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Ground- and First-Excited-Singlet-State Electric Dipole Moments of Some Photochromic Spirobenzopyrans in Their Spiropyran and Merocyanine Form[†]

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The dipole moments of four photochromic derivatives of indolinospirobenzopyran have been studied in their spiro and their open merocyanine form, in dioxane. Determinations have been done by electrooptical absorption measurements (EOAM). To prepare either a pure spiropyran or a pure merocyanine form solution, the experimental setup had to be modified by addition of a second light beam. In this way thermal equilibration between the spiropyran and the merocyanine form and switching from one form to the other induced by the measuring light beam could be avoided. The ground-state dipole moment of the spiro form amounts to (10−15) × 10^{-30} C m and increases strongly to about 60 × 10^{-30} C m with the excitation to the first excited singlet state. The ground-state dipole moment of the merocyanine form is much larger and amounts to (50−60) × 10^{-30} C m. In contrast to the spiro form it decreases to about 40 × 10^{-30} C m, when exciting to the first excited singlet state of the merocyanine form.

1. Introduction

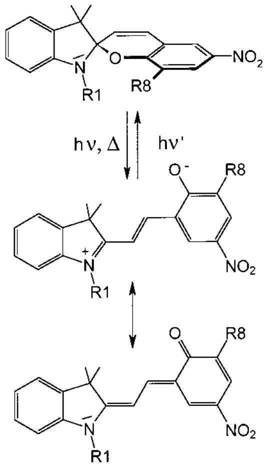
The reversible cleavage of the C−O bond in spirobenzopyrans to yield a merocyanine is an interesting example of photochromism. Since its discovery by Fischer and Hirshberg,[1] the process has been studied under various aspects. References 2 and 3 present a good overview over the wide variety of potential applications of these compounds. The ring-opening process is accompanied by a strong increase of the ground-state dipole moment.[2] But not much is known about the electric dipole moment of the first singlet excited states of the closed and open form.

Hence, in this communication the electric dipole moment in the ground state and first excited singlet state is determined for both forms. The experimental technique involved is generally called electrooptical absorption measurements (EOAM).[4,5] To be able to keep the spiro/mero equilibrium on the desired side, the standard experimental setup described[6] is modified.

2. Experimental Section

2.1. Spirobenzopyrans. Figure 1 presents the photochromic spiropyrans considered in the present communication. They have been prepared by closely following the procedures below.[7]

2.2. Solvents. For EOAM, dioxane only has been used since the investigated compounds were sufficiently soluble in dioxane and a light-induced equilibrium between both forms could be established so as to be able to perform EOAM on both forms. An additional advantage of dioxane is with all EOAM applications that it is not sensitive to electrical break down under high voltage. Dioxane has been bought from Merck (order no. 1.09671). It was rectified and was dried immediately before use over silica (25 mL dioxane over about 1 g each of silica (ICN Alumina N-Super I, order no. 42500, and ICN Alumina B-Super I, order no. 04574, in a small liquid chromatography column).



		R1	
		CH_3	CH_2CH_2COOH
R8	H	MMNS	CMNS
	NO_2	MDNS	CDNS

Figure 1. Photochromism and structure of the studied indolinospirobenzopyrans.

2.3. Experimental Setup of EOAM. The experimental setup used in the present experiment is given in Figure 2.

It corresponds basically to that discussed in refs 5 and 6, with some additions. In Figure 2 the light beam from lamp L1 (Osram XBO 450 W/4) passes through the monochromator M (Carl Zeiss, model MM12Q) and then through the glan prism polarizer P, passing the high voltage measuring cell with its parallel plate electrodes and then falling onto the photomulitplier PM (EMI 9558 QB). The additional light beam from lamp L2 (Osram XBO 75 W/2) passing through filter F2 is collimated into the cell via a quartz window positioned under 45° with respect to the primary beam from lamp L1. In order to avoid scattered

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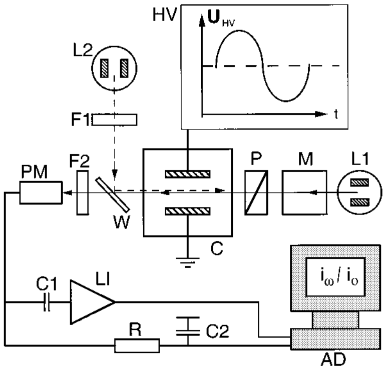

Figure 2. Experimental setup for electrooptical absorption measurements (EOAM) on light induced switchable compounds. (Abbreviations see text).

light from the L2 beam from falling on the photomultiplier, an additional filter F2 is placed in front of the photomultiplier. F1 and F2 are chosen so that the long wavelength light from L1 probing the cell content can pass F2 to reach the photomultiplier, but the short wavelength light from L2/F1 is efficiently blocked by F2. A high DC-electric field of the order of 10^7 V/m from source HV and modulated with frequency 90 Hz is applied to the solution in cell C. The induced electric dichroism then modulates the probing light beam from lamp L1. The resultant modulated component i_ω of the photomultiplier current is fed through a capacitor C1 to a lock-in amplifier (Ithaco, model Dynatrac 393) locked to the modulation phase of the high voltage HV applied to the cell. The average value i_o of the photomultiplier passes a low pass filter R/C2, and a personal computer equipped with a signal processing board (AD, National Instruments, model AT-MIO-16XE-50) calculates i_ω/i_o and from this the quantity AL

$$\mathrm{AL} = (i_\omega/i_o)/((\ln 10)E_{\mathrm{DC}}E_{\mathrm{AC}}) \tag{1}$$

where E_{DC} and E_{AC} are the applied average DC-electric and AC-electric fields.

A laboratory-made program averages i_ω/i_o over a desired time, computes AL according to eq 1, and corrects for a calibration factor. It then displays the average value of AL and its standard deviation. AL is determined as a function of the angle φ between the external electric field and the electric field vector of the light beam determined by the polarizer P, and as a function of the wavenumber ν, determined by the monochromator M. Hence, the primary experimental result is AL(φ,ν). It is used for further evaluation according to Liptay's theory,[4,5] which is shortly described in the next section. Absolute calibration of an EOAM setup is described in ref 8 where absolute AL(φ,ν) values for the compound 4-amino-4′-nitro-biphenyl had been determined, too. All further calibration is done with reference to these values.

2.4. Evaluation of Dipole Moments from EOAM. Liptay's formalism and model[4,5] is used here. Then AL(φ,ν) is related to molecular quantities through the following relationship, where dipole moment terms only are taken into account. Polarizability and transition polarizability terms are neglected here, since they are considered small compared to the relatively large dipole moments of the spiropyran or the merocyanine form of the investigated compounds.

$$\mathrm{AL}(\varphi,\nu) = C + ArD/5 + AsE/30 + ArtF + AstG + AruH + AsuI \tag{2}$$

where $A = A(\nu)$ is the absorbance of the compound to be analyzed at wavenumber ν:

$$r = (2 - \cos^2\varphi) \tag{3}$$

$$s = ((3\cos^2(\varphi)) - 1) \tag{4}$$

$$t = (5hc)^{-1}(\nu/A)\,\mathrm{d}(A/\nu)/\mathrm{d}\nu \tag{5}$$

$$u = (10h^2c^2)^{-1}(\nu/A)\,\mathrm{d}^2(A/\nu)/\mathrm{d}\nu^2 \tag{6}$$

h is Planck's constant and c is the velocity of light.

$t = t(\nu)$ and $u = u(\nu)$ are derived from the first and second derivative of the absorption spectrum and are calculated at the center point of a running third-order polynomial smooth over 39 spectral points with 0.1 nm steps.

To determine AL(φ,ν), the small electric field induced relative changes (i_ω/i_o) of the intensity of the light beam passing the cell must be measured. Due to photon statistics, this means relatively high light intensities. With the photochromic compounds investigated here, such intensities cause the equilibrium between the spiro and the merocyanine form to shift during the measuring time. To avoid this, the additional light beam from lamp 2 (Figure 2) is used which shifts the equilibrium toward the desired side. In the present case this is especially important when studying the merocyanine isomer of the mononitro compounds, since the thermal equilibrium at room temperature and in dioxane lies in these cases on the spiro side. It is likewise important when studying the spiro form of the dinitro compounds, where the thermal equilibrium is shifted toward the merocyanine side.

Because of the light intensity dependent spiro-mero form equilibrium the standard absorption spectrum of the mero isomer can be determined in commercial spectral photometers but with great care, only. Hence such standard UV−vis spectra from a LAMBDA 2 spectral photometer (Perkin-Elmer) have been additionally checked using the same setup (Figure 2) to determine the absorption spectrum $A(\nu)$. As with standard single beam photometers, the absorption spectrum $A(\nu)$ of the mero isomer is determined as $A(\nu) = \log(I_o(\nu)/I(\nu))$, where $I_o(\nu)$ is the photon current on the photomultiplier with no mero form in the cell (lamp 2 switched off, zero absorbance at the mero form absorption band) and $I(\nu)$ the respective photon current under stable equilibrium conditions (lamp 2 switched on, mero form absorbance present in the cell). From this absorption spectrum, t and u then are determined as described above. The agreement was within small error limits.

If nonpolar solutions are only considered and with the approximations discussed above Liptay's more complex formalism reduces to

$$C \approx D \approx 0 \tag{7}$$

$$E = (kT)^{-2}f_e^{\,2}[3(\mathbf{m}\cdot\boldsymbol{\mu}_\mathbf{g})^2 - \boldsymbol{\mu}_\mathbf{g}^{\,2}] \tag{8}$$

$$F = (kT)^{-1}f_e^{\,2}\boldsymbol{\mu}_\mathbf{g}\cdot(\boldsymbol{\mu}_\mathbf{e} - \boldsymbol{\mu}_\mathbf{g}) \tag{9}$$

$$G = (kT)^{-1}f_e^{\,2}(\mathbf{m}\cdot\boldsymbol{\mu}_\mathbf{g})\,(\mathbf{m}\cdot(\boldsymbol{\mu}_\mathbf{e} - \boldsymbol{\mu}_\mathbf{g})) \tag{10}$$

$$H = f_e^{\,2}(\Delta\mu)^2 \tag{11}$$

$$I = f_e^{\,2}(\mathbf{m}\cdot(\boldsymbol{\mu}_\mathbf{e} - \boldsymbol{\mu}_\mathbf{g}))^2 \tag{12}$$

where k is Boltzmann's constant and T the temperature. Here, vectors are bold face.

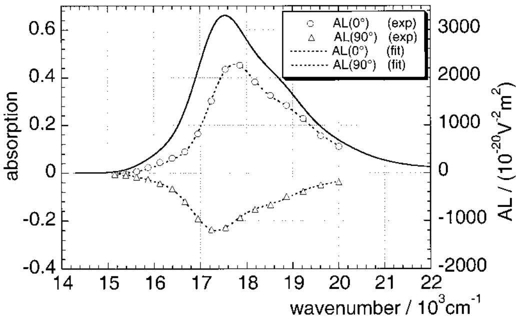

Figure 3. The absorption spectrum of the merocyanine form of CDNS (solid line), determined with a LAMBDA 2 photometer, its electrooptical spectrum AL(φ,ν) at $\varphi = 0°$ (*o o o*) and $\varphi = 90°$ (Δ Δ Δ) and the respective approximations according to eq 2 (dashed lines).

TABLE 1: Values for $E-G$, Determined from EOAM on the Merocyanine Form of Some Photochromic Spiropyrans

compound	$E/(10^{-20}\ \mathrm{V^{-2}\,m^{-2}})$	$F/(10^{-40}\ \mathrm{C\,V^{-1}\,m^2})$	$G/(10^{-40}\mathrm{C\,V^{-1}\,m^2})$
CDNS	50000 ± 1000	−3250 ± 100	−2900 ± 150
MDNS	63700 ± 500	−4560 ± 120	−4550 ± 120
CMNS	48600 ± 600	−2300 ± 200	−2340 ± 200
MMNS	60000 ± 1000	−4300 ± 150	−4400 ± 150

m is a unit vector in the direction of the transition moment in the considered transition, $\boldsymbol{\mu}_\mathbf{g}$ is the ground-state dipole moment effective in solution, and $\boldsymbol{\mu}_\mathbf{e}$ the effective dipole moment of the Franck−Condon excited state which corresponds to the investigated absorption transition. Note that under the condition

$$\boldsymbol{\mu}_\mathbf{g} || \boldsymbol{\mu}_\mathbf{e} - \boldsymbol{\mu}_\mathbf{g} || \mathbf{m}$$

The terms in eqs 8−12 reduce to

$$E = 2(kT)^{-2} f_\mathrm{e}^{\,2} \mu_\mathrm{g}^{\,2} \tag{13}$$

$$F = G = (kT)^{-1} f_\mathrm{e}^{\,2} \mu_\mathrm{g} (\mu_\mathrm{e} - \mu_\mathrm{g}) \tag{14}$$

$$H = I = f_\mathrm{e}^{\,2} (\mu_\mathrm{e} - \mu_\mathrm{g})^2 \tag{15}$$

The electric field acting on a solute molecule is larger than the applied one. This effect is taken into account by the so-called cavity field factor f_e. If the solute molecule is approximated by a point dipole in the center of a sphere, it is

$$f_\mathrm{e} = 3\epsilon/(2\epsilon + 1) \tag{16}$$

where ϵ is the relative permittivity of the solvent. A more sophisticated model which takes into account a nonspherical molecular geometry, in general, does not change results to a considerable amount, see ref 5.

3. Results and Discussion

3.1. The Merocyanine Form. Table 1 comprises the primary results for the terms $E-G$ for the merocyanine form of the studied spiropyrans. Errors are mere statistical errors within a single regression analysis.

As an example, Figure 3 displays the absorption spectrum of the merocyanine form of the compound CDNS, and in addition the electrooptical point by point spectrum AL(φ,ν) and the approximation according to eq 2.

The approximation is quite well; the regression coefficient r^2 is larger than 0.999 in the spectral range used for further evaluation.

TABLE 2: Ground and First Singlet Excited State Dipole Moments of the Merocyanine Form of Some Photochromic Spiropyrans

compound	$\mu_\mathrm{g}/(10^{-30}\ \mathrm{C\ m})$	$\mu_\mathrm{e}/(10^{-30}\ \mathrm{C\ m})$
CDNS	53.8 ± 0.5	37.3 ± 1.4
MDNS	60.7 ± 0.2	39.2 ± 0.9
CMNS	53.0 ± 0.3	40.3 ± 1.5
MMNS	58.9 ± 0.5	37.8 ± 1.3

Table 1 reveals $F \approx G$ from which follows in good approximation for further evaluation of dipole moments that $\mathbf{m} || \boldsymbol{\mu}_\mathbf{g} || \boldsymbol{\mu}_\mathbf{e}$. Hence, eqs 13−15 can be used to determine dipole moments. The results are shown in Table 2. H and I are not further considered since these coefficients are related to the second derivative of the absorption band shape, which cannot be determined with the necessary very high accuracy. This is due to the problems of conserving a stable equilibrium concentration of the merocyanine form during the time necessary to measure the absorption spectrum. Nevertheless, H equals I within the experimental error and thus also supports $\boldsymbol{m} || \boldsymbol{\mu}_\mathrm{g} || \boldsymbol{\mu}_\mathbf{e}$.

Errors are again errors derived from the standard errors of the regression coefficients, from within one regression. Add about 6% as absolute precision error.

In all cases the dipole moment in the ground state of the mero form is large, (53−61) × 10^{-30} C m or about 15−20 D. This is in agreement with what is reported from quantum chemical model calculations with similar compounds: see ref 9. Although 60 × 10^{-30} C m is a large value, it is distinctly less than would be expected for the limiting case of a zwitterionic form. In ref 10 ground and excited-state dipole moments of a class of merocyanines have been reported, also determined by EOAM. In the case of the compound $(CH_3)_2-N-CH{=}CH-CH{=}C-(CN)_2$ a ground-state dipole moment of 40.8 × 10^{-30} C m and a slight positive increase to about 58 × 10^{-30} C m in the first singlet excited state are reported. In contrast, with the benzospirans studied in their merocyanine form in the present communication, a negative change of the dipole moment with the excitation to the first Franck Condon excited singlet state is observed. The excited-state dipole moment amounts to about 40 × 10^{-30} C m or roughly 12 D. This observation is also consistent with results from semiempirical quantum chemical model calculations using AM1 in MOPAC 6.0 after structure preoptimization with Dreiding Force field in CERIUS 2, 4.0 (Molecular Simulations Inc., MSI: Cambridge). The ground-state dipole moments ${}^{\mathbf{th}}\boldsymbol{\mu}_\mathbf{g}$ and for simplicity the first excited triplet state dipole moments ${}^{\mathbf{th}}\boldsymbol{\mu}_\mathbf{T}$ have been calculated, where superscript "th" denotes a theoretical result from model calculations. They are almost parallel and therefore support the assumption above. ${}^{\mathbf{th}}\boldsymbol{\mu}_\mathbf{T}$ is found smaller than ${}^{\mathbf{th}}\boldsymbol{\mu}_\mathbf{g}$, too. For the case of CDNS, Figure 4 shows the dipole moment vectors of these two states.

The fact that the excited state dipole moment is much smaller than what would be estimated from the charge separation in the case of the zwitterionic form supports a more chinoid type first singlet excited state. In ref 11, the ground and excited states, dipole moments of the merocyanine form of MMNS and some closely related spiro benzopyrans in their merocyanine form are determined from solvent shift measurements. Within what can be expected from solvent shift measurements, the reported values of about 42 × 10^{-30} C m for the ground-state dipole moment are in agreement with the results presented here. The first singlet excited-state dipole moment of the merocyanine form of MMNS is reported to be about 12 × 10^{-30} C m in ref 11, which is much less than our values but also show the decrease of the dipole moment with excitation.

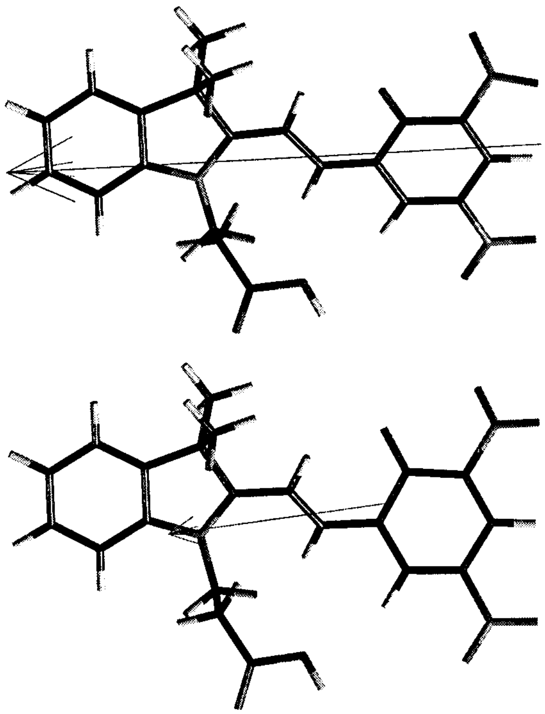

Figure 4. Dipole moment vectors of CDNS in the ground state and the first excited triplet state, as calculated by quantum mechanical model calculations.

TABLE 3: Values for *E*−*G*, Determined from EOAM on the Spiro Form of Some Photochromic Spiropyrans

compound	$E/(10^{-20}\ \mathrm{V^{-2}\,m^2})$	$F/(10^{-40}\ \mathrm{C\,V^{-1}\,m^2})$	$G/(10^{-40}\ \mathrm{C\,V^{-1}\,m^2})$
CDNS	1900 ± 300	1800 ± 200	2600 ± 300
MDNS	1700 ± 200	1550 ± 300	1800 ± 150
CMNS	4200 ± 50	2560 ± 50	2680 ± 40
MMNS	3600 ± 50	2380 ± 70	2540 ± 40

3.2. The Spiro Form. Table 3 represents the primary results for the terms *E*−*G* for the spiro form of the studied spiropyrans. Errors are purely statistical, from within a single regression analysis. The first spiro band is not as isolated as is the first absorption band of the merocyanine isomer. Hence, one should have in mind that the second-order terms in expansion eq 1, that is, *H* and *I*, are no more very reliable. Therefore, they have been omitted here. Because of the same reasoning, in general the results from EOAM in this first spiro absorption band are not as accurate as those from the merocyanine form.

From the values Table 3 the ground and first excited singlet state dipole moment may be derived if some information on the angles between $\boldsymbol{\mu}_g$, $\boldsymbol{\mu}_e$, and $\mathbf{m}$ were available. For this purpose, quantum chemical model calculations (see above) again have been used, and they show that $\boldsymbol{\mu}_g$ and $\boldsymbol{\mu}_e$ can be assumed to be parallel in sufficient approximation, in the case of MMNS and in that of CMNS. The results in Table 4 for these two compounds have been calculated assuming in addition the transition moment to be parallel to $\boldsymbol{\mu}_g$ and $\boldsymbol{\mu}_e$, which is usually the case for larger distance charge-transfer transitions.

As was expected the ground state dipole moment of the spiro form of MMNS and CMNS is much less than that of the merocyanine form and amounts to only 15 × 10^{-30} C m, or 5 D. Quite different from the merocyanine form, the excitation to the first singlet excited-state induces a strong additional charge transfer so that its dipole moment has a value of about 60 × 10^{-30} C m, or about 20 D. It should be mentioned that the results reported here cannot be compared to the results from EOAM reported by Maslak et al.[12] for a series of specially designed spiro compounds. They report dipole moments for the first excited singlet state which in their case is a charge transfer state, involving a charge transfer from the donor to the acceptor side of their compounds, beyond the spiro C.

TABLE 4: Ground- and First-Excited-Singlet-State Dipole Moments of the Spiro Form of Some Photochromic Spiropyrans

compound	$\mu_g/10^{-30}$ C m	$\mu_e/10^{-30}$ C m
CDNS[a]	10.4 ± 0.8	68.8 ± 9.5
MDNS[a]	9.8 ± 0.6	56.9 ± 8.0
CMNS[a]	15.4 ± 0.1	62.3 ± 1.0
MMNS[a]	14.3 ± 0.1	61.8 ± 1.3
CDNS[b]	14.6 ± 1.1	56.2 ± 3.8
MDNS[b]	13.8 ± 0.8	47.3 ± 5.3

[a] Results calculated assuming $\boldsymbol{\mu}_g||\boldsymbol{\mu}_e||\mathbf{m}$. [b] Results calculated assuming $\boldsymbol{\mu}_g||\boldsymbol{\mu}_e$.

In the case of MMNS our results may be compared to those of 4-nitroanisole. Its ground-state dipole moment is reported to be 17.4 × 10^{-30} C m,[13,14] its excited-state dipole moment from EOAM in the gas phase to be 50.3 × 10^{-30} C m,[14] and the results in ref 14 also have shown that the condition $\boldsymbol{\mu}_g||\boldsymbol{\mu}_e||\mathbf{m}$ is fulfilled in very good approximation. The very similar values for 4-nitroanisole and MMNS indicate that the excitation of MMNS in its spiro form into its first electronic absorption band might be highly located in the "benzopyran side" of the spiro-C. Then the assumption $\boldsymbol{\mu}_g||\boldsymbol{\mu}_e||\mathbf{m}$ used for the evaluation of dipole moments of MMNS and CMNS, Table 4, is further sanctioned.

It should be noted that the carboxylic group has no significant effect on the value of the dipole moment. This of course is due to the isolation of the carboxylic group from the rest of the molecule by two methylene groups.

With the compounds CDNS and MDNS the quantum chemical model calculations show an angle between the more or less parallel ground and (triplet − see above) excited-state dipole moment and the 4-nitroanisole axis which differs from zero. Also the fact, that an assumed parallelity $\boldsymbol{\mu}_g||\boldsymbol{\mu}_e||\mathbf{m}$ would result in $\mu_g \approx 10 \times 10^{-30}$ C m which then were smaller than that of the mono-nitro compounds, indicates an angle between $\mathbf{m}$ and $\boldsymbol{\mu}_g$ (and perhaps $\boldsymbol{\mu}_e$).

If the transition moment is yet assumed to have the 4-nitroanisole direction and adopting an angle between $\mathbf{m}$ and $\boldsymbol{\mu}_g$ of roughly 35° from the model calculations, values for the dipole moments can be estimated using eqs 8−10. The results for CDNS and MDNS based on these assumptions are given in Table 4, too, together with results derived under the crude assumption $\boldsymbol{\mu}_g||\boldsymbol{\mu}_e||\mathbf{m}$. Comparison of the results based on both assumptions with respect to the angles between the moments show that changing the assumption does not change the main result much: small μ_g, large μ_e with all four photochromic spiropyrans in their spiro form.

4. Summary

Ground and excited state dipole moments of some photochromic spirobenzopyran compounds in their spiropyran and in their merocyanine form have been determined. The ground state dipole moment of the spiro form is determined to be relatively small (≈5 D), that of the merocyanine form large (≈20 D). Excitation to the first excited singlet state yields in a strongly increased dipole moment in the case of the spiro form (≈20 D) but in a decreased one in the case of the merocyanine form (≈12 D). This is qualitatively consistent with what already had been observed with comparable compounds.[2] On the other hand, the results here cannot be compared with the only existing

EOAM results on spiro compounds in ref 12 since those compounds do not show reversible ring opening and moreover had been designed for a low lying charge-transfer transition between the two moieties.

The photodynamics of the nonthermally reversible photochromism of a related furylfulgide system has been studied in ref 15. The ultrafast photodynamics of the thermally reversible systems CDNS and MDNS is studied in another contribution by Pfeifer-Fukumura et al. to this Festschrift.[16]

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