both the first and second chromene transitions can be followed clearly, the 1290- and 1370-cm^{-1} vibrations, respectively. The ratio of $k_{IC}/k_{PC} \simeq 2.1 \pm 0.5$ for the 1290-cm^{-1} vibration indicates that photochemistry is very competitive with internal conversion in this vibrational sequence. Further, if this were the C–O–C asymmetric stretching frequency which has approximately this value in a conjugated system, the high rate of photochemistry would be explained nicely since the primary photochemical step involves cleavage of the C–O bond.[2] The ratio $k_{IC}/k_{PC} \simeq 8.0 \pm 1.5$ for the 1370-cm^{-1} vibration indicates that photochemistry is much less competitive with internal conversion in this vibrational sequence of the second chromene transition. Thus, the results on β-naphthospiropyran are in agreement with and support the results obtained by Becker, *et al.*,[2] on the chromenes.

Summary

It is clear that the emission transitions of the benzospiropyrans considered are localized on the chromene half of the molecule with the exception of the 5,6′-dinitro derivative in which the emission apparently originates from the indoline portion. Further, the nature of the emissions appears to be valid as assigned. Intramolecular energy transfer between the indoline and chromene portions of the molecule clearly occurs. The relative quantum yields of emission, particularly for the β-naphthospiropyran, show and support a vibronic effect (in excited singlet states) in photochemistry.

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Spectroscopy and Photochemistry of Aryloxiranes[1a]

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Abstract: The absorption spectra of several phenyl-substituted oxiranes in 3-methylpentane at −196° are highly structured and characterized by a 0–0 band at 271 ± 3 nm with a more intense, structureless band at ~230 nm. The fluorescence emission of these compounds occurs at 285–340 nm, with a maximum at 305–310 nm. The isomeric 2,3-bis-α-naphthyloxiranes and tetraphenylepisulfide have also been studied. Irradiation into the 0–0 or higher energy absorption bands causes formation of a colored intermediate. Subsequently, the parent alkene and arylcarbene(s), and carbonyl compound(s) are formed in a manner dependent on oxirane symmetry. Phenyloxirane behaves atypically and no divalent carbon fragments are formed. A consistent mechanistic pathway is proposed to explain the photochemistry and spectroscopy of the oxiranes and their photoproducts.

Several aspects of the spectroscopy and photochemistry of phenyloxiranes have been studied.[2] Griffin and coworkers[3] have found that arylcarbenes are generated in addition to aldehydes and/or ketones upon

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[1] (a) Taken from the thesis submitted by R. O. B. in partial fulfillment of the Ph.D. requirements, University of Houston, Houston, Texas; (b) all spectroscopy and low-temperature photochemistry were conducted at the Department of Chemistry, University of Houston, Houston, Texas 77004; (c) all compounds were synthesized and their gross ambient-temperature photochemistry studied in the Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122. These irradiations were conducted in quartz vessels in a Rayonet chamber reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) equipped with sixteen 8-W low-pressure mercury lamps.

[2] For a preliminary report on this work see: R. S. Becker, J. Kolc, R. O. Bost, H. Dietrich, P. Petrellis, and G. W. Griffin, *J. Amer. Chem. Soc.*, 90, 3292 (1968).

[3] (a) H. Kristinsson and G. W. Griffin, *Angew. Chem. Intern. Ed. Engl.*, 4, 868 (1965); (b) H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, 88, 1579 (1966); (c) H. Dietrich, G. W. Griffin, and R. C. Petterson, *Tetrahedron Lett.*, 153 (1968); (d) P. Petrellis and G. W. Griffin, unpublished results.