

## PHOTOACOUSTIC MEASUREMENTS AND MINDO/3 CALCULATIONS OF ENERGY STORAGE BY SHORT-LIVED SPECIES: THE SPIRO[1,8-*a*]DIHYDROINDOLIZINE-BETAINES SYSTEM<sup>†</sup>

NORMAN A. GARCÍA, GERALD ROSSBROICH and SILVIA E. BRASLAVSKY

*Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34 - 36, D-4330 Mülheim an der Ruhr (F.R.G.)*

HEINZ DÜRR and CARMEN DORWEILER

*F.B. 14.1, Organische Chemie, Universität des Saarlandes, D-6600 Saarbrücken (F.R.G.)*

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### Summary

We have used photoacoustic spectroscopy to measure the difference  $\Delta E$  in internal energy content between spiro[1,8-*a*]dihydroindolizines and short-lived betaines. The energy stored ( $\Delta E$ ) by the betaines varies between 52 and 69 kJ mol<sup>-1</sup>, depending on the particular compound. A linear relationship was established between  $\Delta E$  and the rate constant for the back reaction.

The results of the modified neglect of differential overlap/version 3 (MINDO/3) calculations of a simple model betaine are in good agreement with the experimental data.

### 1. Introduction

Upon absorption of electromagnetic radiation, a compound can deactivate via two possible pathways: radiation processes (*e.g.* fluorescence) or radiationless processes (chemical reaction or relaxation with release of the excess energy as heat). The latter constitutes the source of the signal in photoacoustic spectroscopy (PAS) [2, 3]. Malkin and coworkers [4, 5] used PAS to obtain information on how much light is converted into heat in a particular photoprocess and to thus estimate the yield of the photochemical process.

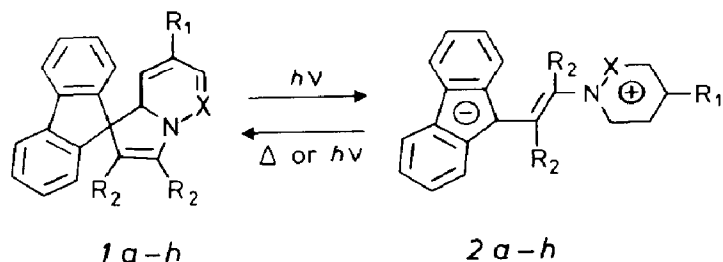
We have applied this method to photochromic systems in which one of the compounds is a short-lived species, in order to measure the difference in energy content between products and reactants.

Photochromic systems have become especially attractive because of their potential in solar-energy conversion. In many cases it is possible to

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<sup>†</sup>Part of these results were presented at the Xth IUPAC Symposium on Photochemistry [1].

calculate the energy stored by evaluating the differences in heat of formation between products and reactants [6]. In other cases, conventional calorimetry or photocalorimetric techniques can be used [7]. The latter methods are applicable only in the case of relatively stable photoproducts. In cases in which short-lived intermediates are produced, PAS becomes a useful technique. The spiro[1,8-*a*]dihydroindolizine **1** [8-10] is a system of this type. These compounds undergo a very facile photochemically induced ring opening (a concerted 1,5-electrocyclic reaction [11]) to give the betaines **2**.



	R <sub>1</sub>	R <sub>2</sub>	X
a	H	CN	N
b	H	CO <sub>2</sub> Me	N
c	H	COMe	N
d	H	CO <sub>2</sub> Me	CH
e	H	CN	CH
f	CO <sub>2</sub> Me	CN	CH
g	CN	CN	CH
h	CH <sub>3</sub>	CN	CH

Fig. 1. The [1,8-*a*]dihydroindolizine–betaine system (1–2).

In this paper we report on (1) PAS studies in which the energy gap between **1** and **2** is evaluated and (2) modified neglect of differential overlap/version 3 (MINDO/3) calculations on compound **3** which serves as a model for structure **2**. Upon comparison of the calculated energy content of **3** with that obtained for an indolizine-like structure [12] the energy gap for the ring opening process can be evaluated.

## 2. Experimental details

The home-made PAS equipment included a stabilized 450 W xenon lamp (PRA model ALH 220) mounted in a housing and an f/3.4 monochromator (Applied Photophysics). The cell was constructed according to the principle of the Helmholtz resonator [13]. This design allows the inner gas volume to be kept small (about 0.08 cm<sup>3</sup> in our case) and, at the same time, separates the microphone from the liquid sample (total liquid volume, about 0.5 cm<sup>3</sup>). The microphone and preamplifier (Brüel and Kjaer 4166 and 2619 respectively) were used in conjunction with two lock-in

amplifiers (Princeton Applied Research, model 186A) to yield amplitude and phase information. The chopping frequency  $\omega$  of the mechanical light modulator and the wavelengths were selected by a microcomputer (Commodore 4032) which was also used to acquire and handle the data from the lock-in amplifiers through a programmable interface (Ithaco 385).

The continuous wave irradiation necessary to maintain a sufficient concentration of **2** for spectral purposes (Fig. 3, below) was performed using a fibre optics source (Oriel 77501 100 W quartz halogen lamp) attached to a 77525 Oriel fibre optics cable.

Since the amplitude of the signal is proportional to  $\omega^{-1.5}$  [14], a relatively low value of  $\omega$  (30 Hz) was used which improved the signal-to-noise ratio. Varying  $\omega$  from 30 to 350 Hz did not produce any change in the results for the energy content in the case of compound **1d**.

The purity of the spiro[1,8-*a*]dihydroindolizine derivatives was controlled by using thin-layer chromatography (TLC) (one spot in SiO<sub>2</sub>-TLC-micro cards, Polygam, Macherey-Nagel; solvent: CH<sub>2</sub>Cl<sub>2</sub>). The concentrations were of the order of 10<sup>-4</sup> M, and the solutions were handled under dim light. No more than two photochromic cycles were used in each measurement, to prevent the oxidation of the betaine form [15]. Conversion was typically about 2%. The amplitude difference between sample and reference was always about 10%. Zinc tetraphenylporphyrin (ZnTPP) was used as a reference, and was prepared by the addition of zinc acetate to a methanolic solution of tetraphenylporphyrin (Aldrich) and purified according to Barnett *et al.* [16].

Spectroscopic grade benzene and ethanol (Merck) were used. A Perkin-Elmer 320 spectrophotometer was employed to measure the absorbances at the selected wavelength. In all cases the absorbance of the sample and the reference were identical to the second decimal place at the irradiation wavelength  $\lambda_{\text{irr}}$ . The spectral resolution ( $\Delta\lambda = 6$  nm) was the same in absorbance and PAS measurements. The spectrum of compound **2b**, which had a lifetime  $1/k$  of 72 s at room temperature (Table 1), was recorded using a fast spectrophotometer with a rotating grating (Omega 10, Bruins Instruments, Munich).

The MINDO/3 calculations were carried out on a Siemens 7561 computer using the MINDO/3 standard version [17]. We are grateful to Professor W. Thiel, Wuppertal University (formerly at Marburg University) for the MINDO/3 program which is included in his modified neglect of diatomic overlap, correlation (MNDOC) version.

### 3. Results

#### 3.1. PAS studies

The rearrangement in the photochromic system spiro[1,8-*a*]dihydroindolizine-betaine (Fig. 1) is based on the photochemical ring opening and closure at the spiro carbon [8]. Typical absorption and PAS spectra are shown in Figs. 2 and 3 respectively. It is known that the photochemical reaction proceeds from the excited singlet state of **1** [18].

TABLE 1

Energy storage for the reaction  $1 \xrightarrow{h\nu} 2$  at room temperature

Compound	$R_1$	$R_2$	$X$	$\lambda_{irr}$ (nm)	$\phi_r^a$	$k_{2 \rightarrow 1}^a$ $\times 10^4$ (s $^{-1}$ )	$\Delta E$ ( $\pm 10\%$ ) (kJ mol $^{-1}$ )		$\Delta H_r^b$ (kJ mol $^{-1}$ ) MINDO/3
							$C_6H_6$	$C_2H_5OH$	
1a	H	CN	N	405	0.78	2.05 <sup>c</sup>	56.4		
1b	H	CO <sub>2</sub> Me	N	390	0.40	138.6 <sup>d</sup>	69.0	62.7	
1c	H	COMe	N	405	0.47	10.74 <sup>e</sup>	57.7	51.4	
1d	H	CO <sub>2</sub> Me	CH	385	0.43	38.8 <sup>d</sup>	60.2	52.7	
1e	H	CN	CH	405	0.70	0.41 <sup>c</sup>	54.3		
1f	CO <sub>2</sub> Me	CN	CH	405	0.65	0.46 <sup>d</sup>	53.1		
1g	CN	CN	CH	405	0.74	0.74 <sup>d</sup>	58.5		
1h	CH <sub>3</sub>	CN	CH	405	0.58	0.22 <sup>d</sup>	52.7		
3	H	CN	CH						69

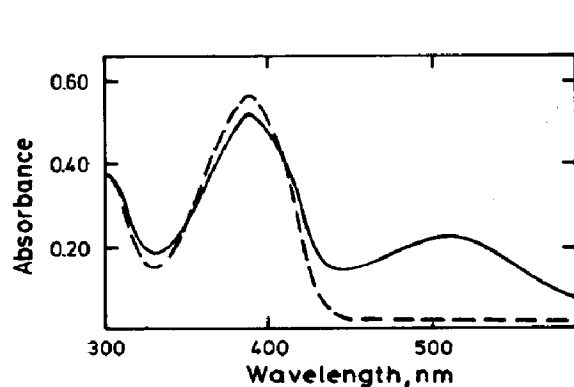
<sup>a</sup>In methylene chloride [8, 10, 18] and corrected for the thermal back reaction [10].<sup>b</sup>Reaction enthalpy for the formation of the betaine 3 from the corresponding indolizine.<sup>c</sup>See ref. 18.<sup>d</sup>See ref. 19.<sup>e</sup>See ref. 9.

Fig. 2. Absorption spectra of spiro[1,8-a]dihydroindolizine (1b) in ethanol: —, before irradiation (1b + 2b); ---, after partial photoconversion to the betaine form (1b). The spectrum of 1b + 2b was recorded using a fast spectrophotometer within 200 ms of irradiating 1b with white light.

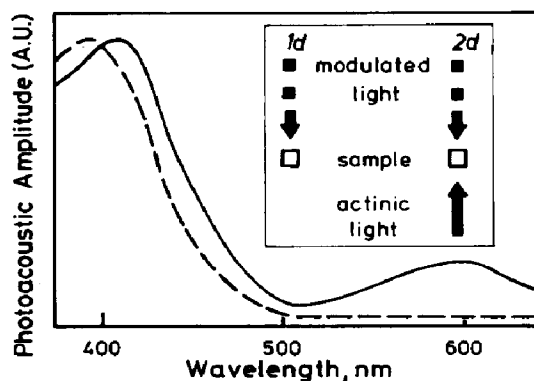


Fig. 3. ---, PA spectra in benzene of the spiro[1,8-a]dihydroindolizine 1d; —, betaine form 2d. The signals of 1d and 2d were registered every 10 nm, allowing 10 min for thermal recovery; the experiment with 2d was performed under continuous irradiation with actinic (white) light through fibre optics from the bottom of the cuvette, in order to maintain a steady concentration of 2d. The maxima of the relative signal amplitudes were normalized to an arbitrary value.

The back reaction (ring closure) is thermally or photochemically induced, depending on the particular substitution pattern. Its rate depends on the polarity of the medium [8]. The rate constants for the thermal process of compounds 2a - 2h are shown in Table 1 [9, 19, 20].

The amplitude  $H_s$  of the PAS signal of the indolizines is related to the reaction energy change  $\Delta E$  through eqn. (1) [4, 5]

$$H_S = \kappa \left( 1 - \frac{\phi_r \Delta E}{N_A h \nu} \right) \quad (1)$$

in which  $\kappa$  is a constant dependent on the experimental conditions (optical and thermal properties of the sample, irradiance, geometry of the cuvette, volume of liquid in the sample,  $\lambda$  and  $\omega$ ) [14],  $N_A$  is Avogadro's number,  $h$  is Planck's constant,  $\phi_r$  the reaction quantum yield and  $\nu$  the frequency of the incident radiation. Fluorescence was neglected in the calculations since the emission quantum yields are of the order of only  $10^{-3}$  [18]. The constant  $\kappa$  (eqn. (1)) can be eliminated by carrying out the measurements relative to a reference (see below) with matched absorbance and under identical geometrical conditions. Since the solutions are dilute, their thermal properties can be considered to be those of the solvent [14]. The product  $\phi_r \Delta E$  is therefore obtained from eqn. (2) [4, 5].

$$\phi_r \Delta E = N_A h \nu \frac{H_R - H_S}{H_R} \quad (2)$$

where  $H_S$  and  $H_R$  are the signal amplitudes of the sample and the reference respectively.

Since the values of  $\phi_r$  vary with wavelength [10, 21], those used for the calculation of  $\Delta E$  (Table 1) were measured at the irradiation wavelength employed in the PAS experiment. The photochemical back reaction was neglected in all cases. For the compound 2a a maximum value of about 0.05 (8% of the direct reaction quantum yield) has been measured, and for compound 2f a value of 0.13 (about 20% of the direct quantum yield) was evaluated [10]. Since the final conversions during the quantitative PAS measurements were very low, the neglect of the back reaction seems justified.

The method is applicable only to the detection of species with lifetimes longer than  $1/\omega$ , since in this case the stored heat will be re-emitted in a time longer than the modulation period [14]. In all the indolizines studied, the lifetime  $1/k$  of species 2 was longer than  $1/\omega$  (see Table 1). The heat detected is normally smaller than that from the reference, which ideally should emit all the absorbed energy as heat in a time much shorter than  $1/\omega$ . ZnTPP in the presence of molecular oxygen (air) was used as the reference, since under these circumstances all radiationless processes are faster than  $1/\omega$  [22].

In correcting for the fluorescence of the reference, values of 0.03 for the fluorescence quantum yield  $\phi_f$  [23, 24] and of  $15\,730\text{ cm}^{-1}$  for the integrated average wavenumber for the ZnTPP fluorescence  $\nu_f$  [25] were used. The observed signal amplitude  $H_R^{\text{obs}}$  of the reference is related to the fluorescence parameters and to the corrected PAS signal amplitude  $H_R$  of the reference through eqn. (3) (which is similar to eqn. (1)).

$$H_R^{\text{obs}} = \kappa \left( 1 - \frac{\phi_f \nu_f}{\nu} \right) = H_R - \kappa \frac{\phi_f \nu_f}{\nu} \quad (3)$$

from which  $\kappa$  and  $H_R$  can be obtained.

Measurements were carried out for several betaine derivatives in benzene and ethanol (Table 1). The quantum yields quoted were measured in methylene chloride [8,10,18]. These values were used to calculate the energy storage in the former solvents, since preliminary results indicated that the quantum yield of the reaction does not depend on the solvent [20]. Methylene chloride could not be used to measure PAS owing to its high volatility.

### 3.2. MINDO/3 calculations on 3

Structure 3, which is a simplified betaine structure (see Fig. 4), was optimized by varying bond lengths and bond angles (assuming  $C_{2v}$  symmetry for the two rings). All dihedral angles were kept constant except for rotations around the C(1)—C(2) and C(3)—N(4) bonds.

The calculated energy minimum for 3 corresponds to a geometry in which the carbocyclic ring is in the plane C(1, 2, 3) and the pyridine ring is perpendicular to this plane (Fig. 5). Calculations of the rotational barrier around C(2)—C(3) show that there is a very small energy difference between the cis and the trans isomers of 3 [12]. The calculated structural parameters and charge densities of 3 are shown in Figs. 6 - 8.

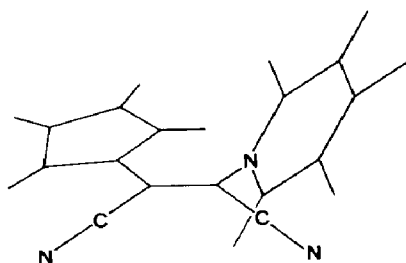
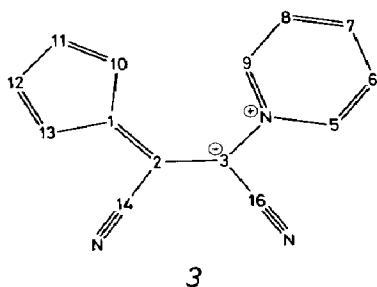


Fig. 4. General numbering scheme for the betaine model compound 3 used in the MINDO/3 calculations.

Fig. 5. Calculated geometry corresponding to the energy minimum of compound 3.

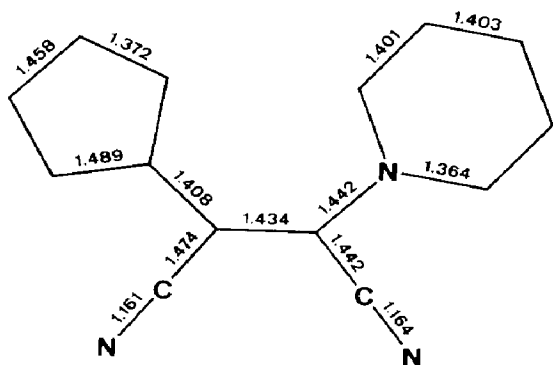


Fig. 6. Calculated bond lengths for compound 3.

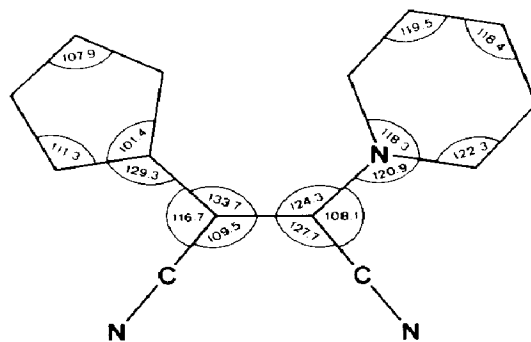


Fig. 7. Calculated angles for compound 3.

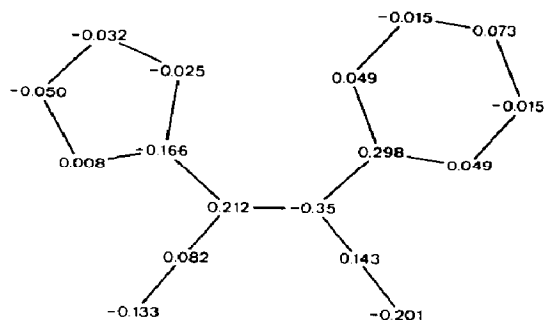


Fig. 8. Calculated electron densities for compound 3.

The C(1)—C(2) bond is 0.026 Å shorter than the C(2)—C(3) bond, the C(3)—C(16) bond is about 0.032 Å shorter than the corresponding C(2)—C(14) bond (Fig. 6), and the five-membered ring has different bond lengths. Finally, large values were obtained for the angles C(1, 2, 3), C(2, 3, 16), C(1, 10, 11) and C(1, 13, 12) (Fig. 7).

For the pyridine ring the structural parameters agree very well with those of the methylpyridinium cation [26].

#### 4. Discussion

The arrangement corresponding to the energy minimum (Fig. 5) allows conjugation throughout the negatively charged cyclopentadienyl—C(2, 3)—alkylidene—C(16)≡N system. As a result the C(3)—C(16) bond length is shorter than that of C(2)—C(14) (Fig. 6).

A comparison of the bond lengths (Fig. 6) suggests furthermore that the actual double bond character is more likely for C(1)—C(2) than for C(2)—C(3). This is also in accord with the finding that the five-membered ring has different types of bond lengths, at variance with what would be expected for a cyclopentadienyl anion [27] having five equivalent bonds. In fact, the bond lengths are closer to a cyclopentadiene structure [17] (Fig. 6). The conjugation is also reflected by the electron densities in 3 which indicate that the negative charge is greater at C(3) than at C(1) (Fig. 8). Conjugation is also optimized through the adoption of large values for the angles C(1, 2, 3), C(2, 3, 16), C(1, 10, 11) and C(1, 13, 12) (Fig. 7) which allows the system to approach a planar structure.

As inferred from previous calculations [12] there is a very small energy difference between the *cis* and the *trans* isomers of 2. Therefore, no isomer is favoured and an equilibrium between the isomers exists, since free rotation is possible around the C(2)—C(3) bond owing to its largely single bond character.

From the PAS studies of 1a - 1h a correlation can be observed between the rate constants of the thermal back reaction  $2 \rightarrow 1$  and the energy stored as shown in Fig. 9. The deviations from a good linear relationship might originate from neglecting the photochemical back reaction (see Section 3

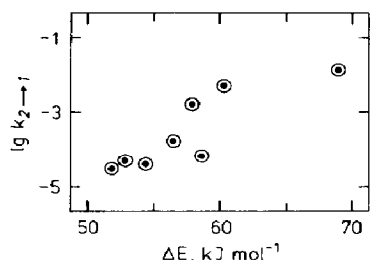


Fig. 9. Logarithm of the  $2 \rightarrow 1$  reaction rate constant in ethylene chloride as a function of the energy  $\Delta E$  stored by the betaines 2 in benzene.

and ref. 10). The value of the quantum yield for the latter reaction is unknown in most cases. From the PAS data and the MINDO/3 calculations it becomes clear that the substituent at C(3) of the betaine 2 is decisive for the stability of these compounds (*cf.* ref. 28).

The variation in  $\Delta E$  with the substitution pattern shows that betaine lifetimes are mainly determined by their energy content. This is also substantiated when the measurements in ethanol and in benzene are compared. The zwitterionic 2 is better stabilized in the more polar medium so that lower average values for  $\Delta E$  result (Table 1). However, considering the large difference in dielectric constant between the two solvents studied, the difference in  $\Delta E$  is relatively small. This can be understood by observing that the charge separation in 2 is far from complete, as inferred from the data given in Fig. 8.

Thus, the conclusion can be drawn that electron withdrawing substituents at C(3) should stabilize the betaines. This result is reflected in Table 1 when the ring closure rate constants of the compounds possessing electron withdrawing substituents (2a, 2e - 2h) are compared with those of the compounds with electron releasing substituents. For instance, 2b shows the highest  $2 \rightarrow 1$  rate constant.

The fact that betaine lifetimes are determined by their energy content (Fig. 9) implies that the solar-energy storage conditions offered by the indolizine-betaine system are not ideal. Extrapolation of the data of Fig. 9 indicates that the required stability of compound 2 (which could eventually be reached through appropriate substitution) would allow only the storage of an extremely small amount of energy.

The enthalpy of formation of the betaine model 3 was calculated to be 744.9 kJ mol<sup>-1</sup>. For an indolizine-like structure related to compound 3 an enthalpy of formation of 676.3 kJ mol<sup>-1</sup> has been obtained [12]. The difference between these two values should be the reaction enthalpy  $\Delta H_r = 69$  kJ mol<sup>-1</sup>. This value is in surprisingly good agreement with the PAS data (see Table 1), considering that the calculations were made for a model compound under ideal gas conditions. The comparison between  $\Delta E$  and  $\Delta H$  is justified since the changes in temperature produced in the PAS cuvette are only of the order of  $10^{-3}$  °C, which would induce extremely small changes in  $\Delta(PV)$ .



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