Table VII. Infrared Data for Dilysine Diamides[a]

Compound	ν_{N-H}	$\nu_{NH_3^+}$	Amide I, $\nu_{C=O}$	COOH, $\nu_{C=O}$	NH_3^+ DEF	Amide II N-H DEF	Amide III	⌬ ring C-H bend
XII	3250 (m)	3060 (m sh)	1658 (s) 1652 (s)	1605 (s sh)	1586 (s)	1555 (s)	1308 (m)	895 (m)[b]
XIII	3315 (m)	3060 (m sh)	1634 (s)	1605 (s sh)	1585 (s)	1547 (s)	1290 (m)	860 (m)[c]
XIV	3305 (m) 3260 (m)	3060 (m sh)	1638 (s)		1582 (s)	1535 (s)	1296 (m)	

[a] Band assignments according to ref 17. [b] 1,2,4,5-benzene ring substitution. [c] 1,4-benzene ring substitution.

Thus the polyamidation of bis(L-lysine)zinc(II) dichloride dihydrate yielded a product containing zinc hydroxide because of partial dissociation of the complex in the basic aqueous phase.

The removal of the metal ion from the polyesters and polyamides yielded six new organic compounds, O,O′-2,5-dichloroterephthaloyl dityrosine, O,O′-terephthaloyl dityrosine, O,O′-isophthaloyl dityrosine, ε-N,ε-N′-2,5-dichloroterephthaloyl dilysine (XII), ε-N,ε-N′-terephthaloyl dilysine (XIII), and ε-N,ε-N′-isophthaloyl dilysine (XIV), which could not have been readily prepared by other methods.

The dityrosine diesters have the ester carbonyl stretching frequency around 1740 cm^{-1}. The significant infrared stretching frequencies of the dilysine diamides are summarized in Table VII.

In this study it was found that the degree of polymerization is primarily governed by the insolubility of the products formed. This appears to be due primarily to the localized charge distribution about the metal ions. Therefore, complexes containing more highly covalent bonds should form polymers of higher molecular weight.

To date no methods for the determination of molecular weights or the degree of polymerization of insoluble chelate polymers have been reported. However, the method described above should be applicable to other chelate polymers prepared by the polymerization of metal chelates containing free functional groups if the metal ion can be removed without destroying other bonds. For high molecular weight polymers this method can tell at least the minimum degree of polymerization. However, for low molecular weight polymers, in which fragments containing the end groups can be isolated, the maximum degree of polymerization can also be determined.

Acknowledgments. The authors wish to thank the Indiana University Chemistry Department for the loan of laboratory space to Ieva O. Hartwell and Dr. George E. Hartwell for many helpful discussions. We also wish to thank the National Science Foundation for financial assistance through Grant G-CP-191.

Photochromic Spiropyrans. I. Absorption Spectra and Evaluation of the π-Electron Orthogonality of the Constituent Halves

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Abstract: The absorption transitions of a series of indolinobenzospiropyrans, at both room temperature and 77°K, for the colorless forms are presented. In addition, spectral data are given for chromenes and an indoline which are treated as models for the appropriate halves of the benzospiropyrans. Analyses of the effect of substitution on the electronic transitions of the model compounds and the benzospiropyrans show that the absorption transitions of the colorless forms are essentially localized on a particular half of the molecule. In addition, a vibrational analysis of the chromene transitions of β-naphthospiropyran is given and shown to be similar to that for dimethylbenzochromene.[2] Assignments of the nature of the absorption transitions, *i.e.*, whether of $\pi^* \leftarrow n$ or $\pi^* \leftarrow \pi$ character, are made for a number of the molecules considered.

Although a great amount of interest has been shown in the spiropyrans as photochromic substances,[3] only a few electronic emission studies and electronic state assignments have been made.[4] The photochromic trans-

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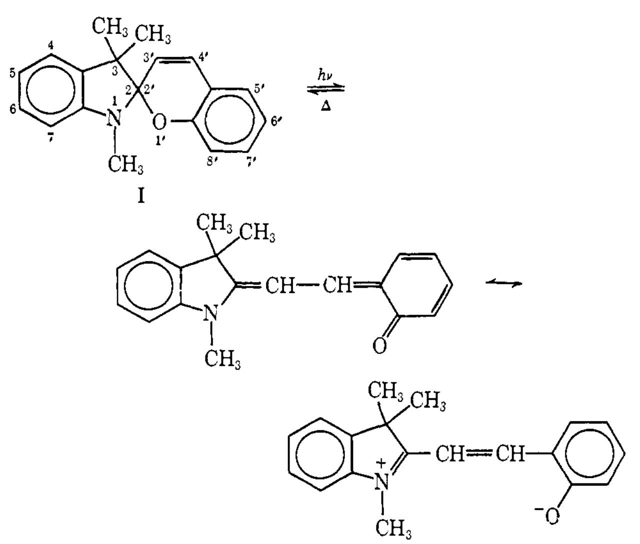
[1] Taken from a dissertation to be submitted in partial fulfillment of the requirements for the Ph.D. degree.

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

[3] In a recent comprehensive photochromism and thermochromism literature survey by the authors, over 75 references were found dealing with the spiropyrans.

[4] (a) C. Balny and P. Douzou, *Compt. Rend., Ser. C.*, **262** (16), 1235 (1966); (b) C. Balny, R. Santus, and P. Douzou, *ibid.*, **262**, 1311 (1966); (c) R. S. Becker and J. K. Roy, *J. Phys. Chem.*, **69**, 1435 (1965).

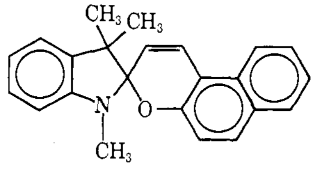
formation is generally considered to involve rupture of the C–O linkage according to the mechanism[5–8]



Thus, the colored modification is considered to consist of a resonance hybrid of a quinoid and a bipolar structure. The initial evidence supporting this mechanism was indirect and based on the resemblance of the absorption spectrum of the colored form to that of the merocyanine dyes.[6] In the course of investigations of the spiropyrans in this laboratory, model compounds for the indoline and chromene portions of the spiropyran were either synthesized or obtained commercially. One result of this was the discovery that the chromenes, some of which occur naturally, were photochromic also. The mechanism proposed was consistent with that for the spiropyrans.[7] Further work involving reaction of the chromene photoproduct with $LiAlH_4$ and then identification of the reduction products provided direct evidence for the above mechanism for the primary process.[8]

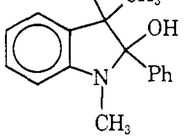
In order to understand fully the photochemical process, the following information is necessary: (1) the assignment of the number and nature of transitions, both absorption and emission, and the determination of whether the transition(s) are "total molecule" in character or restricted to a particular half of the molecule; (2) the effect of temperature on the absorption spectrum; (3) the emission characteristics and nature of the lowest singlet and triplet states; (4) the relative emission quantum efficiency dependence upon the wavelength of excitation; (5) the nature of the absorption of the colored form and the characteristics of the emission; (6) the effect of substitution on the above considerations (3–5); (7) the consequence of sensitization experiments, *i.e.*, whether the colored form can be generated *via* triplet–triplet energy transfer by use of a triplet sensitizer or not.

Solution of these problems will allow assignment of electronic states and determination of the mechanism of the phototransformation. This paper primarily concerns a study of items 1 and 2 above for 1,3,3-trimethylindolinobenzospiropyran (I) and four of its substituted derivatives: 5-chloro, 6′-nitro, 5-chloro-6′-nitro, and 5,6′-dinitro. β-Naphthospiropyran (II) was also studied, primarily because of the striking increase in resolution of the absorption spectrum on cooling from room temperature to 77°K and because of spectral similarities to dimethylbenzochromene.[2]



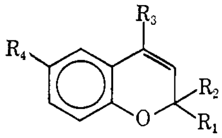
II

Models for the chromene and indoline halves of the molecules were also considered, although a complete study was impossible due to the difficulty of synthesis of some of the models. Only one indoline, 1,3,3-trimethyl-2-hydroxy-2-phenylindoline (III), was available.

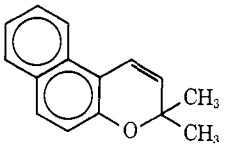


III

Three chromenes, 2,2-diethyl-2H-chromene (IV), 4-phenyl-6-nitro-2H-chromene (V), and 2,2-dimethyl-5,6-benzo-2H-chromene (VI), were available. Thus, comparisons of the absorptions and emissions of the model compounds with those of several of the spiropyrans were possible.



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



VI

This paper concerns the absorption transitions of only the colorless forms of the spiropyrans studied. The absorption spectra of the colorless forms are investigated at both room temperature (~20°) and 77°K. The emission and excitation spectra of the colorless forms are presented in the second part of this series.[9] Assignments of the nature of the emitting states support those of the absorption transitions made here and give some insight into the photochromic mechanism. In addition, for the β-naphthospiropyran (II) and the mononitrobenzospiropyrans a vibronic effect in photochemistry is shown to occur.

Experimental Section

Room temperature and 77°K absorption and per cent transmission spectra were taken on a Cary Model 15 recording spectrophotometer. Quantitative spectra were taken using matched pairs of cells with either Suprasil or optical quartz windows. Qualitative spectra were taken using specially constructed cells with Suprasil windows and approximately 2-mm in path length. These cells, containing the sample, were suspended in a liquid nitrogen containing dewar with flat Suprasil windows.

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(5) R. H. Rim, Y. Hirschberg, and E. Fischer, *J. Phys. Chem.*, **66**, 2470 (1962), and references therein.

(6) R. Heiligman, Y. Hirschberg, and E. Fischer, *J. Chem. Soc.*, **156**, (1961); *J. Phys. Chem.*, **66**, 2465 (1962), and references therein; and J. B. Flannery, Jr., *J. Amer. Chem. Soc.*, **90**, 5660 (1968).

(7) R. S. Becker and J. Michl, *ibid.*, **88**, 5931 (1966).

(8) R. S. Becker and J. Kolc, *J. Phys. Chem.*, 71, 4045 (1967).

(9) N. W. Tyer, Jr., and R. S. Becker, *J. Amer. Chem. Soc.*, **92**, 1295 (1970).

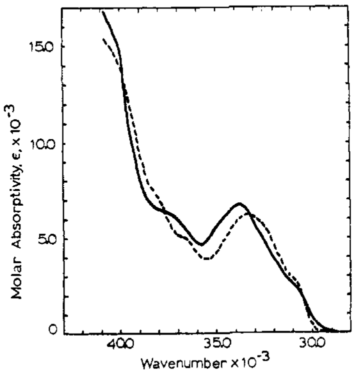

Figure 1. Molar absorptivity *vs.* wave number for 1,3,3-trimethylindolinobenzospiropyran (I) (——) and sum of molar absorptivities *vs.* wave number for 1,3,3-trimethyl-2-hydroxy-2-phenylindoline (III) and 2,2-diethyl-2H-chromene (IV) (- - -) in 3-methylpentane at room temperature.

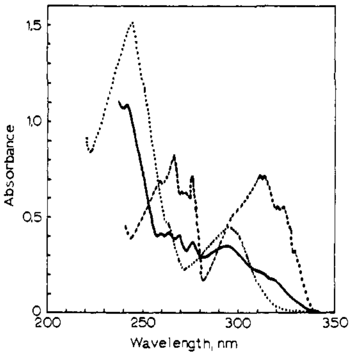

Figure 2. Absorption spectra of ~1.7 × 10^{-4} *M* 1,3,3-trimethylindolinobenzospiropyran (I) (——), 2,2-diethyl-2H-chromene (IV)[2] (- - -), and ~5.1 × 10^{-4} *M* 1,3,3-trimethyl-2-hydroxy-2-phenylindoline (III) (· · · ·) in 3-methylpentane at 77 °K.

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. No purification was attempted but solutions were 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 deoxygenations methods gave clear glasses with no apparent cloudiness.

In order to compare the relative intensities of the first two bands of the β-naphthospiropyran (II), molar absorption coefficients were calculated at room temperature in 3-methylpentane and EPA. The values for the 360- and 347-nm bands were 4570 and 4830 l. mole^{-1} cm^{-1} in 3-methylpentane and 4580 and 4780 l. mole^{-1} cm^{-1} in EPA.

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

Results and Discussion

Examination of the structure of the parent benzospiropyran (I) indicates that the two halves are, topologically, essentially orthogonal. Thus, it might be expected that the π-absorption spectrum could consist of localized transitions belonging to a particular half of the molecule rather than delocalized transitions belonging to the molecule as a whole. Further, a maximum of four emissions, two originating from each half, are possible if there is true orthogonality of the π wave functions and no energy transfer between the two halves.

Absorption of Colorless Forms. In order to determine the accuracy of the prediction of orthogonality of the π wave functions of the two halves, molar absorption coefficients were calculated for the parent benzospiropyran (I), the indoline (III), and 2,2-diethylchromene (IV) in 3-methylpentane at room temperature. The sum of the molar absorption coefficients for the chromene and indoline was compared to that of the parent. The results are shown in Figure 1 as ε *vs.* cm^{-1}. The agreement is generally quite good taking into consideration the errors inherent in the three quantitative determinations. Three additional possibilities could exist to account for the differences. First, the indoline molecule chosen is not the best model possible due to the phenyl group substituted in the 2 position. This substitution might slightly red shift the spectrum from that of the methyl-substituted case and together with some steric ring strain considerations could account for the 560 cm^{-1} difference in the maxima. Further, comparison of the low-temperature absorption spectrum of the indoline (III) with that of the simply substituted indoline, 1,2,3,3-tetramethylindoline,[10] shows good agreement both in relative intensities and position of the transitions. Thus, it is believed that the indoline (III) is a good model and that the phenyl group in III does not add complications because of the spectrum associated with it. Second, there is the possibility of interaction between the methyl groups substituted in the 1 and 3 positions in the indoline half and the lone pair electrons of the oxygen and the hydrogen substituted in the 3′ position in the chromene half. Third, the N and O lone pair electrons are geometrically suitably located for interaction with the π electrons of the halves. Despite all of these potentially complicating features, it is clear that they exert only minor influence and that the π electronic systems are essentially orthogonal. Thus, the absorption transitions of the benzospiropyrans are primarily localized transitions although mixed in certain spectral regions. It is now possible to assign the transitions in benzospiropyran (I) and its derivatives as belonging to or consisting of particular transitions of the individual halves of the molecule.

Indolinobenzospiropyran Parent (I). Comparison of the 77 °K absorption spectrum of the parent benzospiropyran (I) with those of the indoline (III) and diethylchromene (IV),[2] Figure 2 (in addition to those at room temperature), allow an assignment of the transitions in the parent, Table I.

Table I

Compd transitions[a]	Spiropyran (I)	Diethylchromene (IV)	Indoline (III)
1	324 (sh), 312.5 (sh)	311, 313 (sh)	
2	296		295
3	265[b]	265	
4	243.5		244

[a] Band maxima in nanometers, except where noted (sh = shoulder). See Figure 2 for additional spectral detail. [b] A series of resolved bands exist in this region at 276, 270, 265, and 260 nm.

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(10) C. Balny, A. Boukhors, C. Cailly, and R. Gautron, *Compt. Rend., Ser. C*, 263, 360 (1966).

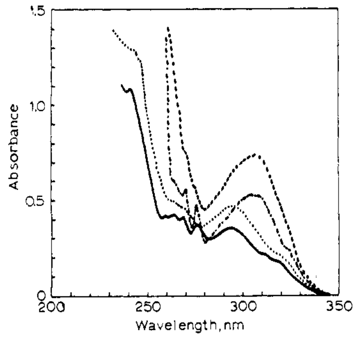

Figure 3. Absorption spectra in 3-methylpentane of 1,3,3-trimethylindolinobenzospiropyran (I) at 77°K (——), 1.7×10^{-4} *M;* at room temperature (····), $\sim 2.6 \times 10^{-4}$ *M;* and of the 5-chloro derivative at 77°K (-·-), 3.6×10^{-4} *M;* at room temperature (---), $\sim 5.5 \times 10^{-4}$ *M*.

The band maxima of the indoline transitions in the parent (I) can be clearly seen, but, due to mixing of the indoline and chromene transitions in the 310- and 265-nm regions, the chromene transitions appear as shoulders on the stronger indoline transitions, Figure 2. Further support for these assignments is provided for by an examination of the effect of substitution on the absorption spectrum. The 5-chlorobenzospiropyran was chosen since the effect of the chloro substitution essentially should be to shift only the indoline transitions if the two halves of the molecule are orthogonal or nearly so.

5-Chlorobenzospiropyran. Examination of Figure 3 shows that the indoline transition with a maximum at 296 nm in the parent has red shifted to 305 nm in the 5-chloro derivative as would be expected from a conjugative substitution. The shoulders at 312.5 and 324 nm in the parent can now be seen at approximately 310 and 324 nm in the 5-chloro derivative. Little or no shift would be expected for the chromene transition. The second indoline transition has shifted in a similar manner to the first although this is not as clear as for the first transition. Thus, the nature of the transitions in the parent appear to be properly assigned.

6′-Nitrobenzospiropyran. In a similar manner, the transitions of the 6′-nitrobenzospiropyran can be assigned, Table II. Figures 4 and 5 show the 77°K absorption spectra of the 4-phenyl-6-nitrochromene (V) and the 6′-nitro derivative, respectively.

Table II

Compd transitions[a]	6′-Nitro derivative	Nitrophenyl-chromene (V)	Indoline (III)
1	340[b]	358	
2	300		295
3[c]	269	279	

[a] Band maxima in nanometers. [b] A series of weakly resolved bands exist in this region at 372.5 (sh), 355, 347.5, 333.5, and 323 nm. [c] Not shown in Figure 5.

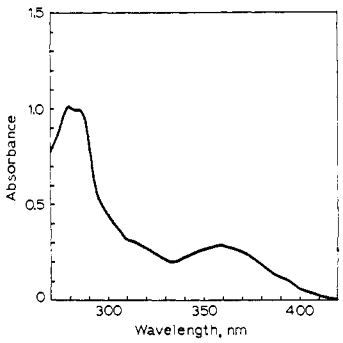

Figure 4. Absorption spectrum of 4-phenyl-6-nitro-2H-chromene (V) in 2-methyltetrahydrofuran at 77°K.

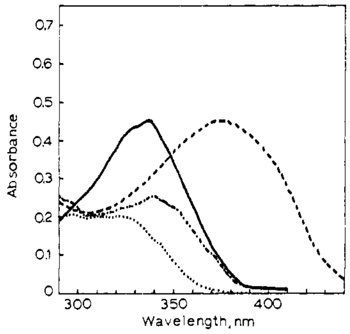

Figure 5. Absorption spectra in 3-methylpentane of the 5,6′-dinitro derivative of benzospiropyran (I) at 77°K (---), saturated solution, at room temperature (——), saturated solution; and of the 6′-nitro derivative of benzospiropyran (I) at 77°K (-·-), $\sim 1.2 \times 10^{-4}$ *M;* at room temperature (····), $\sim 9.5 \times 10^{-5}$ *M*.

The first principal transition of the 6′-nitrobenzospiropyran with a band maximum at 340 nm is assigned to the nitrochromene half of the molecule. There is approximately a 1600-cm^{-1} blue shift of this maxima compared to the nitrochromene (V). However, the nitrochromene (V) itself is not a perfect model since it has a phenyl group substituted in the 4 position which would be expected to red shift the absorption spectrum with respect to the unsubstituted nitrochromene. Comparison of the spectrum of naphthalene with those of 1-phenyl- and 2-phenylnaphthalene indicate shifts of similar magnitude.[11] Furthermore, the solvent used for the nitrochromene (V) spectrum was 2-methyltetrahydrofuran, leading to a further red shift compared to the absorption spectrum of the 6′-nitro derivative in 3-methylpentane. Similar considerations apply for the third transition which is also assigned to the nitrochromene half of the molecule. No problem exists with assignment of the second transition of the 6′-nitrobenzospiropyran to the indoline half of the molecule.

5-Chloro-6′-nitrobenzospiropyran. Figure 6 shows the 77°K absorption spectrum of the 5-chloro-6′-nitrobenzospiropyran. The chloro substitution would be expected to red shift only the indoline transitions. Comparison with Figure 5 shows the first transition to be relatively unaffected in its long-wavelength edge, *i.e.*, it has a shoulder at ~370 nm which corresponds nicely with the shoulder at ~372.5 nm in the 6′-nitrobenzospiropyran. The indoline transition, however, is red shifted and the band appearing at ~310 nm in the 5-chloro-6′-nitro derivative can be assigned to the indoline half of the molecule (parallel in location to the indoline transition at 305 nm assigned for the 5-chlorobenzospiropyran). Similarly, the transitions at 268 and 254.5 nm (not shown in Figure 6) can be assigned to the

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(11) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1951, spectra 195, 290, and 297.

nitrochromene and indoline halves, respectively. These spectral data give strong additional support to the assignments of the transitions for the 6′-nitrobenzospiropyran given above.

5,6′-Dinitrobenzospiropyran. In the case of the 5,6′-dinitro derivative, we did not attempt to assign the bands as belonging to one particular half of the molecule due to the drastic change in the absorption spectrum and lack of a nitroindoline model. Figure 5 shows the room temperature and 77°K absorption spectra of both the 6′-nitro and 5,6′-dinitro derivatives in 3-methylpentane. In the dinitro case, the spectrum is red shifted to such an extent that the solution appears pale yellow at 77°K. It is believed, however, that the transitions due to the nitrochromene half of the molecule lie as previously noted for the two mononitro benzospiropyrans (6′-nitro, 5-chloro-6′-nitro) and that the new long wavelength transition (~370 nm) is now a superposition of the nitroindoline and nitrochromene portions of the molecule. In fact, it is very likely that the longest wavelength portion of the lowest energy transition (max ~370 nm) belongs to the nitroindoline. Further substantiation of this is considered in the paper on emission.[9] In 3-methylpentane the long-wavelength band is much broader than in EPA but the maxima occur at approximately the same wavelength.

Temperature Effects. Similar assignments for the transitions can be made from an examination of the effect of lowering the temperature on the absorption spectra. The benzospiropyran parent (I) and the 5-chloro substituted derivative primarily show increased resolution on lowering the temperature from room temperature to 77°K, Figure 3. The 6′-nitro, the 5-chloro-6′-nitro, and the 5,6′-dinitro derivatives show a marked shifting in their absorption spectra on cooling from room temperature to 77°K, Figures 5 and 6. The latter three molecules have the same basic topology, differing only in the nature of the substitution on the indoline half of the molecule. In all three cases, there is a marked red shift in going from room temperature to 77°K. In the case of the 6′-nitro and 5-chloro-6′-nitro derivatives, there is a marked red shift in the transitions assigned to the nitrochromene half of the molecule while those assigned to the indoline half remain stationary. This is consistent with the observation, Figure 2, that the indoline transitions do not shift on cooling from room temperature to 77°K. For example, the band at ~310 nm in the 77°K absorption spectrum of the 5-chloro-6′-nitro derivative which was assigned to the indoline half of the molecule corresponds to a band at ~312.5 nm in the room temperature absorption spectrum. Similar considerations for the 6′-nitro derivative support the assignment of the transitions previously made. Since the benzospiropyran parent (I) and the 5-chloro derivative show no shifts on lowering the temperature, the nature of the substitution (the nitro group) and its position on the chromene half of the molecule must be responsible for the marked shifting.

Nature of the Transitions. The indoline transitions red shift upon conjugative substitution of a chloro group in the 5 position, as seen by comparison of the spectra of the indoline, the parent benzospiropyran (I), the 5-chloro derivative, the 6′-nitro derivative, and the 5-chloro-6′-nitro derivative. In addition, based on the absorption spectrum of the indoline, the indoline transitions are assigned as $\pi^* \leftarrow \pi$ as are the indoline transitions in the benzospiropyran molecules. This is consistent with and supported by the emissions of the indoline.[9] The indoline has both a fluorescence overlapping the first transition and maximizing at 336 nm, as well as phosphorescence, maximizing at 401 nm, with a lifetime of 1.35 sec. These are assigned as originating from the lowest S_{π,π^*} and T_{π,π^*} states of the indoline (III).

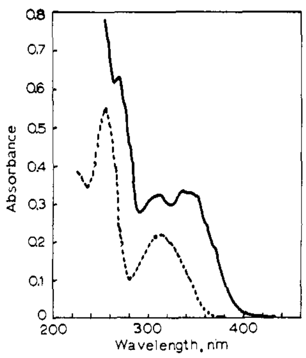

Figure 6. Absorption spectra in 3-methylpentane of the 5-chloro-6′-nitro derivative of benzospiropyran (I) at 77°K (——), ~8.1 × 10^{-5} *M;* at room temperature (- - -), ~5.25 × 10^{-5} *M.*

Little or no shift is noted for any of the absorption bands (at room temperature) in the parent benzospiropyran (I) upon changing the solvent from 3-methylpentane to EPA. Similar results were noted for diethylchromene. In addition, based upon the nature of the transitions in the chromene and the overlap of the fluorescence of the chromene with the first transition,[2] the chromene transitions are assigned as $\pi^* \leftarrow \pi$ as are the chromene transitions in both the parent benzospiropyran (I) and the 5-chloro derivative. The fluorescence of the chromene[2] is assigned as originating from the lowest S_{π,π^*} state. A very weak fluorescence,[9] assigned as originating from a S_{π,π^*} localized on the chromene portion of the molecule, has been found for the parent benzospiropyran (I).

As previously noted, substitution of a nitro group in the 6′ position of the benzospiropyran (I) causes a drastic shift in the absorption spectrum because of shifting of the chromene transitions to longer wavelengths, leaving the indoline transition relatively undisturbed. The shoulders appearing at ~370 nm (77°K) in both the 6′-nitro and 5-chloro-6′-nitro derivatives, in fact, appear to be new transitions localized primarily on the nitro chromophore rather than a shift in the original transitions. Comparison of the spectrum of the 5-chloro-6′-nitro derivative in 3-methylpentane and EPA shows a general loss of structure in the long wavelength bands. The bands previously assigned as belonging to the indoline portion of the molecule remain relatively stationary but the new long wavelength band blue shifts while the chromene band assigned as having $\pi^* \leftarrow \pi$ character in the parent benzospiropyran (I) appears to red shift slightly. It is impossible to determine the exact shifts due to the very weakly resolved structure in 3-methylpentane and the lack of structure in EPA. However, from the shape of the curves and positions of maxima and minima, the shifts can be seen to actually occur as noted. Consequently, the new transi-

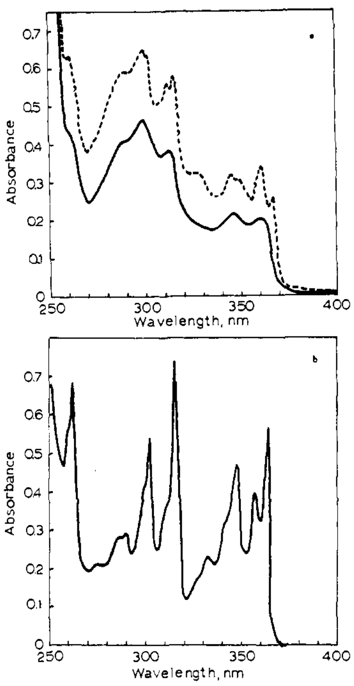

Figure 7. (a) Absorption spectra in 3-methylpentane of the β-naphthospiropyran (II) at 77°K (---), ~2.6 × 10^{-4} *M;* and at room temperature (——), ~2.0 × 10^{-4} *M;* (b) absorption spectrum of 2,2-dimethyl-5,6-benzo-2H-chromene (VI)[2] at 77°K (——) in 3-methylpentane.

Table III. Vibrational Analysis of β-Naphthospiropyran (II) in 3-Methylpentane[a]

Wavelength, nm	Energy, cm^{-1}	ΔE, cm^{-1}	Assignment
366.5	27,277	0	0, 0
360.5	27,731	454	0 + 450[b]
350.0	38,563	1,286	0 + 1,290[b]
344.5	29,019	1,742	0 + 1,290 + 450
326.5	30,619	3,342	0 + 2(1,290) + 450 or 0 + 2(1,290) + 2(450)
315.0	31,737	0	0, 0
312.0	32,042	305	0 + 305[b]
302.0	33,103	1,366	0 + 1,370[b]
299.0	33,435	1,690	0 + 1,370 + 305
291.0	34,354	2,617	0 + 2(1,370)

[a] See ref 2 for a vibrational analysis of 2,2-dimethyl-5,6-benzo-2H-chromene. [b] The 450-, 1290-, 305-, and 1370-cm^{-1} vibrations are 500, 1350, 310, and 1370 cm^{-1}, respectively,[2] in 2,2-dimethyl-5,6-benzo-2H-chromene.

tion seen at long wavelengths in both the 6′-nitro and 5-chloro-6′-nitro derivatives can be assigned as an $\pi^* \leftarrow n$ transition localized on the chromene half of the molecule. This is consistent with the assignment of a sole phosphorescence emission originating from the T_{n,π^*} state for both the 6′-nitro[4c,9] and 5-chloro-6′-nitro[9] derivatives.

β-Naphthospiropyran. In the case of the β-naphthospiropyran (II), the absorption spectrum shows no spectral shift on cooling from room temperature to 77°K in 3-methylpentane. It is particularly interesting to note the dramatic increase in fine structure in going from room temperature to 77°K as shown in Figure 7a. The 77°K absorption spectrum of dimethylbenzochromene[2] is also shown in Figure 7b. A vibrational analysis of the absorption spectrum of β-naphthospiropyran (II) is shown in Table III and the fundamentals are compared with the dimethylbenzochromene. The β-naphthospiropyran transitions originating at 366.5 and 315 nm are equivalent to the first and second dimenthylbenzochromene transitions originating at 364 and 315 nm, respectively, Figures 7a and 7b. Assignment of the 326.5-nm band to a particular transition was impossible until comparison with the vibrational analysis of dimethylbenzochromene was made. Even so, difficulties are encountered because of mixing of the second transition of the chromene half with the first transition of the indoline half (maximum at 295 nm) and a general loss of structure possibly due to interactions of the type discussed earlier for the parent benzospiropyran (I). The shape of the first transition in β-naphthospiropyran notably differs from dimethylbenzochromene in terms of the relative intensities of the 0–0 band and the 450- and 1290-cm^{-1} vibrational components, see Figures 7a, 7b. Several of the vibrational bands seen in the dimethylbenzochromene are not discernible in the β-naphthospiropyran but, in general, the remaining agreement is very good. The 326.5-nm band in the β-naphthospiropyran can be assigned to the first chromene transition although it is difficult to determine whether it represents the 0 + 2(1290) + 450 or 0 + 2(1290) + 2(450) combination bands. Greater difficulties are encountered in the second chromene transition due to the mixing with the first indoline transition. In this case, it appears that the 291-nm band corresponds to 0 + 2(1370) combination band. The indoline transitions are expected to lie as previously noted but due to their broad, structureless character and mixing with the second chromene transition cannot be easily distinguished. On changing solvent polarity from 3-methylpentane to EPA, little or no shift is noted. The absorption transitions of the dimethylbenzochromene are assigned as $\pi^* \leftarrow \pi$ transitions based on the nature of the dimethylbenzochromene bands and the nature and location of the fluorescence.[2] Based on the assignment of the first two transitions of the β-naphthospiropyran as dimethylbenzochromene transitions and the ε values of the bands in this spiropyran, the first two transitions in β-naphthospiropyran are assigned as $\pi^* \leftarrow \pi$. The nature and location of the fluorescence of the β-naphthospiropyran[4c,9] is in accord with this assignment.

Summary

Thus, it is clear that the absorption transitions of the benzospiropyrans are localized on a given half of the molecule and 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, the nature of the transitions appears to be valid as assigned.

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