Time-Resolved Thermodynamic Profile upon Photoexcitation of a Nitrospiropyran in Cycloalkanes and of the Corresponding Merocyanine in Aqueous Solutions

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Dedicated to Professor *André M. Braun* on the occasion of his 60th birthday

The photoconversion of 2′,3′-dihydro-6-nitro-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indole] (**Sp**) to its open merocyanine form (**Mc**) in a series of aerated cycloalkanes (cyclopentane, cyclohexane, and *trans*- and *cis*-decalin) and of the protonated merocyanine (**McH**$^+$) to **Sp** in aqueous solution were studied by laser-induced optoacoustic spectroscopy (LIOAS). The $+(11 \pm 2)$ ml mol^{-1} expansion determined for the ring closure is due to deprotonation of **McH**$^+$ plus the reaction of the ejected proton with the monoanion of malonic acid (added to stabilize **Mc**), an intrinsic expansion and a small electrostriction term. The energy difference between **Sp** and initial **McH**$^+$ is (282 ± 110) kJ mol^{-1}. An intrinsic contraction of $-(47 \pm 15)$ ml mol^{-1} occurs upon ring opening, forming triplet ^{3}Mc in the cycloalkanes, whereas no volume change was detected for the ^{3}Mc to **Mc** relaxation. Electrostriction decreases the ^{3}Mc energy, (165 ± 18) kJ mol^{-1}, to 135 kJ mol^{-1}. The difference in the values of the ring-opening (**Sp** to **Mc**) reaction enthalpy in cycloalkanes as derived from the temperature dependence of the **Sp**$\rightleftharpoons$**Mc** equilibrium, (29 ± 8) kJ mol^{-1}, and from the LIOAS data, $-(9 \pm 25)$ kJ mol^{-1}, is due to the formation of **Mc-Sp** aggregates during steady-state measurements. The **Sp**-sensitized singlet molecular oxygen, $O_2(^1\Delta_g)$, quantum yield (average $\Phi_\Delta = 0.58 \pm 0.03$) derived from the near-IR emission of $O_2(^1\Delta_g)$, was taken as a measure of **Mc** production in the cycloalkanes. These solvents, albeit troublesome in their handling, provide an additional series for the determination of structural volume changes in nonaqueous media, besides the alkanes already used.

Introduction. – The knowledge of the structural volume changes in photochemical reactions [1] is not just of academic interest, but also represents a challenge regarding the possibility of creating materials displaying a reversible volume response towards light [2]. Our major interest in this area is the relationship between the structural volume changes and the type of photoreaction, in order to understand the origin of the molecular structural changes upon excitation of biological photoreceptors [3].

A quantitative correlation was found between the reaction structural volume changes determined by laser-induced optoacoustic spectroscopy (LIOAS) [4] and the entropy changes of the reaction for intramolecular photoinduced electron-transfer reactions of Ru^{II} bipyridyl cyano complexes as well as for photoinduced intermolecular electron-transfer reactions between $Ru(bpy)_3^{2+}$ and the methyl viologen cation, in both cases in aqueous solution containing various monovalent salts. Based on the constancy of the reaction free energy, the changes were attributed to an entropy-enthalpy

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compensation effect related to the changes induced in the H_2O structure by the added salts, which were probed in each case by the photoinduced reaction including a partner that forms H-bonds with H_2O [5–7]. The contractions found upon photoisomerization of azobenzenecarboxylic acids in H_2O were also rationalized in terms of the differences in the chromophore-H_2O specific interactions between the photoisomer and the parent compound [8].

Electrostriction effects have been shown to be of great importance when a dipolar state is created in the highly nonpolar *n*-alkanes [9][10].

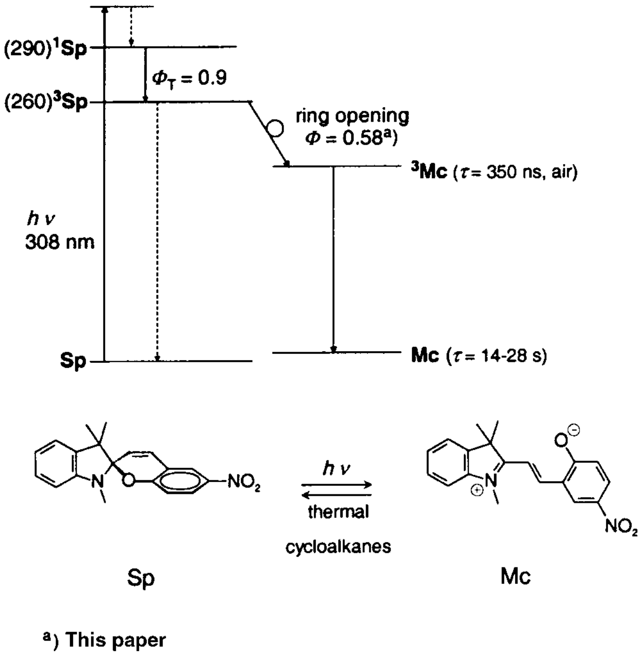
Notwithstanding the differences between the type of molecule-solvent interactions, also in the case of an intramolecular photoinduced electron-transfer reaction in straight chain alkanes, the large structural volume change correlated with the entropy change of the reaction. In these solvents and for the molecule studied, the structural volume change could be attributed to electrostriction and was calculated by means of the equations derived from a continuum model for the solvent [10].

During a study with photoisomerizable bilirubin in albumin, we observed that, for the loosely bound chromophore, the protein has an 'absorbing' role with respect to volume changes [11]. Thus, different types of medium effects may give rise to structural volume changes. In particular, specific chromophore-medium interactions play a predominant role in aqueous media.

We decided, therefore, to take a photochromic system such as a spiropyran [12], which could be studied in several media, to gain understanding of the relative contribution of those medium effects to the structural heat and volume changes. We report in this work LIOAS studies of the ring opening of **Sp** (the closed form of NO_2-BIPS) in a series of aerated organic solvents (cycloalkanes) as well as the ring closure of the corresponding merocyanine form in aqueous solution. Cycloalkanes (instead of alkanes) were chosen due to the better solubility of organic compounds in these solvents and to the smaller topological difference between small and large cycloalkanes (they are all globular molecules) than that existing between short and long alkanes.

The photochemical ring opening of spiropyrans (*Scheme 1*) is very sensitive to structural modifications of the molecular skeleton as well as to solvent and medium effects. In EtOH, H-bond formation between the dipolar state of the merocyanine open form and H-bond donors occurs, making the colored form very long-lived (on the hours scale), whereas in alkanes the lifetime is *ca.* 10–20 s. The 6-nitrospiropyran system has been well studied in alkanes [13][14]. Some properties for the most commonly used 2′,3′-dihydro-6-nitro-1,3,3-trimethylspiro[2*H*-1-benzopyran-2,2′-indole] (NO_2-BIPS) are summarized in *Scheme 1.* The quantum yield for triplet formation upon excitation of the closed form (**Sp**) has been estimated from measurements of singlet molecular oxygen, $O_2(^1\Delta_g)$, sensitization to be very high (*ca.* 90%) [15]. Intersystem-crossing yields mainly a long-lived $n\pi^*$ triplet, which results in the formation of the merocyanine form (**Mc**), whereas *ca.* 10% leads to a short-lived $\pi\pi^*$ triplet, which does not produce **Mc**. The overall quantum yield for ring opening, which occurs *via* the $n\pi^*$ triplet state was shown to be rather high in the absence of oxygen ($\Phi = 0.80$), which implies an efficiency of $\eta = 0.9$ for the production of the merocyanine form from the $n\pi^*$ triplet state. The **Sp** singlet state lifetime is in the subnanosecond range and that of the **Mc** triplet state (^{3}Mc) was reported to be *ca.* 350 ns in air and 6 μs in Ar-saturated solution. Small fluorescence ($\Phi_f \approx 0.01$ for **Mc**) and no phosphorescence at room temperature

Scheme 1. *Ring Opening Reaction of* **Sp** *to* **Mc** *in Organic Solvents, Together with an Energy Scheme Depicting the Various Processes Occurring after Excitation.* The overall quantum yields for the various processes as well as the energies (kJ mol^{-1}) [13][14] of the different states are depicted. See text for the uncertainties in the energy levels of the MC states.



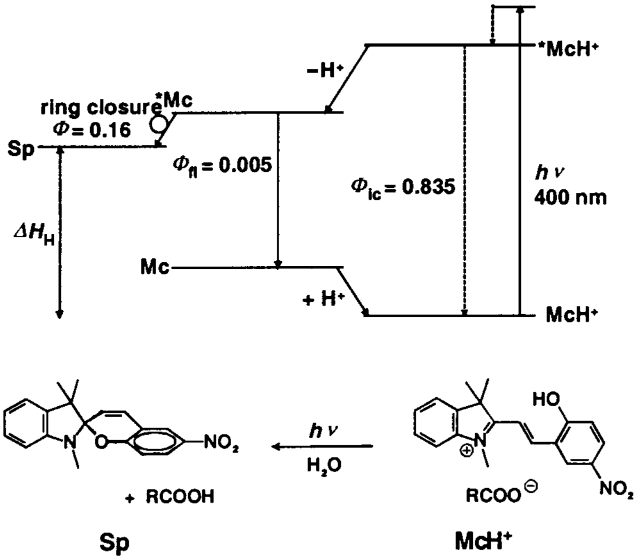
(phosphorescence yield at low temperature is $\Phi_{ph} \approx 0.01$ for **Sp**) are observed [13]. All the above properties make this compound very suitable for LIOAS studies in organic solvents.

The photophysics of H_2O-soluble spiropyrans is not so well-established as that of the spiropyrans in alkanes [16]. It is possible to stabilize the merocyanine form of NO_2-BIPS in H_2O containing acid (*e.g.*, malonic acid) [17–19]. The quantum yield for the photoinduced ring closure of the protonated merocyanine form ($\mathbf{McH^+} \rightarrow \mathbf{Sp}$, *Scheme 2*) has been reported to be 0.16 [19]. Thus, the protonated merocyanine form is also suited for studies in aqueous medium.

During the course of this work, we found that, in analogy to the recent findings during studies with the alkane series [20], also in the cycloalkanes series, it is possible to separate the contributions to the molecular volume changes due to intrinsic effects from those due to interactions with the solvent.

The use of aerated cycloalkane solutions of **Sp** allowed a better evaluation of all parameters, because *i*) the lifetime of the quenched triplet in air-saturated solutions is well within the time window of the LIOAS experiment (several hundreds of nanoseconds) and can be easily separated from that of $O_2(^1\Delta_g)$ in the same solvent, *ii*) the values of $O_2(^1\Delta_g)$ quantum yields, Φ_Δ, equal in turn to the quantum yield of production of ground-state **Mc** upon O_2 quenching of ^{3}Mc, can be readily obtained with high accuracy by monitoring the time-resolved near-IR emission of $O_2(^1\Delta_g)$, and *iii*) the

Scheme 2. *Ring-Closure Reaction of the Protonated Merocyanine Form* (**McH**$^+$) *in H_2O Yielding* **Sp** (from right to left), *Together with an Energy Scheme Depicting the Various Processes Occurring after Excitation.* The yields for the various processes are also included.



value of the energy content of $O_2(^1\Delta_g)$ is well-known, allowing a good determination of the energy distribution in the system after excitation.

Results. – *Photochemical Ring Closure in H_2O.* A typical UV/VIS absorption spectrum of **McH**$^+$ in 10^{-2} M malonic acid, is shown in *Fig. 1*. This spectrum is consistent with those reported in literature [19]. The yellowish solution with absorption maximum at *ca.* 400 nm was stable in the dark. However, when exposed to light for relatively long times, the formation of aggregates was observed. **McH**$^+$ displays fluorescence (*Fig. 1*) for which the quantum yield was determined to be 5×10^{-3} (relative to cresyl violet in ethanol, $\Phi_f = 0.54$ [21]). The maximum at 625 nm (15998 cm^{-1}) and the extremely large *Stokes* shift is taken as an indication that the emission stems from the deprotonated species (**Mc**, *Scheme 2*).

LIOAS Measurements in Aqueous Solution: Data Handling. The LIOAS signals for sample and reference in aqueous solution showed identical form and arrival time, differing only in amplitude. Thus, no deconvolution was applied to the signals in this medium. Two methods were used to separate the structural volume change from the thermal expansion in aqueous solution, in both cases by means of the LIOAS signal amplitudes, *i.e.*, the several-temperatures (ST) and the two temperature (TT)-methods [22]. Both methods take advantage of the strong temperature dependence of the thermal expansion coefficient, β, of H_2O. *Eqn. 1* was used with the ST-method [4][22].

$$\frac{[H_n^S]_T}{[H_n^{ref}]_T} = \alpha + \frac{\Phi_R \Delta V_R}{E_\lambda}\left(\frac{c_p \rho}{\beta}\right)_T \qquad (1)$$

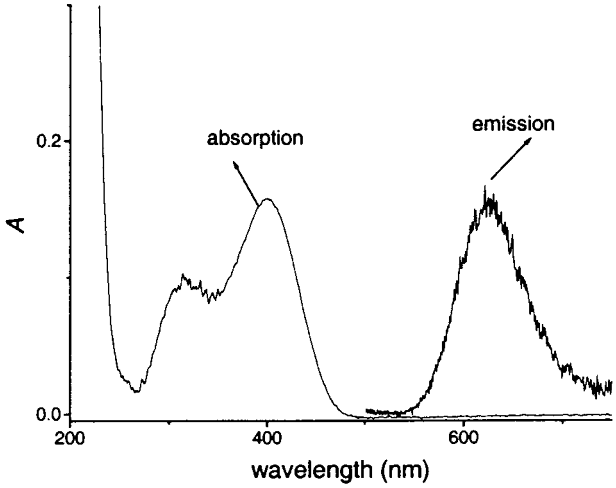


Fig. 1. *UV/VIS Absorption and fluorescence* (excitation at 400 nm) *spectra of* **McH**$^+$ (7×10^{-6} M in H_2O containing 10^{-2} M malonic acid). The emission spectrum (in arbitrary units) is normalized to the 400 nm absorption maximum.

The ratio of fluence-normalized LIOAS signal amplitude for the sample (H_n^S) and for the reference (H_n^{ref}) (of matched absorbances at λ_{exc}) is, thus, related to the ratio of thermoelastic parameters of the medium (the mass density ρ, the heat capacity c_p, and β) and to the laser-wavelength energy per *Einstein*, E_λ (299.07 kJ mol^{-1} at 400 nm). The slope of the plot of the left term in *Eqn. 1 vs.* $(c_p\rho/\beta)_T$ affords the product of the quantum yield of the reaction and the structural volume change per mole of transformed molecules ($\Phi_R\ \Delta V_R$). The intercept of the plot, α, is the fraction of absorbed energy released as heat within the pressure integration time and is related to the energy stored in species living longer than the pressure integration time [4]. The ratio $(c_p\rho/\beta)$ was varied in aqueous solution by varying the temperature [3–6].

The TT method makes use of the relationship $\beta = 0$ K^{-1} at 3.9° ($T_{\beta=0}$) for neat H_2O. *Eqns. 2* and *3* were used with the TT method to obtain the value of the structural volume change and the fraction of heat delivered promptly to the medium [23].

$$\Phi_R \Delta V_R = \frac{[H_n^S]_{T_{\beta=0}}}{[H_n^{ref}]_{T_{\beta \neq 0}}} E_\lambda \left(\frac{\beta}{\rho c_p}\right)_{T_{\beta \neq 0}} \tag{2}$$

$$\alpha = \frac{[H_n^S]_{T_{\beta \neq 0}} - [H_n^S]_{T_{\beta=0}}}{[H_n^{ref}]_{T_{\beta \neq 0}}} \tag{3}$$

It was assumed that the isothermal compressibility κ_T of the solvent (relating the volume change in the sample with the detected pressure pulse) does not change significantly between $T_{\beta=0}$ and the slightly higher temperature at which reference and sample are measured ($T_{\beta \neq 0}$). In our experiments $T_{\beta \neq 0} = 10°$. The LIOAS signal is inversely proportional to κ_T, which for H_2O at 3.9 and 10° differs by less than 5%.

LIOAS measurements at $T_{\beta=0}$ are shown in *Fig. 2*. Under the same conditions for which the LIOAS reference compound EB (in 10^{-2} M malonic acid) did not give any signal, the **McH**$^+$ solution showed a clear positive signal [$\Phi_R\,\Delta V_R = (1.76 \pm 0.1)$ ml mol^{-1}], indicative of an expansion upon photoreaction. The data, together with $\Phi_R = 0.16$ and *Eqn. 2*, afford a value of $\Delta V_R = +(11 \pm 0.5)$ ml mol^{-1}. With *Eqn. 3*, $\alpha = 0.84$ is obtained.

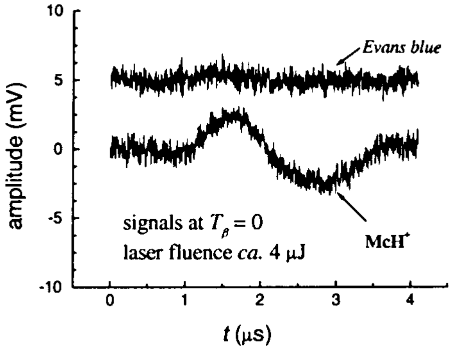


Fig. 2. *LIOAS Signals of the reference compound* Evans *blue and of* **McH**$^+$ (in H_2O containing 10^{-2} M malonic acid; $T_{\beta=0} = 3.8°$; $\lambda_{exc} = 400$ nm)

The ratio of sample and reference fluence-normalized signals at several temperatures is represented in *Fig. 3*. Fitting the data (slope $= (6 \pm 1) \cdot 10^{-3}$ ml/kJ, intercept (0.84 ± 0.06)) with *Eqn. 1* and again with $\Phi_R = 0.16$ affords an expansion of $\Delta V_R = +(11 \pm 2)$ ml mol^{-1}. The ST and TT methods clearly give the same results. We assumed that the quantum yield does not change over the small temperature range analyzed.

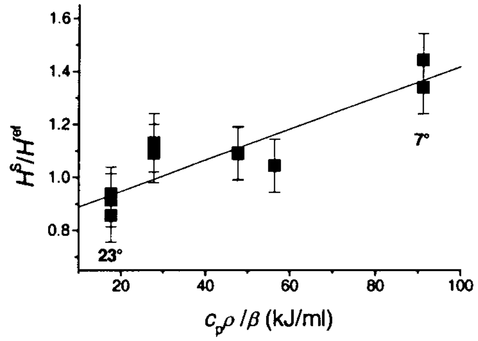


Fig. 3. *Ratio of fluence-normalized LIOAS signal amplitudes of absorbance-matched sample* (H_n^S, **McH**$^+$) *and reference* (H_n^{ref}, *Evans* blue) *solutions at various temperatures in H_2O containing 10^{-2}* M *malonic acid* ($\lambda_{exc} = 400$ nm $(0.1 \leq A_{400} \leq 0.2)$

Simple energy-balance considerations lead to *Eqn. 4* relating the energy stored in a long-lived species plus the energy released by emission with the α value (either the intercept in *Fig. 3* or the value from *Eqn. 3*) and the molar energy of the laser pulse, E_λ.

$$(1-\alpha)\,E_\lambda = \Phi_{\mathbf{McH}\to\mathbf{Sp}}\,\Delta H_R + \Phi_{fl}\,E_{00} \tag{4}$$

With $\Phi_f = 5 \times 10^{-3}$ (see *Exper. Part*) and the singlet-state energy of the merocyanine form (E_{00} *ca.* 220 kJ mol^{-1}) [15], a value of 1.1 kJ mol^{-1} is calculated as the energy released as radiation ($\Phi_{fl}\,E_{00}$). With $\alpha = 0.84$, $\Phi_{\mathbf{McH}\to\mathbf{Sp}} = 0.16$, and $E_\lambda = 299.07$ kJ mol^{-1}, a value $\Delta H_R = (282 \pm 110)$ kJ mol^{-1} is obtained for the enthalpy difference between ground-state **McH**$^+$ and **Sp** in aqueous solution. No $O_2(^1\Delta_g)$ could be detected for **McH**$^+$ in these solutions and Φ_Δ was estimated to be $< 10^{-1}$ on the basis of the signal observed with TSPP^{4-}.

Photochemical Ring Opening in Nonpolar Solvents. Typical UV/VIS absorption spectra of NO$_2$-BIPS and the calorimetric reference compound OHB in cyclohexane are shown in *Fig. 4*. Also depicted (*Inset* in *Fig. 4*) is a VIS spectrum of **Mc** obtained after irradiating a 2×10^{-5} M NO$_2$-BIPS cyclohexane solution with a few 308-nm laser flashes. It displays maxima at 570 and 620 nm, which do not change shape or relative intensity upon reduction of the initial NO$_2$-BIPS concentration below 10^{-6} M.

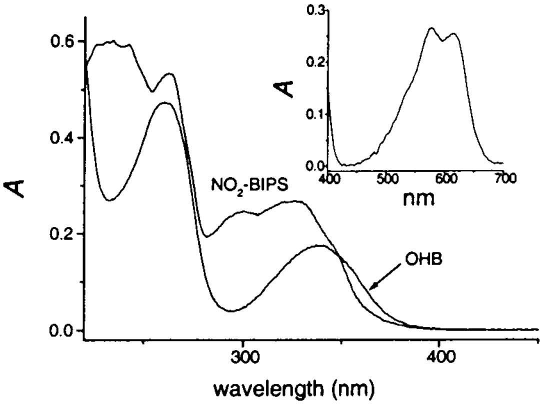


Fig. 4. *UV/VIS Absorption spectra of NO$_2$-BIPS and of the calorimetric reference OHB in cyclohexane. Inset:* Visible absorption spectrum of **Mc** in cyclohexane obtained directly after excitation of NO$_2$-BIPS with laser pulses at 308 nm.

Upon O_2 quenching of ^{3}Mc, **Mc** is produced with the same quantum yield as $O_2(^1\Delta_g)$, according to the reaction mechanism (*Eqns. 5–8*).

$$\mathbf{Sp} \rightarrow {}^1\mathrm{Sp} \tag{5}$$

$$^1\mathrm{Sp} \rightarrow {}^3\mathrm{Sp} \tag{6}$$

$$^3\mathrm{Sp} \rightarrow {}^3\mathrm{Mc} \tag{7}$$

$$^3\mathrm{Mc} + O_2(^3\Delta_g) \rightarrow \mathrm{Mc} + O_2(^1\Delta_g) \tag{8}$$

Thus, the **Sp**-sensitized $O_2(^1\Delta_g)$ quantum yield, Φ_Δ, in air-saturated cycloalkanes is a measure of the **Mc** quantum yield in these solutions, similar to those used during the LIOAS measurements. In any case, no difference was observed in the Φ_Δ values between O_2- and air-saturated cycloalkane solutions, for all four solvents (comparisons between air- and O_2-saturated solutions of **Sp** in cyclohexane are shown in *Fig. 5, Inset b*). This lack of difference is understandable in view of the long lifetime of the ^{3}Mc state (> 1 μs).

The values of Φ_Δ obtained from the ratio of the total energy-dependent plots of the prompt amplitude of the near-IR $O_2(^1\Delta_g)$ emission for sample and reference (data for cyclohexane are shown in *Fig. 5*), were $\Phi_\Delta = 0.60 \pm 0.05$ (cyclopentane), 0.55 ± 0.05

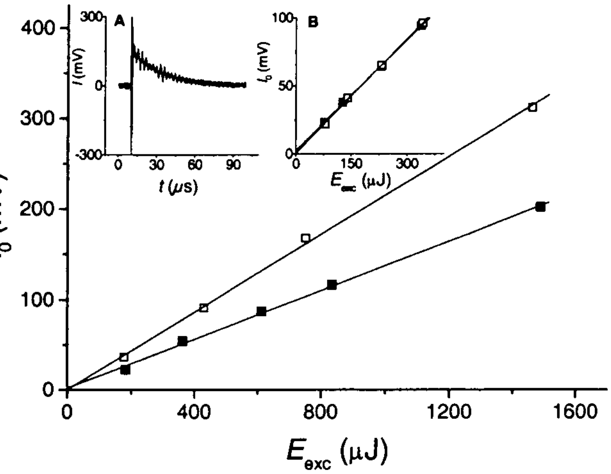


Fig. 5. *Total laser-pulse energy-dependent zero-time amplitude* (I_0) *of the sensitized near-IR* $O_2(^1\Delta_g)$ *emission at 1270 nm.* Excitation ($\lambda_{exc} = 308$ nm) of absorbance matched ($A_{308} = 0.20$) cyclohexane solutions of (□) PN, O_2-saturated, (■) NO_2-BIPS, air-saturated. *Inset A:* decay of the 1270 nm emission from an air-saturated cyclohexane solution of NO_2-BIPS. The lifetime of $O_2(^1\Delta_g)$ is $\tau_\Delta = 23$ μs. *Inset B:* Zero-time amplitude of the near-IR emission *vs.* total laser-pulse energy upon excitation of an (■) air-saturated and an (□) O_2-saturated cyclohexane solution of NO_2-BIPS.

(cyclohexane, average from data derived from measurements *vs.* PN and *vs.* TPP), 0.58 ± 0.05 (*cis*-decalin), and 0.57 ± 0.05 (*trans*-decalin). The value in cyclohexane is smaller than the reported $\Phi_\Delta = 0.8$ [15], and used as the upper limit for the triplet yield. The reason for the discrepancy most probably is that the previous value was determined by comparison with the reference in a different solvent than that used for the sample.

LIOAS Measurements in Nonpolar Solvents: Data Handling. Eqn. 9 was used to separate heat release (q_i) and structural volume changes (ΔV_i). Both effects contribute to the amplitudes, φ_i, recovered by deconvolution [24][6].

$$E_\lambda \varphi_i = q_i + \Phi_i \Delta V_i \left(\frac{c_p \rho}{\beta}\right) \tag{9}$$

E_λ is the molar excitation energy, and Φ_i is the quantum yield of the particular step analyzed. The ratio of thermoelastic parameters ($c_p\rho/\beta$) varies within the cycloalkane series, similar to the case of the alkanes [9][10][25][26].

The LIOAS signals obtained upon excitation of **Sp** in aerated cyclohexane, of the reference, the result of the fitting and the distribution of the residuals upon deconvolution are shown in *Fig. 6*. Also shown are the signals in an O_2-purged cyclohexane solution. Two exponential terms were enough to obtain a good fitting of the data in all four solvents and under all conditions (air, O_2, and Ar). The lifetime (τ_1) associated with the first component of the function recovered upon deconvolution was in every case in the range 0.5–5 ns and did not depend on the nature of the gas present (air, O_2, or Ar). The lifetime associated with the second component τ_2 depended on the solvent and on the type of gas present. It was $\tau_2 > 650$ ns in Ar-saturated, (235 ± 40) ns

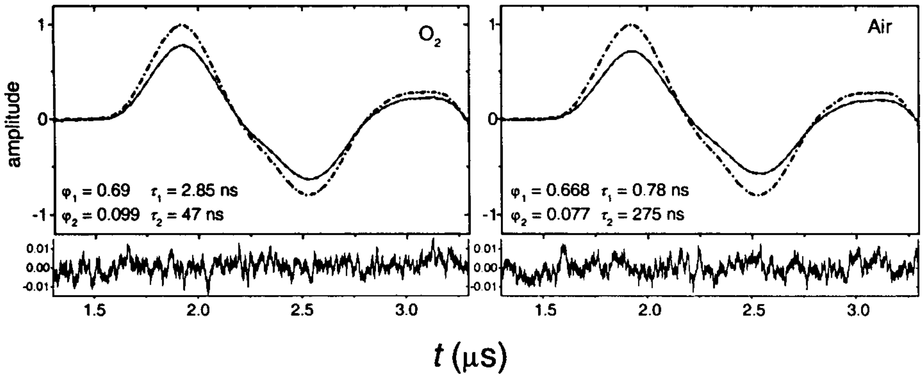


Fig. 6. *LIOAS Signals* (solid line) *of NO_2-BIPS in air-saturated* (right panel) *and oxygen saturated* (left panel) *cyclohexane at 20°*. $\lambda_{exc} = 308$ nm. $A_{308} = 0.2$, together with the signal of an absorbance-matched solution of the reference (OHB, dashed line), the fitted curve (pointed line overlapping the sample signal), and the error distribution. The results of the fitting routine are included in each panel.

in air-saturated, and (45 ± 10) ns in O_2-saturated cyclohexane solutions. The quenching rate constant by O_2 of the energy storing species roughly derived from these data and taking into account the O_2 solubility in cyclohexane is $k_q = 2 \times 10^9$ M^{-1} s^{-1}. The average values of τ_2 in the air-saturated solutions of **Sp** in the other three cycloalkanes were (286 ± 33) ns in cyclopentane, (402 ± 18) ns in *trans*-decalin, and (544 ± 76) ns in cis-decalin.

Due to the time window of the LIOAS experiment, $\tau_2 < 30$ ns were difficult to properly separate from τ_1, this making problematic the analysis in the O_2-saturated solutions. On the other hand, $\tau_2 > 2$ μs are also difficult to determine, this impairing the determination of this lifetime in the Ar-saturated solutions.

On the basis of its lifetime and the rate of its quenching by O_2, the second component of the LIOAS signals is assigned to the ^{3}Mc decay, either non-quenched in Ar, or O_2-quenched (*Eqn. 8*), in both cases decaying to **Mc**. The first component produced in a time $\leq \tau_1$ is attributed to ^{3}Mc formation.

Energy balance considerations lead to *Eqn. 10*, relating the fraction of absorbed laser energy evolved upon formation of ^{3}Mc ($\alpha_1 = q_1/E_\lambda$, q_1 is the heat associated with the first component of the biexponential function with lifetime τ_1, *Eqn. 9*) with the energy of the storing species (^{3}Mc), E_T, and the quantum yield of its formation $\Phi_T = \Phi_\Delta = 0.58 \pm 0.05$ (average of the value in the four cycloalkanes).

$$(1 - \alpha_1)\, E_\lambda = \Phi_\Delta\, (E_T) + \Phi_{fl}\, E_{00} \tag{10}$$

As no fluorescence has been reported for **Sp** [12–15], the second term on the right side of *Eqn. 10* can be neglected. Combination of *Eqns. 9* and *10* leads to *Eqn. 11*, used to calculate the energy content of the triplet as well as the volume change concomitant with its formation, ΔV_T, from the LIOAS data in the four cycloalkanes.

$$(1 - \varphi_1)\frac{E_\lambda}{\Phi_\Delta} = E_T - \Delta V_T\left(\frac{c_p\rho}{\beta}\right) \tag{11}$$

The left side of *Eqn. 11*, for absorbance-matched solutions of sample and reference in the four cycloalkanes, and with $E_\lambda = 388.04$ kJ mol^{-1}, is plotted in *Fig. 7,a*, *vs.* the ratio of thermoelastic parameters of the four cycloalkanes, $c_p\rho/\beta$, taken from the literature (see below, *Table 2*) [25].

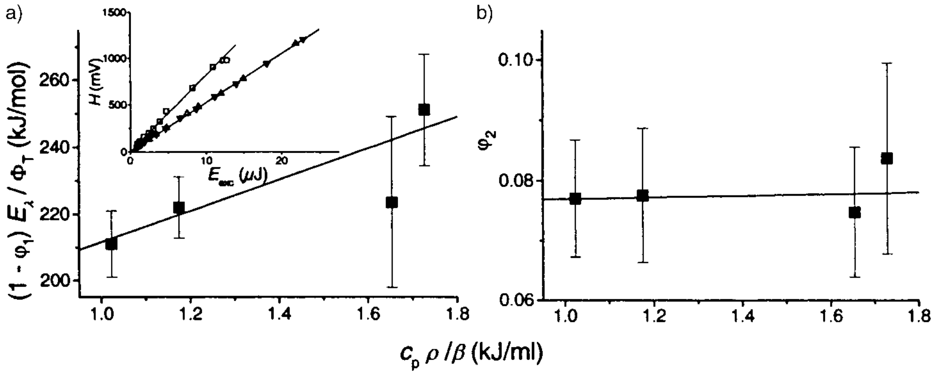


Fig. 7. a) *Left side of Eqn. 11* (fraction of free energy stored in species produced in less than 5 ns per phototransformed mol of **Sp**) *after laser* (308 nm) *excitation of* **Sp** *in various aerated cycloalkanes* ($A_{308} = 0.2$). The calorimetric reference was an absorbance-matched solution of OHB in the respective solvent. b) *Normalized amplitude* (φ_2) *associated with the second component of the pressure wave* (τ_2 *ca.* 300 ns, exact value depending on the solvent) vs. ($c_p\rho/\beta$) *for the four solvents.* Values are the average of three independent series of experiments. *Inset:* Total laser pulse energy-dependent LIOAS amplitude for absorbance-matched ($A_{308} = 0.16 \pm 0.002$) (□) O_2-saturated OHB, and (△) Ar- and (▼) O_2-saturated NO_2-BIPS cyclohexane solutions.

The slope of the line in *Fig. 7,a* is (47 ± 14) ml and the intercept is (165 ± 18) kJ. The values obtained for slope and intercept are very sensitive to the value of Φ_Δ. Only a thorough purification of the cycloalkanes (see *Exper. Part*) eliminated the residual absorption and emission upon excitation with 308 nm and afforded reproducible Φ_Δ data. In addition, the LIOAS data obtained in particular for *trans*-decalin were extremely sensitive to the storage time of the purified solvent. Just few days of storage (even when kept in the dark and under Ar) resulted in nonreproducible data with this solvent.

The total maximum amplitude (H) (no deconvolution) of the LIOAS experiments performed with Ar-, air-, and O_2-saturated cycloalkane solutions of **Sp** showed no differences in the slopes of the laser total energy-dependent plots (*e.g.*, for cyclohexane in *Fig. 7*, inset). The reason obviously lies in the small difference between the energy stored and the structural volume change produced when the triplet is formed in Ar-saturated solutions and when $O_2(^1\Delta_g)$ and **Mc** are formed (albeit in different amounts) in air- and O_2-saturated solutions, especially taking into account that radiationless deactivation upon excitation at 308 nm constitutes the largest part of the LIOAS signal.

Upon O_2 quenching of ^{3}Mc, the energy is stored by $O_2(^1\Delta_g)$ with a molar-energy content $E_\Delta = 94.1$ kJ mol^{-1} [27] (with a lifetime in cycloalkanes much longer than the pressure integration time of our experiment, *e.g.*, 23 μs in cyclohexane) [28] and by **Mc**.

Eqn. 12 is used to derive the energy stored by the relaxed open **Mc** form from the measured $\alpha_2 = 0.076 \pm 0.008$ (*Fig. 7,b*).

$$E_\lambda \alpha_2/\Phi_\Delta = E_T + E_\Delta + E_{\mathbf{Mc}} \qquad (12)$$

Temperature Effect on the **Sp**$\rightleftharpoons$**Mc** *Equilibrium.* ΔH_R for the equilibrium in cyclohexane was determined by studying the temperature effect on the constant, K_{eq}. For this purpose, the temperature-induced absorbance changes were monitored.

The spectra of a 2.3×10^{-2} M **Sp** solution in cyclohexane at 25° and at 60° are shown in *Fig. 8*. With the absorption coefficient at 600 nm of $\varepsilon_{600} = 4 \times 10^{-4}$ M^{-1} cm^{-1} [13–15], the values of $K_{eq} = 1.6 \times 10^{-6}$ and 5.6×10^{-6} at 25° and 60°, respectively, were obtained. With these values, $\Delta H_R = (29 \pm 8)$ kJ mol^{-1} is calculated, in the same range as the values reported in the literature for similar solvents (*Table 1*) and higher than the value determined by LIOAS (albeit within the large error of the LIOAS data, *vide supra*). However, the UV/VIS absorption spectra show that the colored (**Mc**) species is different in this case. The colored form obtained by heating (*Fig. 8*) shows a broad

Table 1. *Reaction Enthalpy, ΔH_R, for the Reaction* **Sp** → **Mc** *as Determined by the Influence of Temperature on the Steady-State Equilibrium Between the two Forms of NO_2-BIPS in Various Solvents*

Solvent	ΔH_R (kJ mol^{-1})	Reference
Benzene	18.4 ± 1.6	[36]
Cyclohexane	13.4	[12a]
Decalin	25.1	[12a]
Decalin[a])	23 to 31	[37]
Cyclohexane	29 ± 8	this work

[a]) Various substituted NO_2-BIPS.

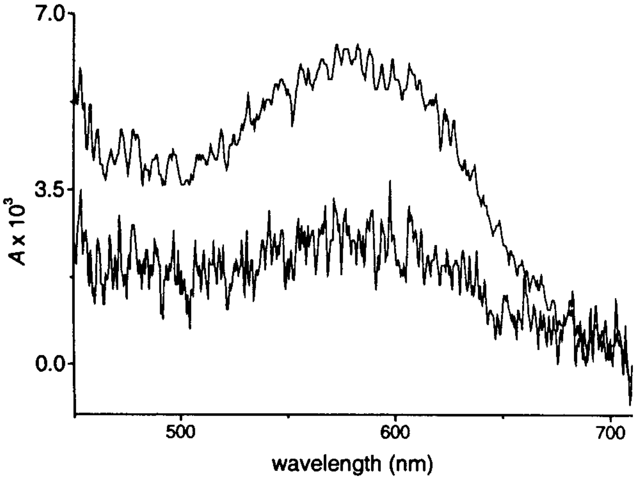


Fig. 8. *VIS Part of the absorption spectra of a 0.023*M *solution of NO_2-BIPS in cyclohexane at 25°* (bottom) *and at 60°* (top)

spectrum without structure that differs from that obtained upon photoexcitation of low concentration solutions (see *Inset* in *Fig. 4*).

Due to the relatively high concentration needed for, as well as to the time available for the open form to react with **Sp** during the temperature-dependent studies, we attribute this spectral differences to complex formation between the resulting open form and **Sp** (see *Discussion*).

Discussion. – *Volume Changes.* Reaction volume changes (ΔV_R) in dilute solutions may be regarded as the addition of two terms: a change in *i*) the intrinsic volume and in *ii*) the interactions with the solvent [29].

A change of the intrinsic volume of a solute is in principle attributed only to a change in the *Van der Waals* volume. This change may originate in the breaking or formation of bonds and in the change of bond lengths due to radical formation or ionization. A rotation or isomerization alone should not influence very much the *Van der Waals* volume, but it might strongly affect the solvent sphere around a molecule. The interaction with the solvent is of great interest and it may consist of formation or breaking of H-bonds, proton release or uptake, H_2O formation, electrostriction (contraction or expansion) of solvent molecules upon charge creation (or annihilation), and change in solvent spheres. At low concentrations (10^{-4} – 10^{-6} M) solute-solute interactions should play no important role, although attention has to be paid to aggregation or cluster formation.

We regard the total value of ΔV_R as the sum of several contributions, as described below for each of the media.

Photochemical Ring Closure in Aqueous Solutions. The ring closure of **McH**$^+$ may be dissected as consisting of four steps: proton ejection, ring closure of **Mc** to **Sp**, protonation of the malonic acid monoanion, and electrostriction due to the large dipole-moment change upon ring closure. The volume changes corresponding to each of these steps are either known or can be calculated. The electrostriction volume in H_2O may be calculated with the *Drude-Nernst Eqn. 13* (as a crude approximation, since this equation is not appropriate for H_2O) describing the volume change in a solvent with dielectric constant ε of a species with a dipole moment μ in a cavity of radius r [5][20].

$$\Delta V_{el} = -\frac{(\mu_{\mathbf{Sp}}^2 - \mu_{\mathbf{Mc}}^2)}{r^3} \frac{3}{(2\varepsilon + 1)^2} \frac{\delta\varepsilon}{\delta p} \tag{13}$$

With, as a first approximation, the dipole moment change reported by *Levitus et al.* [30] for the ring opening of **Sp** in organic solvents, *i.e.*, $\mu_{\mathbf{Sp}} = 6.4$ to $\mu_{\mathbf{Mc}} = 14.2$ D, and the radius $r = 4.1$ Å obtained by taking the average *Van der Waals* volume and equating it to a sphere volume, together with $\delta\varepsilon/\delta p = 3.68 \times 10^{-8}$ Pa^{-1} [25], and $\varepsilon = 78$ [25], a value of ΔV_{el} *ca.* +0.6 ml mol^{-1} for the ring closure in H_2O is calculated. Notwithstanding that this calculation does not take into account the possible solvent-induced polarization of the **Mc** form, 0.6 ml mol^{-1} is much smaller than the observed 11 ml mol^{-1}. Other contributions should be thus considered, especially because the reaction of a zwiterionic species in aqueous solution necessarily involves strong specific interactions with the H_2O dipoles.

The proton ejection corresponds to a contraction of – 5.5 ml mol^{-1}, as determined by several groups [31]. The change in the *Van der Waals* volume upon ring closure (– 2 ml mol^{-1}) was calculated with the PM3 program. However, this calculation does not consider the formation of charged species. The intrinsic volume change derived from the LIOAS data in cycloalkanes (*vide infra*) would be 47 ml mol^{-1} for the reaction **Mc** → **Sp**.

The largest volume contribution should be attributed to the protonation of the malonic acid monoanion, the most abundant species at pH 5. The first dissociation of malonic acid has been determined by densitometry to produce a reaction volume of – 10 ml mol^{-1} [32].

We thus apply the following (*Scheme 3*) for the reaction in H_2O which leads to a rough estimate of the structural volume change:

Scheme 3. *Estimation of Structural Volume Change in Aqueous Solution with Malonic Acid.*

$$\mathbf{McH^+} \longrightarrow \mathbf{Mc} + \mathbf{H^+} \qquad \Delta V_{\mathrm{H+}} = -\ 5.5\ \mathrm{ml\ mol^{-1}}$$

$$\mathbf{Mc} \longrightarrow \mathbf{Sp} \qquad \Delta V_{\mathrm{vdW}} > -\ 2\ \mathrm{ml\ mol^{-1}}$$

$$\Delta V_{\mathrm{el}}\ \mathit{ca.} +\ 0.6\ \mathrm{ml\ mol^{-1}}$$

$$\mathrm{H^+ + R(CO_2H)COO^-} \longrightarrow \mathrm{R(COOH)_2} \qquad \Delta V_{\mathrm{prot}} = +10\ \mathrm{ml\ mol^{-1}}$$

$$\Delta V_{\mathrm{R}} = \Delta V_{\mathrm{vdW}} + \Delta V_{\mathrm{prot}} + \Delta V_{\mathrm{H+}} + \Delta V_{\mathrm{el}}\ \mathrm{ca.} + 3\ \mathrm{ml\ mol^{-1}}$$

Taking into account the various approximations (the error is at least 5 ml mol^{-1}), the estimated value is not far from our measured $+(11 \pm 2)$ ml mol^{-1} for the ring closure of **McH**$^+$ to **Sp** in H_2O in the presence of malonic acid. In fact, as will be discussed in the next section, it is possible that the intrinsic volume change for the **McH**$^+$ → **Sp** reaction is much larger (and positive) than that calculated with PM3.

According to the above considerations, the major contributions to the reaction volume change are the deprotonation of **McH**$^+$ and the protonation of the malonic acid monoanion, in addition to the intrinsic volume change (*vide infra*).

Similar considerations should apply to the calculation of ΔH_R. However, at the moment, we cannot separate the various contributions to the measured heat, which, in any case, bear a large error, especially due to the large value of the prompt heat (*Eqn. 9*).

Photochemical Ring Opening in Nonpolar Solvents. By considering that both reaction-volume change and enthalpy change are a sum of an intrinsic term (I) and a solvent term due to electrostriction (el), and, taking into account that the first amplitude (φ_1) of the biexponential function is associated with the ^{3}Mc formation, it is possible to write $\Delta V_T = (\Delta V_{\mathrm{IT}} + \Delta V_{\mathrm{elT}})$, and $\Delta E_T = (\Delta H_{\mathrm{IT}} + \Delta H_{\mathrm{elT}})$ (T for the properties associated with ^{3}Mc) in *Eqn. 11*, and *Eqn. 14* is readily obtained.

$$(1-\varphi_1)\frac{E_\lambda}{\Phi_\Delta} = (\Delta H_{\mathrm{IT}} + \Delta H_{\mathrm{elT}}) - (\Delta V_{\mathrm{IT}} + \Delta V_{\mathrm{elT}})\left(\frac{c_p\rho}{\beta}\right) \qquad (14)$$

Herbrich and *Schmidt* [20] recently observed a linear relationship between the calculated pressure derivative of the free energy due to electrostriction (q_p) and the values of the ratio ($\beta/c_p\,\rho$) in alkanes. Based upon the following line of arguments, this observation justified the use of the alkane series in conjunction with *Eqn. 11* (= *Eqn. 14*) in order to derive structural volume and enthalpy changes of photoinduced reactions in those solvents. Upon photoinduced formation of a species of different dipole moment (μ) than the parent compound, the volume change due to electrostriction ΔV_{el} in a solvent of dielectric constant ε and isothermal compressibility κ_{T} is given by *Eqn. 15* (derived from the *Clausius Mossotti* approximation for q_p) [10][20][33].

$$\Delta V_{\mathrm{el}} = -(\mu^2/r^3)\,q_p = -(\mu^2/r^3)(\varepsilon+2)(\varepsilon-1)/(2\varepsilon+1)^2\,\kappa_{\mathrm{T}} \tag{15}$$

Herbrich and *Schmidt* noted that the empirically found linear correlation (with a negligible intercept) between q_p and ($\beta/c_p\,\rho$) for alkanes means that $\Delta V_{\mathrm{el}}\ (c_p\rho/\beta) =$ constant $= -0.24\ \mathrm{N_A}\ (\mu^2/r^3)$ kJ mol^{-1} $= \Delta H_{\mathrm{el}}$ [20]. The constancy of the term $[\Delta V_{\mathrm{el}}\ (c_p\rho/\beta)]$ in the solvent series explains why the plot of the left side of *Eqn. 14 vs.* ($c_p\rho/\beta$) leads to a linear plot even when ΔV_{el} varies with the solvent. This observation allows the separation of the value of the intrinsic enthalpy change, ΔH_{I}, inasmuch as the electrostrictive term turns out to be $\Delta H_{\mathrm{el}} = [\Delta V_{\mathrm{el}}\ (c_p\rho/\beta)]$ [20] (provided that the solvent effect is due only to electrostriction, a very reasonable assumption in the case of the alkanes [10]).

We also find a similar linear correlation, *i.e.*, $q_p = -0.005 + 0.222\ (\beta/c_p\rho)$ within the series of cycloalkanes used in this work (see footnote in *Table 2* regarding the calculation of the values for *cis*-decalin, according to the method developed by *Marcus* [34]). Therefore, also in this series, the term $[\Delta V_{\mathrm{el}}\ (c_p\rho/\beta)]$ should be a constant. In fact, with *Eqn. 15*, the difference in dipole moment between **Sp** and **Mc** ($\mu_{\mathrm{Sp}} = 6.4$ and $\mu_{\mathrm{Mc}} = 14.2$) [30] and r = 4.1 Å as above, the values of ΔV_{el} are calculated for the four solvents (*Table 2*) and the term $[\Delta V_{\mathrm{el}}\ (c_p\rho/\beta)]$ (= ΔH_{el}, last column in *Table 2*) is effectively a constant with a relatively small deviation. The invariance of the term is a solvent property, which obviously means that ΔH_{el} should also be constant for the photoproduction of triplet ^{3}Mc upon **Sp** excitation.

The slope of the plot of *Eqn. 13* (*Fig. 7,a*) thus affords $\Delta V_{\mathrm{IT}} = -(47 \pm 15)$ ml mol^{-1} devoid of electrostriction for the process **Sp** → ^{3}Mc in cycloalkanes.

The near-zero slope of the plot in *Fig. 7,b* indicates that there is no detectable volume change during the transformation ^{3}Mc → **Mc**. Therefore, the intrinsic volume change **Sp** → **Mc** calculated on the basis of the data in the cycloalkane series is $\Delta V_{\mathrm{I}} = -(47 \pm 15)$ ml mol^{-1}. This value is much larger than the change in the *Van der Waals* volume of *ca.* 2 ml mol^{-1} calculated with the Alchemy program and PM3 as the difference between 174.28 for **Mc** and 172.11 ml mol^{-1} for **Sp**. A contraction of $\Delta V_{\mathrm{I}} = -(47 \pm 15)$ ml mol^{-1} is a large value justified on the basis of the formation of a zwitterionic species from a neutral one. A strong shortening of bonds may be expected, but are not considered in the calculations.

With the solvent-dependent electrostrictive volume change, $\Delta V_{\mathrm{el}} = -25$ ml mol^{-1} calculated, *e.g.*, for cyclohexane (*Table 2*), $\Delta V_{\mathrm{R}} = \Delta V_{\mathrm{I}} + \Delta V_{\mathrm{el}} = -(71 \pm 20)$ ml mol^{-1} is obtained, higher than the values derived from the pressure-dependent experiments

Table 2. *Properties of the Cycloalkanes Used*

Solvent	$c_p\rho/\beta$ ^a) [kJ ml^{-1}]	ε ^b)	κ_T ^c) [Pa^{-1}] 10^9	Viscosity [N s m^{-2}] 10^3	ΔV_{el} ^d) [ml mol^{-1}]	ΔH_{el} ^f) [kJ mol^{-1}]
Cyclopentane	1.0238	1.968	1.358	0.416	– 30.1	– 31
Cyclohexane	1.1755	2.024	1.120	0.898	– 25.4	– 30
trans-Decalin	1.6545	2.197	0.759	2.128	– 17.2	– 28
cis-Decalin	1.7282	2.172	0.720^e)	3.381	– 17.6	– 30

^a) c_p: Specific heat; ρ: mass density; β: expansion coefficient [25]. ^b) ε: dielectric constant [25]. ^c) κ_T: isothermal compressibility at 25° [34]. ^d) Calculated with *Eqn. 15* and κ_T. ^e) Calculated by *Y. Marcus* (University of Jerusalem) with *Eqn. 9* in *Marcus* and *Hefter* [34] and the density, the isobaric expansivity, and the vapor pressure from *Riddick et al.* [25] for *trans-* and *cis*-decalin and a calculated V_x value (*Eqn. 6* in *Marcus* and *Hefter* [34]) for ten atoms. The value for *cis*-decalin was then corrected with a similar difference as that found between the experimentally measured (0.759 GPa^{-1}) and the predicted (0.714 GPa^{-1}) values of κ_T for *trans*-decalin. According to *Y. Marcus* (private communication), the value of κ_T for *cis*-decalin should be lower than that for the *trans* isomer due to the better packing of the former. ^f) $\Delta H_{el} = \Delta V_{el}\,(c_p\rho/\beta)$.

with three spiropyrans, *i.e.*, the presently studied NO_2-BIPS, 2′,3′-dihydro-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2-indole]-8-carboxylic acid, and 2′,3′-dihydro-1′,3′,3′-trimethyl-8-nitrospiro[2*H*-1-benzopyran-2,2′-indole]-6-carboxylic acid). Those experiments afforded information about the activation volumes for both the ring-opening and the ring-closure reactions in several solvents, as well as about the reaction volumes. Reaction volumes which should include all effects (reaction and solvent movements) in the range -7 to -22 ml mol^{-1} were reported for the ring opening, depending on the solvent [35].

In the most complete of these studies, however, the solvents used were of a different nature than the cycloalkanes used in this work, such as $CHCl_3$, 1,2-dichloroethane, acetone, and DMSO and the concentrations needed for those studies were in general larger than those in the present LIOAS experiments (10^{-5}M) [35].

The data obtained with *trans*-decalin have a larger error than the other points (see *Fig. 7*), probably due to the higher instability of this solvent. Without the *trans*-decalin values, the slope of the plot in *Fig. 7,a* is $\Delta V_{IT} = -(57 \pm 5)$ ml mol^{-1}, a still larger value with a smaller error than the value including all four cycloalkanes.

We note that, although the viscosity does change over the solvent series (*Table 2*) [25], it should not have a strong influence on the photophysics of **Sp**. It has been shown that the photophysical properties of the NO_2-BIPS solutions begin to change at temperatures around 173 K in methyltetrahydrofuran or in methylcyclohexane/methylpentane mixtures, where viscosity is much higher than the highest one used in our work [13]. Consequently, viscosity effects were not considered in our analysis.

Enthalpy Changes. Table 1 shows the literature values for the enthalpy change as reported for the same type of photochromic systems in several solvents [12][36][37]. The intercept in *Fig. 7,a* (*Eqn. 14*) is $\Delta H_{IT} + \Delta H_{elT} - \Delta V_{elT}\ (c_p\rho/\beta) = (165 \pm 19)$ kJ mol^{-1}. With the value $\Delta H_{elT} = -30$ kJ mol^{-1}, constant within the solvent series (*Table 2*) (*vide supra*), the electrostriction-stabilized triplet energy is calculated to be 135 kJ mol^{-1}, reasonable in view of the efficient quenching by O_2, affording $O_2(^1\Delta_g)$ with energy $E_\Delta = 94.1$ kJ mol^{-1} [27].

The intercept in *Fig. 7,b*, $\alpha_2 = 0.076 \pm 0.008$, together with *Eqn. 12* yields the energy content of the open ground-state **Mc** species $E_{\mathrm{Mc}} = -(9 \pm 25)$ kJ mol^{-1}. Although this value is different from that obtained with the steady-state method (*Table 1*), it falls within those values when taking into account the large cumulative error derived from the procedure used for its calculation.

Disregarding again the value for *trans*-decalin, $\Delta H_{\mathrm{IT}} = (155 \pm 6)$ kJ mol^{-1} and $E_{\mathrm{T}} = (125 \pm 8)$ kJ mol^{-1} are obtained. With $\alpha_2 = 0.067 \pm 0.002$ (without *trans*-decalin) and *Eqn. 12*, $E_{\mathrm{Mc}} = -(14 \pm 12)$ kJ mol^{-1} , *i.e.*, essentially no energy difference with the ground-state **Sp**. However, the difference between the UV/VIS spectra of the photogenerated **Mc** form (*Fig. 4*, inset) and the thermally generated colored form **Mc** (*Fig. 8*) indicates that the species observed with the two methods might be different. This might be the origin of the discrepancy between the enthalpy difference determined by the steady-state method (*Table 1*) and by LIOAS.

Already in 1968, *Flannery* [36] recorded the spectra of the photoinduced and the thermal products of **Sp**. The two spectra in benzene were not identical and the difference could not be explained on the grounds of increased concentration of **Sp** alone. One important difference between the two spectra is the absorption around 450 nm, which is absent in the spectrum of the photoinduced species. The aggregation and complexation of spiropyrans in nonpolar solvents has already attained a lot of attention and the general consensus is that a complex of **Sp** and **Mc** can be relatively easily formed. This complex can then form higher aggregates, depending on irradiation and concentration [38].

The merocyanine form of the spiropyrans was reported to aggregate or form dimers that absorb at *ca.* 490 nm [37]. Two monomeric species absorbing at 555 and 590 nm have been reported [12a], although recently one monomeric species of a substituted **Mc** has been shown to have a structured absorption in this region indicating that the two peaks may belong to the same species [38b]. These two maxima are observed especially well for the photoinduced transient in cycloalkanes. It has also been speculated that the two bands correspond to different **Mc** conformers [17][35c]. We conclude that dimerization or higher aggregation should be taken into account during the determination of the reaction enthalpy by the temperature dependence of the equilibrium constant for spiropyrans. This effect should be of no influence for the determinations by LIOAS inasmuch as only the processes during few ns to µs after the laser pulse are monitored.

The enthalpy change in H_2O is rather high and probably due to a large hydrophobic effect of the photoproduced **Sp**.

Entropy Changes. Structural volume changes in unconstrained media (such as solutions are) are expected to have the same sign as entropy changes since both quantities are related to the degree of order in a system. In fact, the structural volume changes measured with LIOAS for an intramolecular electron transfer reaction in nonpolar solvents were quantitatively related with the entropy changes through one of the *Maxwell* relations [10]. For intra- and intermolecular electron transfer reactions in aqueous media, however, an empirical relation was found between both quantities [5][7]. It is evident that while reactions in nonpolar solvents can be treated with equations that handle the medium as a continuum experiencing only an expansion or a contraction due to induced-dipole interactions, those of molecules forming specific bonds with the solvent, such as H-bonds with H_2O that break and reform during the reaction, cannot be treated in a similar manner.

We do not know what is the quantitative correlation between the total ΔV_r and ΔS_r in this reaction. Based on our previous work [10], we calculate ΔS_{el} with the *Maxwell* relation $\Delta S_{el} = \beta/\kappa_T \Delta V_{el}$. *E.g.*, with $\beta/\kappa_T = 1.07$ J ml^{-1} K for cyclohexane [25] and $\Delta V_{el} = -25$ ml mol^{-1} (*Table 2*), a value of $\Delta S_{el} = -27$ J mol^{-1} K^{-1} is obtained for the ^{3}Mc (and for the **Mc**) production in cyclohexane. Most probably, this is just a lowest limit for ΔS_r in absolute terms (*i.e.*, $\Delta S_R < -27$ J mol^{-1}), since the intrinsic contraction during the **Sp** → **Mc** transformation should also lead to a negative entropy contribution. With the value of ΔS_{el}, the entropic term due to electrostriction at 293 K is $T\Delta S_{el} = -8$ kJ mol^{-1} in cyclohexane. Thus, with $\Delta H_R = +(9 \pm 25)$ kJ mol^{-1} and the above considerations $\Delta G_R > 17$ kJ mol^{-1} for the **Sp** → **Mc** reaction in this solvent (see *Table 3*).

Table 3. *Thermodynamic Parameters Determined by LIOAS for the Photoreactions* **McH$^+$ → Sp** *in Aqueous Solution and* **Sp → Mc** *in Cycloalkane Solvents*

Parameter	Aqueous solution **McH$^+$ → Sp**	Cyclohexane **Sp → Mc**
ΔV_R [ml mol^{-1}]	+11 ±2	−71 ±20
ΔS_R [J mol^{-1} K^{-1}]	–	< −27[a])
TΔS_R [kJ mol^{-1}] (at 298 K)	–	< −8[a])
ΔH_R [kJ mol^{-1}]	+282 ±110	+9 ±25
ΔG_R [kJ mol^{-1}]	–	> 17[a])

[a]) Experimental ΔH_R value in the four cycloalkanes together with the ΔS_{el} value for cyclohexane with $\beta = 0.00122$ K^{-1} and $\kappa_T = 1.14 \times 10^{-6}$ kPa^{-1} [25] ($\beta/\kappa_T = 1.07$ J cm^{-3} K^{-1}): see text.

The quantitative relationship between the ΔV_R values and the ΔS_R values in the aqueous solutions is not easy to assess, because several effects should contribute to ΔS_R. A quantitative correlation between ΔV_R and ΔS_R in aqueous media was possible only for cases in which medium effects dominate the value of ΔV_R and therefore determine the value of ΔS_R [5][7]. Thus, it is not possible to calculate the free energy for the ring closure of McH$^+$ in aqueous solutions from the data available so far.

General Conclusions. The present results indicate that the alkane variation method can be extended to an array of cyclic alkanes, with a $(c_p\rho/\beta)$ range comparable to that for linear alkanes [9][10][26][39]. The differences between cyclic and linear alkanes lie mainly in the generally better solubility in the former and in the relatively constant shape of the solvent molecules. Still, the variation in $(c_p\rho/\beta)$ is relatively small in comparison with that in H_2O at various temperatures. Similar to the case of the linear alkanes [20] the constancy of the term $[\Delta V_{el}\ (c_p\rho/\beta)]$ within the cycloalkane series permits the separation of the intrinsic and electrostrictive terms both in the enthalpy and in the volume change. However, a problem related to the use of the cycloalkanes is the purification of the solvents which involves a tedious procedure.

The study of the **Sp** ring opening in cycloalkanes and the **McH$^+$** ring closure in aqueous solutions confirms our previous conclusions regarding the fundamental difference between the forces determining the chromophore-medium interactions in both media. While, in H_2O, deprotonation, protonation, and polar interactions are the main factors, in cycloalkanes reorganization attributed to electrostriction constitute the major forces.

LIOAS provides good parameters for the triplet state formed in sub-ns times and with lifetimes in the hundreds of ns in air-saturated solutions, whereas the data for the final merocyanine bear large errors. However, an important conclusion is that the comparison of steady-state and time-resolved methods seems to afford different results for the reaction enthalpy and for the reaction volumes, *i.e.*, in a time-resolved photochemical method a species is promptly induced and its properties measured, whereas during the classical steady-state thermal or pressure equilibration methods, higher concentrations and longer times are required, allowing the reactive species to further react and form aggregates.

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Experimental Part

General. The abs. of the samples and calorimetric reference (matched within 2%) at the laser excitation wavelength ($0.1 \leq A(\lambda_{exc}) \leq 0.2$) were recorded with a *Shimadzu UV-2102* PC spectrophotometer before and after the LIOAS measurements. Temp. changes between 3° and 25° did not change the abs. at the excitation wavelength (400 nm) of McH^+ and EB aq. soln.

Compounds. 2′,3′-Dihydro-6-nitro-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indole] (NO_2-BIPS) was obtained from *Aldrich*. Organic solvents were purified by multiple distillation before use and checked for the absence of absorbance at 308 nm and for the lowest possible LIOAS signal upon excitation with 308 nm. This required repeated distillation under vacuum at 10 mbar. The protonated species was obtained by the following procedure. NO_2-BIPS was dissolved in EtOH, flashed at 308 nm until it reached maximum coloration. The solvent was swiftly evaporated in the dark. The material thus obtained was dissolved in 0.01M malonic acid, filtered through a 0.2 μm filter and kept in the dark. The pH of the nonbuffered solns. was 5. The yellow soln. was stable for several weeks. *Evans* blue (EB, *Aldrich*) in aq. solns. and *ortho*-hydroxybenzophenone (OHB, *Merck*, recrystallized from EtOH) dissolved in org. solvents were used as the calorimetric references. 5,10,15,20-Tetraphenylporphyrin (TPP) and phenalenone (perinaphtenone, PN) were used as references for the $O_2(^1\Delta_g)$ determinations in cycloalkanes. 5,10,15,20-tetrakis(4-sulfonatophenyl)porphine ($TSPP^{4-}$) was used as a $O_2(^1\Delta_g)$ reference in aq. soln.

Laser-Induced Optoacoustic Spectroscopy. Aqueous Solutions. The LIOAS setup was as already described [3–10]. A *Lambda Physik/EMG101 MSC* excimer laser (XeCl) pumped a *FL2000* dye laser with *Furan 2* dye for the production of the 400 nm pulses. The measurements in acidic aq. soln. were performed in the dark and the sample solns. were stirred between measurements. The solns. were in general not degassed. In some cases, the solns. were bubbled for 10 min. with solvent-saturated Ar or O_2. The Pb-Zr-Ti piezoelectric transducer (*Vernitron*, resonance frequency 1 MHz) was pressed against the cuvette wall parallel to the excitation beam and cuvette-detector contact was established with Si-grease. The ceramic detector was preferred over the film detector because of its higher sensitivity [4]. The cuvette-detector contact remained fixed during a measurement series of the sample and the calorimetric reference. The signal was amplified and subsequently recorded by a transient digitizer (*Tektronix TDS 684 A*) connected to a workstation. The first acoustic wave amplitude (H), *i.e.*, the first maximum to first minimum difference, was used in the aq. solns. The pressure integration time was *ca.* 350 ns with the 0.5 mm slit used to shape the laser beam, so transients between 35 ns and 5 μs could be detected by means of deconvolution procedures. A linear dependence with zero intercept of H with laser total pulse energy was observed for the experiments in aq. media for total laser energies < 20 μJ. The cell was thermostated to ±0.2°. The temp. was measured before the photophysical measurements by placing the thermometer (a digital *Pt100*) in the excitation volume inside the cuvette containing EtOH. The desired temp. for the cooling solvent was determined with EtOH in the cuvette and kept constant during the experiment. The samples excited by the laser during the LIOAS measurements showed no sign of aggregation by either visual inspection or by UV/VIS abs. The only difference before and after measurement was a slight decrease of the abs. ($<5\%$) at the maximum which was taken into account by taking the average of initial and final absorbances.

Nonpolar solvents. The signals from 10 shots of the 15 ns pulses at 308 nm ($\equiv 388.04$ kJ mol^{-1}) of the XeCl excimer laser were averaged, stirring the cycloalkane solns. of NO_2-BIPS in between the shots. 100 Traces were averaged with the solns. of the calorimetric reference. The number of averaged signals was kept to a minimum in order to avoid product accumulation. With the 0.5 mm slit, the acoustic transient time was *ca.* 400 ns in cycloalkanes. Linear total pulse energy dependences of the signal amplitude were obtained up to 50 μJ for NO_2-BIPS in cycloalkanes. All neat org. solvents gave small LIOAS signals upon excitation at 308 nm. This was most probably due to residual absorbance unobservable with a spectrophotometer. In the repeatedly distillated cycloalkanes (*vide supra*) the intensity of this signal was less than 2% of the signals with NO_2-BIPS solns.

Deconvolution (performed with the Sound Analysis program, version 1.13, *Quantum Northwest, Inc.*, Spokane, WA) of the sample signal with the instrumental response was used in the case of the cycloalkane solns. The instrumental response was determined with an OHB solution of the used cycloalkane as calorimetric reference. Three independent series of experiments, each one with freshly prepared solns. were carried out at 20°. Good fit of the LIOAS signals from NO_2-BIPS in org. solvents was obtained upon convolution of the reference signal with a double exponential function describing the time-dependent pressure evolution in the sample. For the LIOAS experiments, concentrations were $1-2 \times 10^{-5}$M. A volume of $0.5 \times 6 \times 10$ mm was irradiated by a single laser shot of *ca.* 20 μJ pulse^{-1}, and the cuvette was stirred for *ca.* 10 sec. Under these conditions dimerization and aggregation should be minimized.

Ring-Closure Quantum-Yield Determination. The quantum yield for ring closure in aq. solns. under our conditions of temperature, concentration, air equilibration, and pH, was determined by measuring the disappearance of the colored form at 400 nm as a function of the number of 400 nm laser shots (converted into photon number). The molar abs. coefficient $\varepsilon_{400} = 2.3 \times 10^4$ M^{-1} cm^{-1} [19] and the measured fluorescence quantum yield $\Phi_f = 5 \times 10^{-3}$ were used for the calculations. The value obtained $\Phi_r = 0.16$ was identical to that reported previously [19].

$O_2(^1\Delta_g)$ Quantum-Yield Determination. The quantum yield for $O_2(^1\Delta_g)$ formation, Φ_Δ, of NO_2-BIPS in air- and in O_2-sat. cycloalkanes was determined as previously described, by monitoring the time-resolved emission at 1270 nm of the $O_2(^1\Delta_g)$ phosphorescence with a liquid N_2-cooled Ge diode [40]. The decay was extrapolated to zero time and the prompt amplitude was compared to that of the ref. soln. at matched abs. (± 0.005). TPP in cyclohexane with $\Phi_\Delta^{TPP} = 0.73$ (determined against phenalenone in cyclohexane, with $\Phi_\Delta = 0.91 \pm 0.03$, as recommended in [41]) was used as a reference. Phenalenone was also used in all four solvents with a value of Φ_Δ considered identical to that in cyclohexane. This is justified by the constant value of Φ_Δ for phenalenone in several solvents [41]. Care was taken to shake the sample between each of the ten laser shots performed to average the $O_2(^1\Delta_g)$ decay traces. The decay lifetime of the NO_2-BIPS-sensitized $O_2(^1\Delta_g)$ signal in cyclohexane was $\tau_\Delta = 23$ μs (*vide infra*, *Inset* in *Fig. 5*), identical to the value reported for the $O_2(^1\Delta_g)$ lifetime in this solvent [28b].

The same procedure was followed for the determination of Φ_Δ in aq. solns. Comparison was made to the signal of $TSPP^{4-}$ ($\Phi_\Delta = 0.53 \pm 0.05$ [42]).

Calculations of *Van der Waals* volumes were performed with a PC after minimization with the PM3 method in the Alchemy program.

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