statistical methods (SHELX86), and 115 parameters were refined. Water hydrogen atoms were included as located. All other hydrogen atoms were included in calculated positions after they had been located. $R = 0.067$, $wR = 0.193$, refined against $|F^2|$. b) Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-410414 (**5**) and CSD-410413 (**3**).

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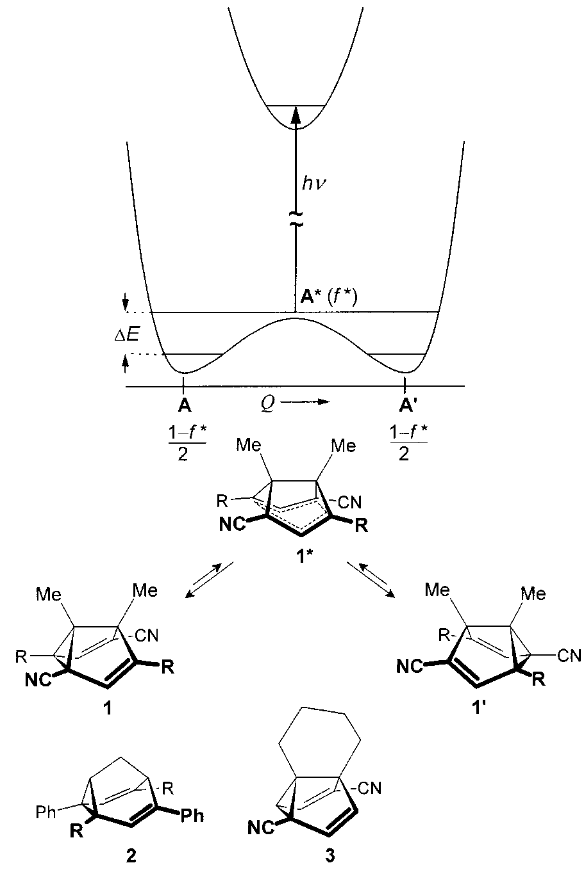
The Equilibrium between Localized and Delocalized States of Thermochromic Semibullvalenes and Barbaralanes—Direct Observation of Transition States of Degenerate Cope Rearrangements

Helmut Quast* and Maximilian Seefelder

Dedicated to Professor William von Eggers Doering on the occasion of his 80th birthday

The Möbius–Hückel concept provides a *theoretical* link between pericyclic transition states and normal molecules.[1] As yet an *experimental* link has not existed. Von E. Doering's seminal design and first examples of molecules that are fluxional because of a very fast degenerate Cope rearrangement[2] were followed by Zimmerman's discovery of semibullvalene[3] and the demonstration that the ground state and the transition state for its Cope rearrangement differ in energy by just a few kcal mol^{-1}.[4] Hoffmann and Stohrer[5] and Dewar and Lo[6] predicted substitution patterns for semibullvalenes that would lower and eventually abandon this energy gap, and thus result in stable delocalized, bishomoaromatic semibullvalenes.[7] A similar formal mutation of shallow degenerate double-well potentials into single-minimum systems is known from the pyramidal inversion of ammonia and its derivatives.[8]

The discovery that the semibullvalenedicarbonitrile **1a** is thermochromic suggested an equilibrium between the classical, localized structure **1a** and its delocalized, bishomoaromatic isomer **1a***, which was estimated to be higher in energy by about 11 kJ mol^{-1} (Scheme 1).[9] Subsequently, the semibullvalenes **1b**[10] and **3**[11] and the barbaralanes **2b**[12] and **2c**[13] showed that thermochromism is common to degenerate systems with extremely low Cope barriers.[14] We report here the quantitative analysis of this phenomenon. Enthalpy differences of as little as 1 kJ mol^{-1} are found to govern the equilibrium between the two degenerate ground states **A**, **A′** and the species **A*** which absorb at long wavelengths. The latter are interpreted as higher, delocalized states, located just above the flat potential barrier between the two ground states, namely, where vibronic interaction is strong.



1a: R = H; 1b, 2b: R = Ph; 2c: R = CN

Scheme 1.

UV/Vis spectra were recorded at various temperatures for degassed solutions of **1**–**3** in butyronitrile. This solvent was chosen because it is sufficiently transparent in the near-UV region and has a broad temperature range in the liquid state. Careful attention has been given to the reversibility of the temperature-driven changes in the spectra. The absorbance was corrected for the thermal expansion of the solvent with the help of density data[15] and refers to a temperature of 298 K.

For the determination of the enthalpy difference ΔH^0 between the differently absorbing species by means of the temperature-dependent long-wavelength bands, we regard their integrated absorbance A_{int} as a measure of the fraction f^* which exists in the higher state **A***. The integrated absorbance A_{int} is obtained by deconvolution of the UV/Vis spectra with Gauss curves[16] (Figures 1–3). Toward this end, Gauss curves

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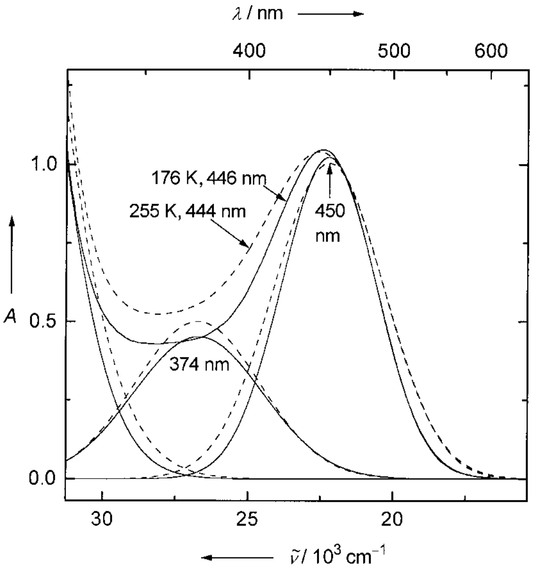


Figure 1. UV/Vis spectra of $\mathbf{1b} \rightleftharpoons \mathbf{1b}^* \rightleftharpoons \mathbf{1b}'$ recorded in degassed butyronitrile ($c = 7.69 \times 10^{-4}$ mol L^{-1}), and the calculated Gauss curves at the highest (dashed curves) and lowest temperature (solid curves).

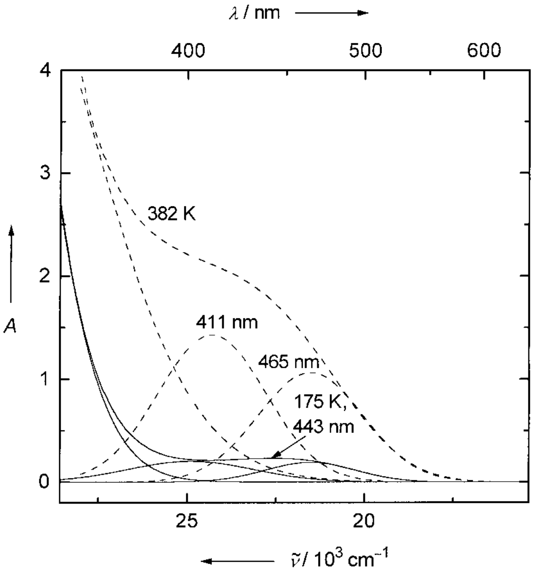


Figure 2. UV/Vis spectra of $\mathbf{2b} \rightleftharpoons \mathbf{2b}^* \times \mathbf{2b}'$ recorded in degassed butyronitrile ($c = 2.84 \times 10^{-3}$ mol L^{-1}), and the calculated Gauss curves at the highest (dashed curves) and lowest temperature (solid curves).

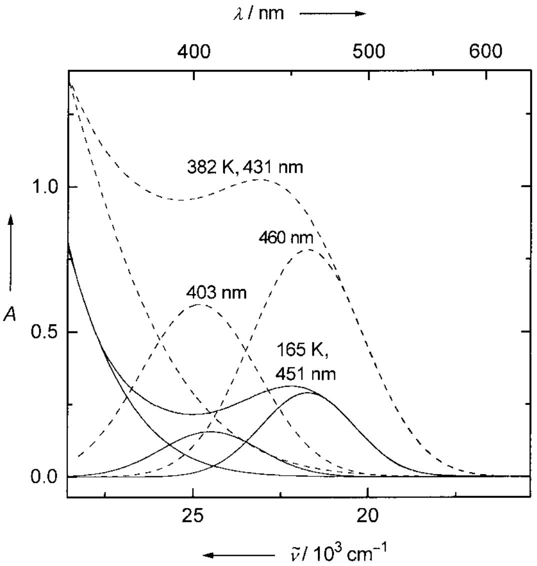


Figure 3. UV/Vis spectra of $\mathbf{2c} \rightleftharpoons \mathbf{2c}^* \times \mathbf{2c}'$ recorded in degassed butyronitrile ($c = 1.25 \times 10^{-3}$ mol L^{-1}), and the calculated Gauss curves at the highest (dashed curves) and lowest temperature (solid curves).

with fixed maxima were fitted to the long-wavelength tails of the spectra. The wavelength of the maxima were determined from the spectra recorded at the lowest temperatures, where the interfering Doppler broadening of the intense short-wavelength absorptions is smallest. The best fit obtained by variation of the wavelength of the maxima afforded the $\lambda^*_{\max}$ values that were also employed at higher temperatures. We note that the ΔH^0 values depend only slightly on the precise position of these maxima. In fact, deliberate variation of $\lambda^*_{\max}$ by ±10 nm resulted in only the small errors given in Table 1. Likewise, insignificant errors of less than 0.05 kJ mol^{-1} were introduced by the choice of smaller or larger (±10 nm) long-wavelength sections of the UV/Vis spectra for the fitting of the Gauss curves.

While single Gauss curves sufficed for the near-UV spectra of the semibullvalenedicarbonitriles **1a**[9] and **3**,[11] the near-UV/Vis spectra of the higher substituted systems **1b**, **2b**, and **c** could *not* be reproduced in that way. Surprisingly, subtraction of the calculated long-wavelength Gauss curve from the total spectrum uncovered a pronounced shoulder at the steep ascent toward shorter wavelengths, which indicated the presence of a second temperature-dependent band of similar intensity (Figures 1–3). The strong overlap with the intense absorptions at shorter wavelengths precluded the calculation of the integrated absorbance of this band with a precision sufficient for a quantitative analysis.[17]

The expression of the equilibrium constant K for the two degenerate states **A**, **A′** and the higher state **A*** [Eq. (1)] is solved for f^*. Replacement of f^* in the Lambert–Beer law [Eq. (2); where $\varepsilon^*_{\text{int}}$ = integrated extinction coefficient of the

Table 1. Enthalpy differences (ΔH^0) between the ground states **A**, **A′** and the higher states **A***, as well as the integrated extinction coefficients ($\varepsilon^*_{\text{int}}$) as computed by a least-squares fit of Equation (4) to the integrated absorbance versus temperature data. The error in ΔH^0 results from a deliberate variation of $\lambda^*_{\max}$ by ±10 nm; the statistical error is about 0.005 kJ mol^{-1}. The squares of the correlation coefficients (r^2), and estimated maxima ($\lambda^*_{\max}$) and calculated extinction coefficients ($\varepsilon^*_{\max}$) for the long-wavelength band of **A*** are also listed.

Compound	ΔH^0 [kJ mol^{-1}]	$\varepsilon^*_{\text{int}}\,10^{-3}$ [L mol^{-1} cm^{-2}]	r^2	$\lambda^*_{\max}$ [nm]	$\varepsilon^*_{\max}\,10^{-3}$ (T [K]) [L mol^{-1} cm^{-1}]
$\mathbf{1a} \rightleftharpoons \mathbf{1a}^* \rightleftharpoons \mathbf{1a}'$	11.06 ± 0.44	50.6	1.0000	360	9.2 (255)
$\mathbf{1b} \rightleftharpoons \mathbf{1b}^* \rightleftharpoons \mathbf{1b}'$	0.82 ± 0.14	24.5	0.9997	450	5.1 (255)
$\mathbf{2b} \rightleftharpoons \mathbf{2b}^* \rightleftharpoons \mathbf{2b}'$	5.51 ± 0.18	17.3	0.9989	465	5.0 (259)
$\mathbf{2c} \rightleftharpoons \mathbf{2c}^* \rightleftharpoons \mathbf{2c}'$	3.30 ± 0.23	17.0	0.9991	460	4.7 (253)
$\mathbf{3} \rightleftharpoons \mathbf{3}^* \rightleftharpoons \mathbf{3}'$	8.58 ± 0.23	38.3	0.9999	360	5.3 (259)

temperature-dependent long-wavelength band [L mol^{-1} cm^{-2}]; c = total concentration [mol L^{-1}]; d = path length [cm]],[18] which has been shown to be valid for **1a**[9] and **2c**, yields the relationship between A_{int} and the thermodynamic parameters of the equilibrium [Eq. (3)]. The overall entropy difference ΔS^0 is the sum of the entropy difference that is due solely to the difference in symmetry numbers σ between **A**, **A′** and **A***, $R\ln(\sigma_{\mathbf{A},\mathbf{A}'}/\sigma_{\mathbf{A}^*})$, and a second term that contains all other contributions to ΔS^0.[19] We obtain the simplified, approximate Equation (4) by assuming that the latter have the same value for **A**, **A′** and **A***, and **A*** has a structure of twofold rotational symmetry, that is, $\sigma_{\mathbf{A}^*} = 2$ (see below).[20] Equation (4) may also be derived on the basis of the symmetry-corrected equilibrium constant $K_{\text{corr}} = [\mathbf{A}^*]/[\mathbf{A}] = 2f^*/(1-f^*)$ instead of $K = [\mathbf{A}^*]/([\mathbf{A}]+[\mathbf{A}'])$ [Eq. (1)] and the assumption that the entropy difference between **A** and **A*** is zero. The least-squares fit of Equation (4) to the A_{int} versus temperature data yielded the two parameters $\varepsilon^*_{\text{int}}$ and ΔH^0. The approximation is supported by satisfactory agreement between the experimental data points and the computed curves, and by excellent correlation coefficients. The squares of the latter are listed in Table 1 together with the calculated parameters $\varepsilon^*_{\text{int}}$ and ΔH^0.

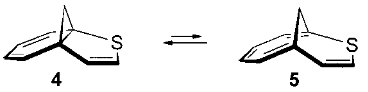
$$K = \frac{f^*}{1-f^*} = \exp\left(-\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}\right) \tag{1}$$

$$A_{\text{int}} = \varepsilon^*_{\text{int}}(f^* c)\, d \tag{2}$$

$$A_{\text{int}} = \varepsilon^*_{\text{int}} c d \left(1 + \exp\frac{-\Delta S^0}{R} \exp\frac{\Delta H^0}{RT}\right)^{-1} \tag{3}$$

$$A_{\text{int}} \approx \varepsilon^*_{\text{int}} c d \left(1 + 2\exp\frac{\Delta H^0}{RT}\right)^{-1} \tag{4}$$

Credence is lent to the analytical procedure by its application to the thermochromism reported by Okazaki et al. for the fluxional system $\mathbf{4} \rightleftharpoons \mathbf{5}$.[21] Calculation of A_{int} ($\lambda^*_{\max} = 350$ nm) from the five published UV/Vis spectra and the least-squares fit of an equation, which is identical to Equation (4) except for the lack of the pre-exponential factor 2, to the A_{int} versus T data yielded $\Delta H^0 = 3.8$ kJ mol^{-1}. This value agrees well with the difference between the free enthalpies $\Delta G^0(303\,\text{K}) = 4.2$ kJ mol^{-1}, which was estimated on the basis of chemical shifts in the ^{13}C NMR spectra.[21]



4 **5**

The temperature dependence of the fractions f^* that exist in the higher state **A*** was calculated from Equations (2) and (4) and is displayed in Figure 4. The f^* versus T curves are determined only by the enthalpy difference ΔH^0 between the two states. A cursory inspection of Figure 4 allows an explanation of previous, puzzling observations: The yellow semibullvalenedicarbonitriles **1a** and **3** completely fade at temperatures below 200 K, while, in the case of **1b** sizeable amounts of the orange-red species survive even on cooling with liquid nitrogen.

The enthalpy differences ΔH^0, which were derived from variable-temperature UV/Vis spectra recorded for butyronitrile solutions (Table 1), are composed of the gas-phase enthalpy differences $\Delta H^0_{\mathbf{A}/\mathbf{A}^*}$ and the solvation terms $(\Delta H_{\mathbf{A}})_{\text{BN}}$ and $(\Delta H_{\mathbf{A}^*})_{\text{BN}}$, which stem from the transfer of **A**, **A′** and **A***, respectively, from the gas phase to the butyronitrile solvent [Eq. (5)].

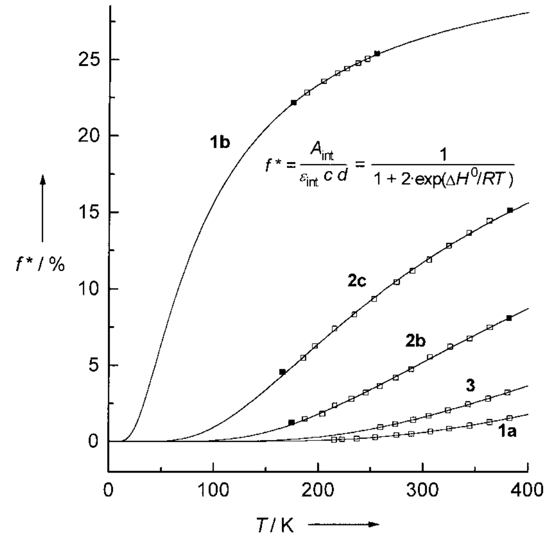


Figure 4. Temperature dependence of the fractions f^* that exist in the higher state **A*** of the thermochromic semibullvalenes **1**, **3**, and the barbaralanes **2**. Filled squares correspond to the UV/Vis spectra displayed in Figures 1–3.

$$\Delta H^0 = \Delta H^0_{\mathbf{A}/\mathbf{A}^*} + (\Delta H_{\mathbf{A}^*})_{\text{BN}} - (\Delta H_{\mathbf{A}})_{\text{BN}} \tag{5}$$

We interpret[12] the gas-phase enthalpy differences $\Delta H^0_{\mathbf{A}/\mathbf{A}^*}$ on the basis of the ubiquitous system of adiabatic energy hypersurfaces that consists of a symmetrical, shallow double-well ground-state potential and a single-minimum excited-state potential (Scheme 1).[22] Recently, Zilberg et al. demonstrated that this system can be readily derived for semibullvalene with the valence bond configuration-mixing method. They calculated the energy gap between the two adiabatic surfaces at the geometry of the transition structure on the lower surface to be 5.16 eV, a value which corresponds to a Franck–Condon transition at $\lambda_{\max} = 240$ nm.[23] By taking into account the effects of the substituents, we note that the UV/Vis properties of the higher states **A*** of the present *substituted* semibullvalenes and barbaralanes (Table 1) are in accord with Zilberg's $\lambda_{\max}$ value for the transition structure of semibullvalene and the UV absorptions predicted for C_{2v}-semibullvalene by Borden, von R. Schleyer et al.[24]

Within the limits of this simple model, the species **A*** which absorb at long wavelengths are considered as vibronic eigenstates that are located just above the low potential barrier toward the degenerate Cope rearrangement $\mathbf{A} \rightleftharpoons \mathbf{A}'$. Thus $\Delta H^0_{\mathbf{A}/\mathbf{A}^*}$ corresponds to $N_{\text{L}}\Delta E$ (N_{L} = Loschmidt's number), where ΔE is the energy of the transition with the exceptional fundamental frequency associated with the vibration along the reaction coordinate.

Unfortunately, gas-phase enthalpy differences are not directly available, and possible relations between ΔH^0 values measured for solutions and the structures of the compounds are obscured by solvent effects.[25] The values of ΔH^0 are very small indeed and in the range of van der Waals and other weak solute–solvent interactions.[26] Only in the case of **1a** can the enthalpy difference ΔH^0 between **A**, **A′** and **A*** be compared with the barrier for the degenerate Cope rearrangement $\mathbf{A} \rightleftharpoons \mathbf{A'}$, $\Delta G^{\neq}(200\,\mathrm{K}) = 14.4\,\mathrm{kJ\,mol^{-1}}$ (in chlorodifluoromethane/[D$_6$]dimethyl ether).[27] Those barriers are too low to be determined by ^{13}C NMR spectroscopy for the other compounds, and any estimates based on increments for substituents[27] must assume their additivity, which can hardly be justified. Nevertheless, qualitative arguments on the basis of cooperative steric and electronic substituent effects, and constant solvation terms support the conclusion that the ΔH^0 values roughly parallel the heights of the Cope barriers.

Taking together all experimental observations and theoretical arguments, one cannot escape the conclusion that the species **A*** are indeed vibronic states above the potential energy maximum between the shallow wells **A** and **A′**, and, consequently, correspond to transition states. In terms of a conventional structural representation, they are delocalized, bishomoaromatic semibullvalenes and barbaralanes. While experimental investigations of transition states have so far been the domain of femtosecond chemistry[28] or other highly sophisticated techniques,[29] thermochromic semibullvalenes and barbaralanes allow the observation of transition states even with one's naked eye.

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