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Photochromism of spironaphthooxazines having electron-donor substituents

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Abstract

Spectral and photochromic properties of spironaphthooxazines (SNOs) with piperidine and morpholine substituents have been studied at different temperatures in various solvents. It has been recognized that introduction of these substituents in naphthooxazine fragment leads to fluorescence of the initial form of SNO molecules at low temperatures, which disappears with temperature rise. The dependences of the photoinduced form of spectral characteristics on temperature and concentration make it possible to assume the aggregation of the molecules of photoinduced form in non-polar solvents. It is proposed that the coloured form of substituted SNOs has a bipolar structure with a positive charge on piperidine or morpholine nitrogen atom contrary to the quinonoic form of unsubstituted SNO.

Keywords: Photochromism; Spironaphthooxazines; Electron donor

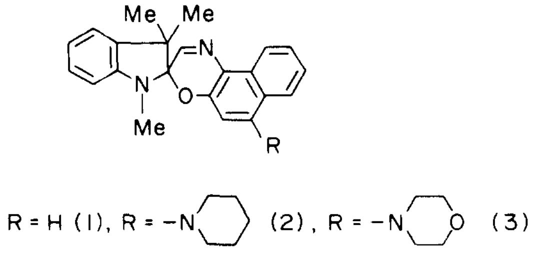
1. Introduction

Basic research on photochromic materials has been increasing in recent years as a result of scientific interest and possible commercial applications. When in crystalline form or dispersed in rigid polymer matrices, photochromics appear to be promising in areas such as display systems, microfilms, computers and communication systems [1].

Photochromism of spironaphthooxazines (SNOs) is the subject of extensive investigations nowadays owing to their higher photostability in comparison with well-known indolinospiropyranes (ISPs) [2]. The mechanism of photochromism of SNOs is similar to that of ISPs and involves heterolytic cleavage of the C–O spirobond of the oxazine ring to give highly coloured isomers, photomerocyanines, which undergo ring closure to reproduce SNOs either upon heating or by irradiation with visible light. Photochromic properties of SNOs are highly sensitive to their structure and environment.

In our previous papers [3–5] the influence of NO_2 group introduced by direct chemical reactions into different positions of SNOs on spectral luminescence and photochromic characteristics of some SNOs has been studied. It has been shown that in solutions the wavelength of the absorption maximum of coloured form of nitrosubstituted SNOs shifts to blue and the rate constant *k* of ring closure decreases as the polarity of the medium increases. From these results we have concluded that the coloured form of nitrosubstituted SNOs has a bipolar structure in solvents of different polarity contrary to the quinonoic form of unsubstituted SNO. Furthermore, it has been shown that nitrosubstituted SNOs have luminescence in contrast with unsubstituted SNO. The scheme of electronically excited levels and transitions between them have been proposed to explain the interpretation of electronic absorption and emission spectra [4].

At the same time, data on the influence of the electron-donor substituent on the spectral and photochromic properties of SNOs are rather scarce [6,7]. So in this paper, we present the results of spectroscopic and photochromic study of two SNOs having electron-donor substituents: 1′,3′,3′-trimethyl-6-piperidinospiro[indoline-2′,3-3H-naphtho[2,1-b][1,4]-oxazine] and 1′,3′,3′-trimethyl-6-morpholinospiro[indoline2′,3-3H-naphtho[2,1-b][1,4]-oxazine].



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Comparison of the experimental results for the SNOs **2** and **3** with those for unsubstituted SNO **1** makes it possible to establish the influence of electron-donor substituents in the naphthooxazine fragment on the photochromic behaviour of SNOs.

2. Experimental details

2.1. Materials

Compounds **1–3** used in this work were prepared and purified as described in [8]. Nuclear magnetic resonance and thin layer chromatography techniques showed no trace of impurities in these samples.

Ethanol, acetonitrile, dimethylformamide (DMF), acetone, toluene, butyl acetate, heptane and light petroleum ether (PE) purified by standard methods were used as solvents.

2.2. Spectroscopic study

All spectral luminescence and kinetic measurements were carried out using a classic spectrofluorophosphorimeter assembly based on two monochromators. A 1000 W xenon arc lamp powered by a stabilized rectifier was used as an excitation source. The excitation wavelengths were selected with a grating monochromator with a concave diffraction grating having 1200 lines mm^{-1}, an aperture ratio of 1:2.5 and reversible linear dispersion of 16 A mm^{-1}. A quantum counter based on rhodamine B solution in ethylene glycol (3 g dm^{-1}) served for excitation wavelength correction. A grating monochromator with a grating having 1200 lines mm^{-1}, an aperture ratio of 1:6 and a reversible linear dispersion of 13 A mm^{-1} was used as a recording monochromator. The luminescence signal after passing through the recording monochromator, photomultiplier and ''inlet–outlet'' adapter was numerically treated on an IBM PC. Luminescence spectra were corrected taking account of the quantum spectral sensitivity of the recording installation. A phosphoroscope, analogous to that in [9], was used for recording the phosphorescence.

To record the absorption spectra the above installation was used as a single-beam spectrometer with a hydrogen lamp as UV light source and an incandescent lamp as a visible light source.

All spectral measurements were carried out in a quartz rectangular cell placed in a thermostatic quartz Dewar flask, controlling the temperature to within ± 1 °C.

For 365 nm photocolouration, a 1000 W high pressure mercury lamp (light intensity, 3×10^5 mol s^{-1} dm^{-3}) and a set of glass filters were used.

The concentrations of the compounds were varied in the range 10^{-4}–10^{-6} mol dm^{-3}.

3. Results and discussion

Compounds **2** and **3** as well as **1** exhibit strong photochromic properties, i.e. they are transformed under light action from the initial state A into the coloured form B, which returns to the uncoloured state in the dark. The transition $A \xrightarrow{h\nu} B$ includes spirobond C–O dissociation and *cis–trans* isomerization, resulting in formation of the B form with a planar configuration and intensive light absorbance in the visible region of the spectrum.

The presence of an electron-donor substituent in the molecules of **2** and **3** results in considerable differences of their photochromic characteristics from those of **1**.

3.1. Initial form

As seen from Fig. 1, the absorption spectra of the initial forms A(**2**) and A(**3**) in all solvents used have a pronounced red shift in comparison with the spectrum of A(**1**), which may be connected not only with the evident bathochromic influence of the electron-donor substituent [10,11], but also with the possible appearance of new electronic transitions of $n\pi^*$ nature in A(**2**) and A(**3**).

The last assumption is indirectly proved by the existence of A(**2**) and A(**3**) molecule fluorescence at 77 K in all solvents used (Fig. 1), which is not observed for A(**1**) at any temperature [12,13]. The results obtained for A(**3**) are qualitatively similar to those for A(**2**). We therefore concentrate on the results for the A(**2**) sample. Two facts allow us to attribute the observed fluorescence to A(**2**) molecules.

(1) Inspection of Fig. 1 indicates the identity of band positions in the absorption spectrum and luminescence excitation spectrum of A(**2**). Some differences observed in band intensities seem to be connected with the dependence of the quantum yield of photocolouration on the excitation wavelength.

(2) The observed fluorescence intensity decreases during the photocolouration process.

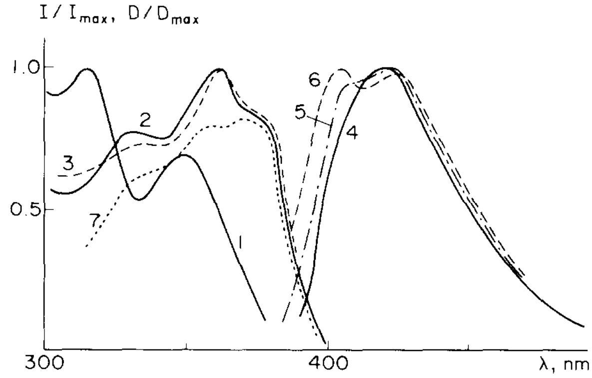


Fig. 1. Absorption (curves 1–3), luminescence (curves 4–6) and luminescence excitation (curve 7) spectra of A(**1**) (curve 1), A(**2**) (curves 2 and 4–7) and A(**3**) (curve 3) molecules in heptane at 300 K (curves 1–3) and 77 K (curves 4–7). The A(**2**) concentration is 10^{-3} mol dm^{-1} (curve 4), 10^{-5} mol dm^{-1} (curve 5)and 10^{-6} mol dm^{-1} (curve 6).

No phosphorescence of A(**2**) and A(**3**) have been observed.

The position and form of the absorption spectra of A(**2**) and A(**3**) do not depend practically on the concentration nor on the medium polarity, whereas the fluorescence spectra of A(**2**) and A(**3**) in non-polar heptane and PE vary considerably with increasing concentration, as shown for A(**2**) in Fig. 1. This dependence is absent in polar solvents (DMF and EtOH). Moreover, the fluorescence intensity decreases gradually with increasing temperature from 77 K and vanishes completely when the solvent melts. Earlier we have found an analogous temperature effect on luminescent properties for spiroanthrooxazines (SAOs) [14–16]. Luminescence of unsubstituted SAO has been assumed to arise only in aggregated states, most probably dimers. These dimers are formed by two molecules of SAO, anthrooxazine fragments of which are situated one under another along their long axis. SAO luminescence has been observed in a non-polar medium even at 300 K, and that of bis-SAO also in polar solvents at 300 K [16]. Taking into account that A(**1**) shows no luminescence even at 77 K, and that the presence of piperidine or morpholine substituents in A(**2**) or A(**3**) sterically prevents the formation of dimers analogous to SAO, we conclude that disappearance of the fluorescence of A(**2**) and A(**3**) with increase in temperature is connected with the appearance of non-radiative internal conversion of the excited state $A^* \rightsquigarrow A_0$. The latter is usually absent in a glassy or crystalline solvent at low temperatures [17]. Thus A(**2**) and A(**3**) molecules exist in monomer form in a polar environment even at low temperatures and in non-polar solvents their aggregation takes place.

3.2. Photoinduced form

The absorption spectra of coloured forms B(2) in heptane, DMF and EtOH as functions of temperature are shown in Fig. 2. The range of temperature changes was 77–300 K for EtOH (it becomes glassy at 77 K) and from melting point to 300 K for DMF and heptane. As has been pointed out earlier [12,13], the absorption spectra of B(**1**) are temperature independent in solvents of different polarities.

Photocolouration of samples was carried out by two methods. In the first case the solutions were irradiated at a low temperature up to the maximum value of the optical density of the B form absorbance band. Then spectrum transformations were recorded on gradual temperature increase. In the second case, freshly made solutions were cooled to the given temperature and then dyed to a fixed stationary state; the absorption spectra were recorded under constant UV light action. The spectral characteristics of B(**2**) at any temperature were obtained independent of photocolouration method. Spectra of B(**2**) changed with temperature only in heptane.

So the B(**2**) spectrum in heptane at 186 K consists of two bands with maxima at 560 and 535 nm (Fig. 2). The absorbance band at 560 nm vanishes gradually with increase in temperature. As recording of the absorption spectra in heptane is impossible below its melting point, analogous measurements were conducted for solutions of **2** in PE, which becames glassy at a lower temperature. Gradual disappearance of the long-wave band in the absorption spectrum of B(**2**) took place in PE as well as in heptane in the range 77–300 K. The relative intensity of the long-wave band increases with increase in concentration and its disappearance with temperature rise becomes more pronounced.

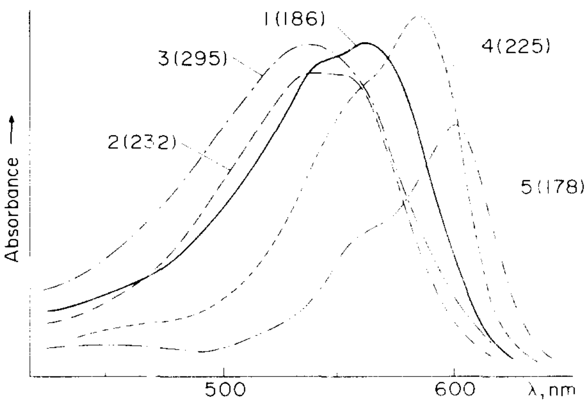


Fig. 2. Absorption spectra of B(**2**) in heptane (curves 1–3), DMF (curve 4) and EtOH (curve 5). The recording temperature is given in parentheses.

Spectra of B(**3**) are also temperature independent in polar solvents; their temperature dependence in non-polar solvents is consistent with that for B(**2**).

The dependence of the absorption spectra of photoinduced form on temperature known for ISP is connected with the existence of different stereoisomers of B form. These stereoisomers have individual spectral characteristics and exist in thermodynamic equilibrium depending on temperature and medium properties [1,18,19].

Any explanation of the temperature dependence of photoinduced form absorption spectra of **2** and **3** must account for and be consistent with the following observations.

(1) Transformations of the absorbance spectra of B(**2**) and B(**3**) with temperature change in non-polar solvents are qualitatively similar to those for ISP.

(2) Absorption spectra of B(**2**) and B(**3**) are temperature independent in polar EtOH and DMF. Contrary to this, in the case of ISP the temperature dependence of absorption spectra is more pronounced in a polar medium [19].

(3) The relative intensity of the band at 560 nm increases in the spectrum of B(**2**) with concentration increase in heptane and PE at low temperatures.

From these data we conclude that the temperature changes in B(**2**) and B(**3**) absorption spectra are not caused by the presence of different stereoisomers. Only aggregation of B(**2**) and B(**3**) molecules takes place in non-polar solvents.

The positions ν_B of long-wave maxima of B(**1**)–B(**3**) absorption spectra in solvents of different polarities are listed in Table 1. From these data it is evident that the bathochromic shift of absorption spectra for all coloured forms is observed with solvent polarity increase. Moreover, the position of ν_B

Table 1
Photochromic properties of SNO **1–3**

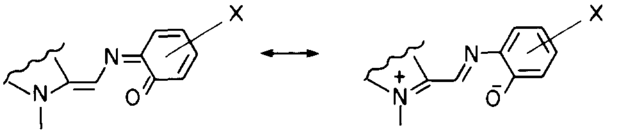
SNO	Parameter (units)	Value for following solvents						
		Ethanol	Acetonitrile	DMF	Acetone	Toluene	Butyl acetate	Heptane
B(**1**)	$\nu_B{}^a$ (cm^{-1})	16400	16480	16530	16780	16890	17240	18020
	E_A (kcal mol^{-1})	20.6	16.7	15.8	–	–	–	10.7
	$k_T{}^b$ (s^{-1})	0.61	1.12	1.08	0.99	0.28	0.55	0.16
B(**2**)	$\nu_B{}^a$ (cm^{-1})	16600	17120	17240	17360	17860	18020	18690
	E_A (kcal mol^{-1})	13.9	–	11.9	–	–	–	4.2
	$k_T{}^b$ (s^{-1})	1.91	0.75	0.31	0.37	0.07	0.06	0.04
B(**3**)	$\nu_B{}^a$ (cm^{-1})	16805	–	17090	17240	17540	17566	18520
	E_A (kcal mol^{-1})	14.3	–	14.2	–	–	–	–
	$k_T{}^b$ (s^{-1})	1.02	–	0.83	–	0.07	0.08	0.05
	$E_T{}^c$ (kcal mol^{-1})	51.9	46.0	43.8	42.2	33.9	–	30.9
	ϵ^c	24.3	37.5	36.7	20.7	2.4	5.0	1.9

[a] At 300 K.
[b] At 294 K.
[c] Data from [20].

in B(**1**)–B(**3**) spectra correlates with Dimroth's polarity parameter E_T of solvents usually used for dyes [20].

Nevertheless, some differences between the solvatochromic behaviour of B(**1**) and that of B(**2**) and B(**3**) are observed. Firstly, one can expect by analogy with the A form that the electron-donor substituent in B(**2**) and B(**3**) will cause a long-wave shift of $\nu_B{}^2$ and $\nu_B{}^3$ compared with $\nu_B{}^1$ in all solvents used. However, as seen from Table 1, both $\nu_B{}^2$ and $\nu_B{}^3$ are greater than $\nu_B{}^1$ in all cases. It should be mentioned that the relationship $\nu_B{}^2 > \nu_B{}^3 > \nu_B{}^1$ holds true in all solvents except EtOH. Secondly, the absolute values of $\nu_B{}^2$ and $\nu_B{}^3$ shifts between non-polar heptane and polar EtOH are greater than that of $\nu_B{}^1$ (2030 cm^{-1}, 1720 cm^{-1} and 1620 cm^{-1} respectively). These disagreements are believed to arise from the difference between the B(**1**) and the B(**2**) and B(**3**) structures.

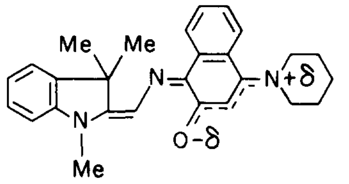
It is well known that coloured forms of photochromic spirocompounds exist as mesomeric equilibrium between quinonoic (Q) and bipolar (BP) structures [1,21]:


Q BP

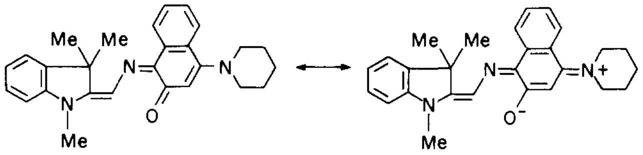
As has been shown earlier [21], B(**1**) exists in quinonoic form in non-polar solvents and its contribution to the bipolar structure rises slightly with increase in solvent polarity.

If it is supposed that this equilibrium occurs in B(**2**) and B(**3**), then long-wave absorption bands of these compounds should lie in a long-wave region in comparison with that of B(**1**) because of the electron-donor properties of piperidine and morpholine substituents. That is, the relationships $\nu_B{}^1 > \nu_B{}^2$ and $\nu_B{}^1 > \nu_B{}^3$ have to be fulfilled, as well as in the case of their uncoloured forms. However, experimental results lead to the opposite relation, namely $\nu_B{}^2 > \nu_B{}^3 > \nu_B{}^1$.

To explain this disagreement we made a suggestion that B(**2**) exists in the following structure:

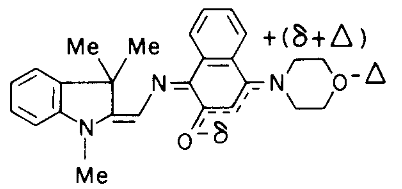


which is an intermediate between Q and BPA forms:


Q BPA

Within the limits of the model of linear oscillators [10,11], for which the applicability to the coloured form of ISP has been previously shown [18,19], the long-wave band in the absorption spectrum of a dye is caused by charge oscillation in the chain of conjugated bonds between auxochrome and antiauxochrome. The longer this chain and the greater the difference between donor–acceptor properties of auxochrome and antiauxochrome, the more this band is shifted towards the red region. Comparison of BP and BPA structures, having identical auxochromes and antiauxochromes, shows that BPA must be characterized by more short-wave absorbance. Experimental data are consistent with this hypothesis.

It is reasonable to suppose that this representation holds true for B(**3**) too. However, in the last case the inductive effect of the oxygen atom in a morpholine substituent leads to an increase in the differences between the electron-donor and electron-acceptor properties of auxochrome and antiauxochrome in comparison with those of B(**2**). Consequently, the following structure can be attributed to B(**3**):



According to [10,11], this oxygen atom effect should result in the red shift of ν_B^3 compared with ν_B^2, as in fact occurs.

Moreover, it is clear that the spectra of the bipolar forms B(**2**) and B(**3**) must be more sensitive to solvent polarity than the Q form of B(**1**). This explains the greater shift for ν_B^2 and ν_B^3 than that for ν_B^1 in going from heptane to EtOH. The positive solvatochromism of B(**1**), B(**2**) and B(**3**) is connected with the fact that electronically excited states of these molecules are more polar than the ground states. Probably, the electronically excited state has a BP structure for all compounds.

An analogous BPA structure can exist also in other SNOs having secondary amine as a substituent in positions 6, 7 or 9 of the naphthooxazine fragment.

It is natural to expect that the difference in structures of coloured forms will also have an effect on the kinetic parameters of their dark decolouration process. In spite of the fact that decolouration of B(**1**), B(**2**) and B(**3**) proceeds monoexponentially, the absolute values of rate constants k_T^1, k_T^2 and k_T^3, the activation energies E_A^1, E_A^2 and E_A^3 and their dependence on solvent polarity differ considerably (see Table 1). It is obvious that the k_T^1 values are determined not by solvent polarity parameter E_T but by its dielectric constant ϵ. A plot of ln k_T^1 and ln k_T^2 vs. ϵ^{-1} is shown in Fig. 3. The relationship between experimental values of ln k_T and ϵ^{-1} is linear in good approximation for B(**1**) and it is almost absent for B(**2**). The value of k_T^1 in EtOH drops out from the common dependence, possibly owing to the specific intermolecular interactions. Note that the relationship between ln k_T and $(\epsilon-1)/(2\epsilon+1)$ is linear too for B(**1**) and is absent for B(**2**). Any correlation between ln k_T^3 and ϵ is also absent.

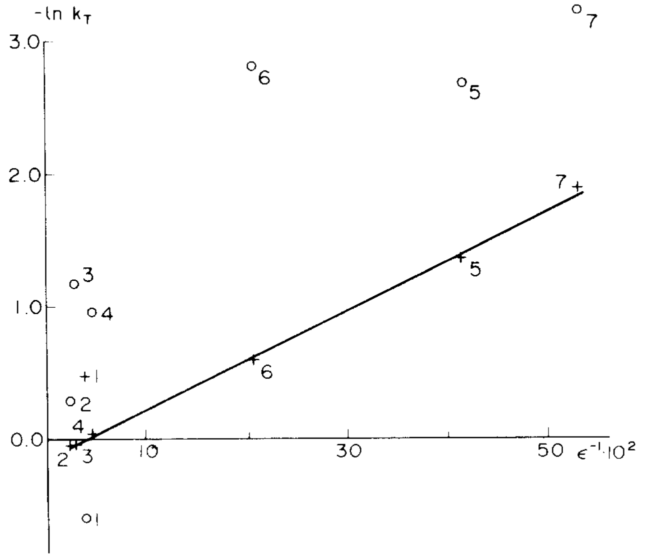
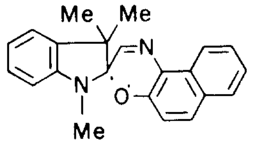
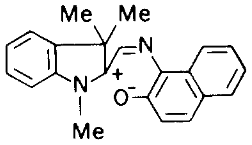


Fig. 3. Dependence of ln k_T on ϵ^{-1} for B(**1**) (∗) and B(**2**) (○) in different solvents: curve 1, EtOH; curve 2, acetonitrile; curve 3, DMF; curve 4, acetone; curve 5, toluene; curve 6, butyl acetate; curve 7, heptane.

We used the Hughes–Ingold theory [20] in order to explain k_T dependence on ϵ. According to [20], higher polarity of any activated complex in comparison with those of the initial state leads to a rise in the reaction rate with increase in ϵ. If the state of the B molecule after the *cis–trans* isomerization process directly before closing of the oxazine ring is considered, an activated complex of decolouration reaction of B(**1**) occurs and its structure may be presented as either biradical or bipolar forms:





Since B(**1**) exists as a non-polar quinonoic structure B, as has been shown above, the dependence of k_T on ϵ should be almost absent in the case of the nonpolar biradical transition state. The linear relationship between k_T and ϵ shows that the activated complex has a bipolar structure. This assumption agrees with data earlier obtained for ISPs [22].

The transition states in the decolouration reaction of B(**2**) and B(**3**) are reasonably suggested to have also the bipolar structure and, since the initial states of B(**2**) and B(**3**) are bipolar too (BPA), the dependence of k_T^2 and k_T^3 on solvent polarity has a complicated nature.

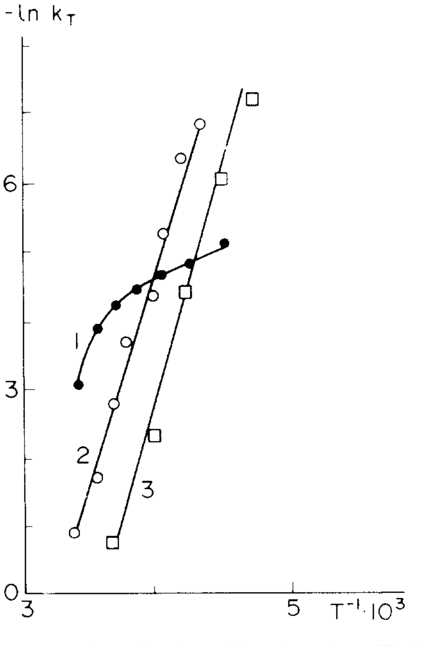


Fig. 4. Arrhenius dependence for thermal decolouration of B(**2**) in heptane (curve 1), DMF (curve 2) and EtOH (curve 3).

It should be noted that the E_A values for B(**2**) and B(**3**) differ considerably from those for B(**1**) even in polar solvents, where the Arrhenius dependence is well accomplished for all these compounds (Table 1). This difference is likely to be the result of the differences between their coloured form structures. The dependence of ln k_T^2 on T^{-1} is non-linear in non-polar heptane (Fig. 4) contrary to that of ln k_T^1. The E_A^2 value for this solvent given in Table 1 was obtained by averaging over whole temperature interval. This agrees with the above-mentioned conclusion that B(**2**) molecules exist in an aggregated state in non-polar solvents; their aggregation degree depends upon temperature.

4. Conclusions

So, our study has shown that the introduction of an electron-donor secondary amine substituent in the 6 position of naphthooxazine fragment of SNO leads to significant changes in photochromic properties in comparison with that of unsubstituted SNO.

The first distinction involves the appearance of A(**2**) and A(**3**) luminescence; this emission competes with C–O spirobond dissociation. Consequently, the quantum yield of C–O spirobond dissociation in A(**2**) and A(**3**) is smaller than that in A(**1**); the latter was established in [13] to be 1 at 77 K.

The second distinction is linked to the realization of a novel photoinduced form for A(**2**) and A(**3**), namely a bipolar structure with a positive charge on the N atom of the electron-donor substituent. This structure is more favourable than the quinonoic structure B(**1**) for formation of dimers and more complicated aggregates, which is in agreement with our experimental results in non-polar solvents.

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