

**THERMOCHROMISM AND PHOTOCHROMISM OF
ARYL-SUBSTITUTED ACYCLIC AZINES
X: RELATIONSHIP BETWEEN MOLECULAR GEOMETRY AND
FLUORESCENCE OF ANTHRANYL-SUBSTITUTED COMPOUNDS†**

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Summary

The *EE* and *EZ* isomers of 9-anthraldehyde azine (II) do not show any fluorescence either at room temperature or at low temperatures. The *ZZ* isomer shows monomer–excimer fluorescence strongly dependent on temperature as is characteristic of bridged anthracene compounds. The differences in fluorescence behaviour are discussed with respect to the molecular geometry of the three isomers of II.

1. Introduction

Our investigations of aryl-substituted 2,3-diazabutadienes (azines) of the structure given in Fig. 1 have shown that photochromism based on *E–Z* isomerization about the C=N bond is a general property of this class of compounds [1]. We have studied the mechanism of both the photochemical [2, 3] and the thermal [4, 5] isomerization and have shown that steric and electronic effects markedly influence both the absorption spectra and the photochemical properties of the azines. Therefore, it was interesting to find out to what extent these effects influence the fluorescence behaviour of this class of compounds.

Regardless of the molecular structure, none of the azines investigated fluoresce (fluorescence quantum yield $\phi_F < 10^{-4}$) unless they are protonated

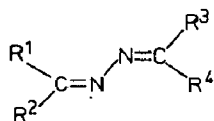


Fig. 1. 2,3-Diazabutadiene (azine).

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on the nitrogen atom [6 - 8]. However, if, owing to non-bonded interactions, an aryl substituent is twisted out of the molecular plane and the π -electron conjugation between this aryl substituent and the azomethine residue is largely interrupted, then this substituent, as an uncoupled subchromophore, will show a more bathochromic absorption than the azomethine residue and exhibit its own fluorescence [9]. This holds true, for example, for *Z* isomers of 9-anthranil-substituted azines as shown in Fig. 2 for benzophenone-9-anthraldehyde azine (I) (Fig. 1: $R^1 \equiv R^2 \equiv$ phenyl, $R^3 \equiv$ 9-anthranil, $R^4 \equiv$ H).

9-Anthraldehyde azine (II) (Fig. 1: $R^2 \equiv R^3 \equiv$ 9-anthranil, $R^1 \equiv R^4 \equiv$ H) has three *E-Z* isomers. Since the photochemically producible [1, 10] *EZ* and *ZZ* forms are considerably twisted around the *Z*-configured C—C (anthranil) bond [11, 12] the absorption spectrum of the *ZZ* isomer largely corresponds to that of anthracene (Fig. 3). Hence, for twisted *EZ* and *ZZ* isomers fluorescence properties similar to those of *Z*-I can be expected.

The *ZZ* structure derived from the electronic absorption spectrum of the third isomer with the lowest r_F value (thin-layer chromatography on silica gel [1, 10]), which can be produced by irradiation with light of wavelength $\lambda' = 436$ nm, is the only one of the three isomers which can adopt a molecular geometry such as that postulated for the formation of excimers [13] by a slight torsion around the single N—N bond. Thus, searching for a characteristic excimer fluorescence is another method of obtaining evidence

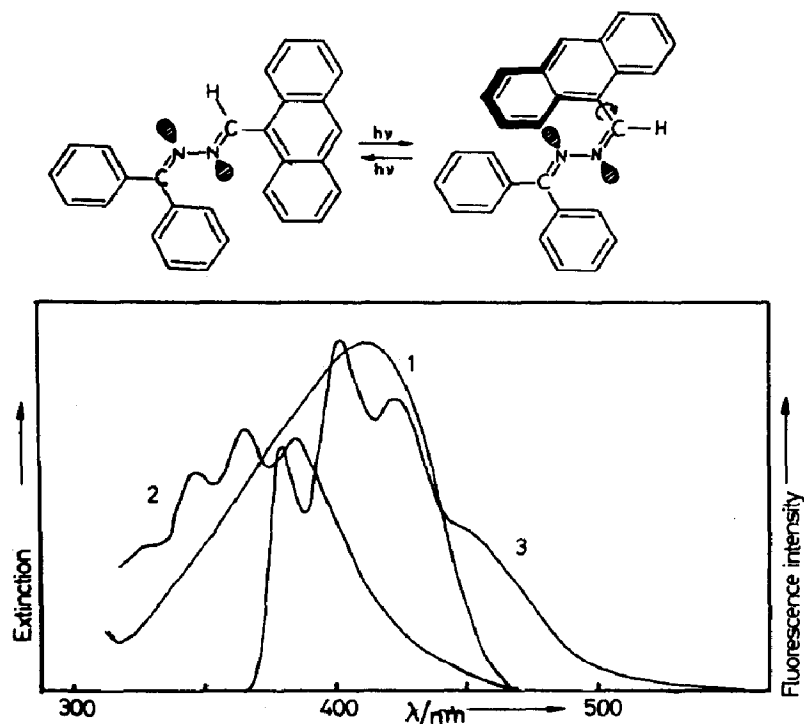


Fig. 2. Electronic absorption spectra of *E*-I (curve 1) and *Z*-I (curve 2) in toluene at room temperature, and the fluorescence spectrum of *Z*-I (curve 3) in methylcyclohexane-isopentane (50vol.%–50vol.%).

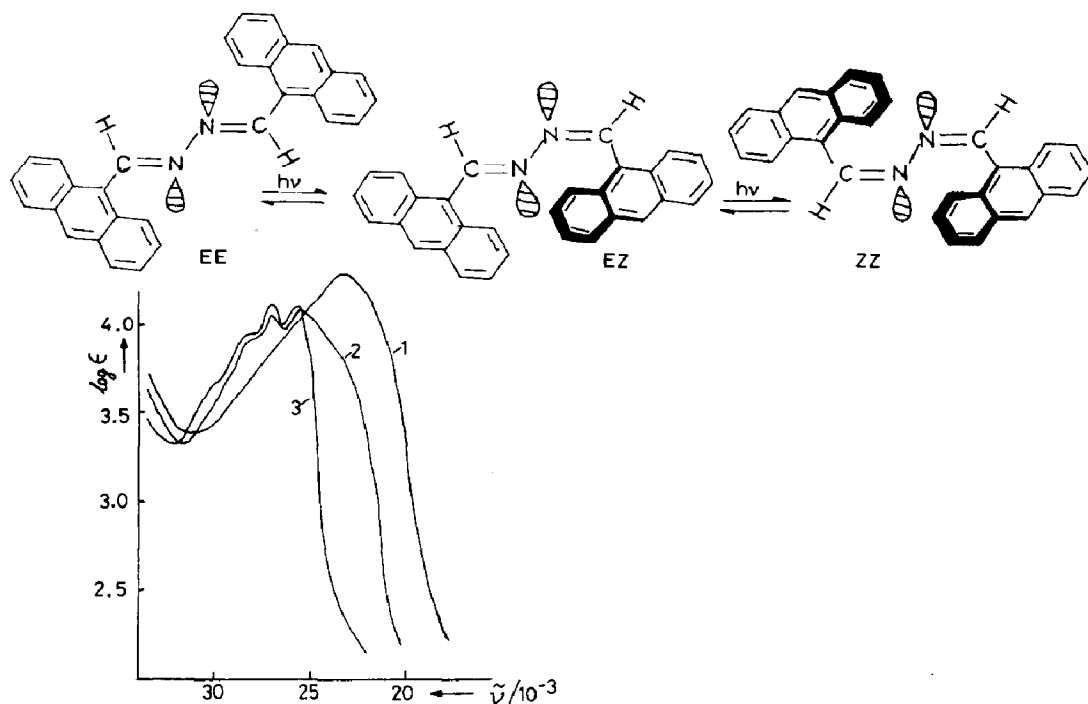


Fig. 3. Electronic absorption spectra of the *E-Z* isomers of II at room temperature in toluene: curve 1, *EE*-II; curve 2, *EZ*-II; curve 3, *ZZ*-II.

for the molecular geometry of selected isomers of aryl-substituted azines. Therefore, we have studied the relationship between geometry and fluorescence behaviour in detail using II as an example.

2. Results and discussion

Irrespective of the polarity of the solvent, the thermodynamically stable, only slightly twisted [11] *EE* isomer of II does not show any fluorescence ($\phi_F < 10^{-4}$) either at room temperature or at low temperatures (about 77 K). These experimental facts correspond with results obtained with phenyl, mesityl, fluorenyl, 9-acridinyl and other 9-anthracenyl-substituted azines [9]. For the *E* and *EE* forms, the lowest electron excited state has predominantly $n\pi^*$ character [3, 12] so that, owing to the radiation lifetime of $n\pi^*$ states being usually longer than that of $\pi\pi^*$ states, radiationless deactivation processes are favoured. In contrast with, for example, 9-anthraldehyde, the nature of the lowest electron excited state is maintained in spite of relative shifts in the position of the $\pi\pi^*$ and $n\pi^*$ states owing to the acceptor ability of the solvent [3, 14]. This explains why, regardless of the solvent, no fluorescence can be detected with this class of compounds.

With the *EZ* isomer, one of the 9-anthracenyl substituents is considerably twisted out of the molecular plane [11]. The resulting interruption of the conjugated π -electron system leads to a hypsochromically shifted absorption

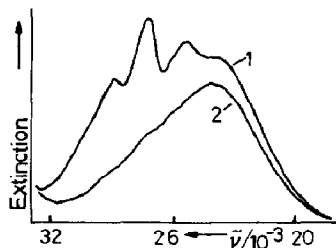


Fig. 4. Electronic absorption spectra of *EZ*-II (curve 1) and III (curve 2) at room temperature in toluene.

band with the vibrational structure characteristics of anthracene (see Fig. 3). The longest wavelength absorption band is, however, predominantly determined by the chromophore of the π -electronically uncoupled anthranyl-substituted azomethine residue [15] which is comparable with the non-fluorescing acetone-9-anthraldehyde azine (III) (Fig. 1: $R^1 \equiv H$; $R^2 \equiv 9$ -anthranyl; $R^3 \equiv R^4 \equiv CH_3$) (see Fig. 4). Thus, despite the torsion of one C—C (anthranyl) bond on *EZ*-II, even at low temperatures, no fluorescence is expected. This was confirmed by experiment.

The *ZZ* isomer of II, in which both C—C (anthranyl) bonds are strongly twisted, shows two different fluorescence emissions strongly dependent on temperature and shown representatively by the spectra in Fig. 5. In accor-

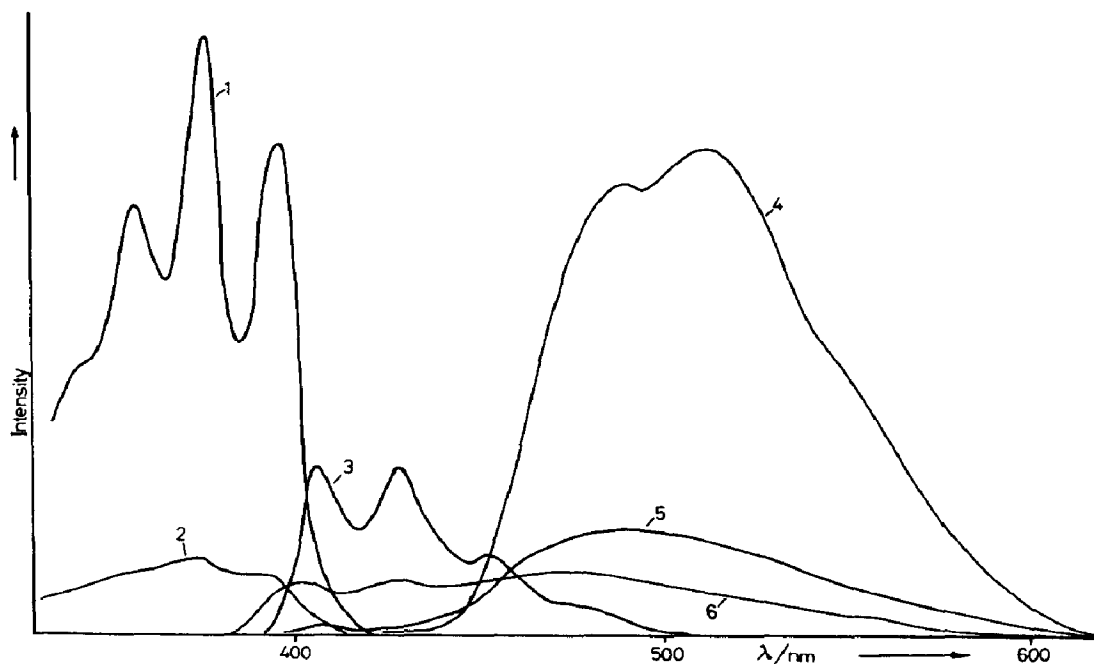


Fig. 5. Fluorescence spectra of *ZZ*-II at various temperatures: curve 3, 77 K; curve 4, 173 K; curve 5, 233 K; curve 6 (the fluorescence intensity is amplified by the factor 10), 293 K. Fluorescence excitation spectra at 293 K (curve 2), and at $T < 233$ K (curve 1) in methylcyclohexane-isopentane (50vol.%–50vol.%). Excitation wavelength, 350 nm; emission wavelength for fluorescence excitation spectra, 500 nm.

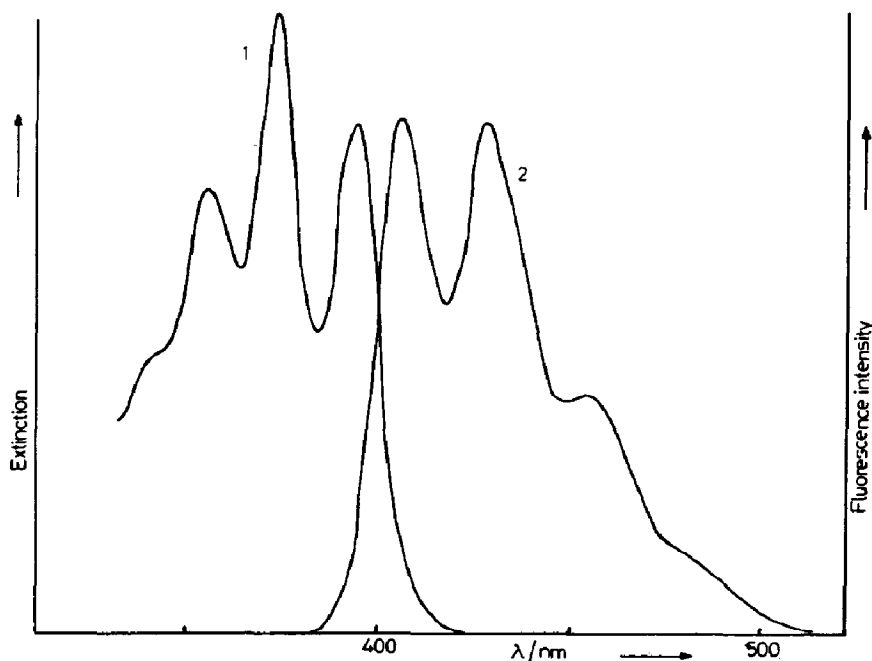


Fig. 6. Fluorescence spectrum ($\lambda_{exc} = 350$ nm) (curve 2) and fluorescence excitation spectrum ($\lambda_F = 430$ nm) (curve 1) of ZZ-II in rigid solution at 77 K in methylcyclohexane-isopentane (50vol.%-50vol.%).

dance with an excimer fluorescence, the fluorescence excitation spectra are independent of the emission wavelength at any temperature.

In rigid solution at 77 K, only the emission which is the mirror image of the absorption spectrum is observed (Fig. 6). The fluorescence excitation spectrum is in accord with the absorption spectrum. This is understandable, because for ZZ-II, in contrast with EE-II, the longest wavelength absorption band is determined by the subchromophore of the π -electronically uncoupled 9-anthranlyl substituent, and hence fluorescence of the anthracene itself occurs. The same facts hold true with Z-I (see Fig. 2) [9].

In fluid solution a dual fluorescence is observed with an excimer fluorescence band characteristic of bridged anthracene compounds [13] (Fig. 5). Making use of the equation

$$\phi_{F, S} = \frac{\int I_S d\lambda}{E_S'} \frac{E_{ref}'}{\int I_{ref} d\lambda} \frac{n_S^2}{n_{ref}^2} \phi_{F, ref} \quad (1)$$

where I is the fluorescence intensity, ϕ_F the fluorescence quantum yield, $E' \leq 0.05$ the extinction at the irradiation wavelength, n the refractive index, and the subscripts S and ref refer to the sample (ZZ-II) and the reference standard (quinine sulphate in 0.1 N H_2SO_4) respectively, the fluorescence quantum yield of the monomer of ZZ-II was calculated. The quantum yield of the excimer fluorescence was determined from the relation of the integrated excimer-to-monomer fluorescence intensity (Table 1). Neglecting additional temperature-dependent deactivation processes both in the monomer (mon) and the excimer (exc), the relationship

TABLE 1

Fluorescence quantum yields of the monomer ($\phi_{F, \text{mon}}$) and the excimer ($\phi_{F, \text{exc}}$) of ZZ-II at various temperatures in 50vol.%methylcyclohexane-50vol.%isopentane

T (K)	$\phi_{F, \text{mon}}$	$\phi_{F, \text{exc}}$
293	0.001	0.003
233	0.002	0.056
173	0.003	0.340
138	0.004	0.056
77	0.090	—

$\ln \phi_{F, \text{exc}}/\phi_{F, \text{mon}}$ vs. T^{-1}

allows an estimation of the bond enthalpy of the excimer as $\Delta H \leq 20 \text{ kJ mol}^{-1}$. At temperatures below 200 K, at least two maxima occur in the range of the excimer band. In this region, two or more bands whose relative intensity ratio is temperature dependent are possibly superimposed. These facts suggest the existence of distinct excimers caused by different conformational isomers. The occurrence of such conformational isomers of bichromophoric anthracenes has been described previously [16].

From investigations on sterically crowded linked anthracenes and various anthracenophanes it was concluded that the molecular geometry of the emitting excimer state of linked anthracenes appears to be one in which the two aromatic moieties are only partially overlapping, or they may be in an angular arrangement [13]. Inspection of Dreiding molecular models of the isomer which is considered to be the ZZ form [1, 10] suggests a molecular geometry resulting from torsion around the N—N bond. Such an isomer is able to form an excimer state characterized by a structureless emission band around 500 nm. This single-(N—N)-twisted ZZ structure for II is represented in Fig. 7. The emission spectrum of C₃-linked D,L-diastereoisomeric bis[α -(9-anthryl)ethyl] ether [17], for example, supports the structural similarity of the two compounds in terms of the relative position of the anthranyl substituents (compare Fig. 6 in ref. 17 with Figs. 5 and 7).

Obviously, the thermodynamically stable conformation of ZZ-II does not exhibit the single-(N—N)-twisted structure shown in Fig. 7, because in

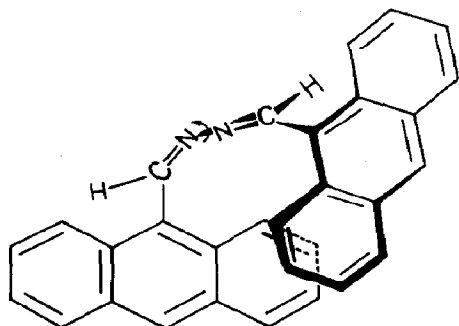


Fig. 7. Single-(N—N)-twisted ZZ-II.

rigid solution ($T \approx 77$ K) only a fluorescence of the monomer is observed (see Fig. 6). Moreover, the absorption spectrum does not indicate an interaction of anthranyl substituents in the ground state as observed in the case of D,L-bis[α (9-anthryl)ethyl] ether [17].

In fluid solution, changes in conformation gain in significance and in the electron excited state the molecular geometry necessary for the formation of an excimer state (see Fig. 7) can be predominantly produced by torsion around the N—N single bond. Such a molecular geometry, necessary for the formation of the excimer, is only possible for the *ZZ* isomer and can be reached neither with the *EZ* nor with the *EE* isomer. This is confirmed by the fact that an excimer fluorescence with these isomers is not found.

Thus, *ZZ*-II is the first example of a C_4 -linked anthracene with a C=N—N=C bridge at which excimer fluorescence could be detected.

3. Experimental details

The procedures for preparing the azines I and II have been given elsewhere [18] or have been carried out analogously with III (prepared from the acetone hydrazone and 9-anthraldehyde). The *EZ* and *ZZ* isomers of II were produced by irradiation with wavelength $\lambda' = 488$ nm (argon ion laser (VEB Carl Zeiss, Jena, G.D.R.)) and with $\lambda' = 436$ nm, respectively, starting with the thermodynamically stable *EE* form. A high pressure mercury lamp (HBO 200, VEB Narva, Berlin, G.D.R.) was used as light source, and monochromatic radiation ($\lambda' = 436$ nm) was selected with an interference filter 436 nm (VEB Carl Zeiss, Jena). The *E-Z* isomer enriched by irradiation in solution was used directly for the fluorescence measurements without isolating it from the isomer mixture.

The absorption spectra were recorded with the spectrometer CARY 17 (U.S.A.), and the fluorescence measurements were achieved by means of an automatically correcting spectrofluorometer-phosphorometer FICA 55 (ARL, France). The fluorescence quantum yield ϕ_F was determined relative to that of quinine sulphate in 0.1 N H_2SO_4 ($\phi_F = 0.51$ [19]). The extinction E' at the irradiation wavelength was always equal to or less than 0.05.

The temperature dependence of ϕ_F was measured in a self-constructed controllable low temperature cuvette. The measurement of the temperatures took place in the cuvette ($\Delta T = 1$ K). The values of the fluorescence quantum yield determined were not corrected because the temperature influences on the refractive index n and the concentration partially compensate each other.

References

- 1 K. Appenroth, M. Reichenbächer and R. Paetzold, *J. Photochem.*, 14 (1980) 39.
- 2 K. Appenroth, M. Reichenbächer and R. Paetzold, *J. Photochem.*, 14 (1980) 51.
- 3 K. Appenroth, M. Reichenbächer and R. Paetzold, *J. Photochem.*, 24 (1984) 65.

- 4 K. Appenroth, M. Reichenbächer and R. Paetzold, *Tetrahedron*, 37 (1981) 569.
- 5 K. Appenroth, M. Reichenbächer and R. Paetzold, *Z. Chem.*, 23 (1983) 149.
- 6 A. Weller and H. Wolf, *Liebigs Ann.*, 657 (1972) 64.
- 7 K. Appenroth, M. Reichenbächer and R. Paetzold, *Z. Chem.*, 23 (1983) 414.
- 8 K. Gustav and S. Vettermann, *Wiss. Z. Univ. Jena, math.-naturwiss. Reihe*, 29 (1980) 715.
- 9 K. Appenroth, E. Birckner and M. Reichenbächer, *Z. Chem.*, 26 (1986) 106.
- 10 K. Appenroth, M. Reichenbächer and R. Paetzold, *Z. Chem.*, 23 (1983) 413.
- 11 K. Gustav and S. Vettermann, *Z. Chem.*, 18 (1978) 456.
- 12 R. Paetzold, M. Reichenbächer and K. Appenroth, *Z. Chem.*, 21 (1981) 412.
- 13 H.-D. Becker, *Pure Appl. Chem.*, 54 (1982) 1589.
- 14 M. Kupfer, A. Henrion and W. Abraham, *Z. physik. Chem. (Leipzig)*, 267 (1986) 705.
- 15 K. Gustav and S. Vettermann, *J. prakt. Chem.*, 326 (1984) 485.
- 16 A. Castellan, J.-P. Desvergne, R. Lesclaux and J.-C. Soullignac, *Chem. Phys. Lett.*, 106 (1984) 117.
- 17 H.-D. Becker and K. A. Andersson, *J. Org. Chem.*, 47 (1982) 354.
- 18 M. Reichenbächer, K. Appenroth and R. Paetzold, *Z. Chem.*, 24 (1984) 21.
- 19 W. R. Ware and W. Rothmann, *Chem. Phys. Lett.*, 39 (1976) 449.