193. Photoformation of (*Z*)-Isomers in Diarylazomethines

Part IV[1])

Direct and Sensitized Photoisomerization of Pyridyl Analogues of Benzylidene-aniline and Absorption Spectra of their (*Z*)-Isomers

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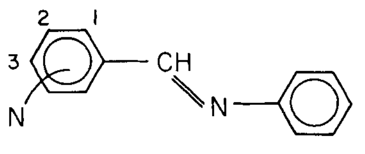
Summary

UV irradiation of solutions of the (*E*)-isomers of five (out of the possible six) monopyridyl analogues at reduced temperatures results in extensive (80–90%) conversion into the corresponding (*Z*)-isomers. The process is reversible both thermally and photochemically. The (*Z*)-isomers are stable at temperatures below –80°, and their absorption spectra were estimated. Biacetyl-photosensitized (*E*)→(*Z*) isomerization was observed, with (*Z*)-contents of *ca.* 70% at the photostationary state.

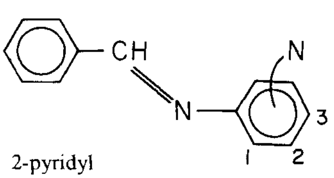
1. Introduction. – In previous publications [1–3] we have described the reversible photoformation of (*Z*)-isomers of a variety of diarylazomethines, Ar–CH=N–Ar′ and Ar–C(CH_3)=N–Ar′, where Ar and Ar′ are phenyl, substituted phenyl, or naphthyl, all of which exist in solution as the (*E*)-isomers. (*Z*)→(*E*) thermal reversion is fast at room temperature but can be stopped by cooling to about –70 °C. Photosensitized (*E*)→(*Z*) conversion was also observed.

We now report on a similar investigation of the pyridyl analogues **1** and **2**.

These five compounds have been described by *Perkampus & Behjati* [4] in connection with their photocyclodehydrogenation to azaphenanthrenes.



1a 3-pyridyl
1b 2-pyridyl
1c 1-pyridyl



2a 2-pyridyl
2b 1-pyridyl

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[1]) Part III: [1], Part II: [2], Part I: [3].

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2. Results. – *Direct (E)→(Z) Photoisomerization, and Absorption Spectra of the (Z)-Isomers.* UV irradiation of Ar-flushed solutions of all five compounds below −80 °C (below −120 °C for **2b**) resulted in remarkable changes in the absorption spectra, generally similar to those described earlier [1–3], *i.e.* pronounced decreases in the absorbance in the long-wavelength part of the spectrum and increases in the short-wavelength part. Photostationary states (PSS) are established at appropriately low temperatures, and vary with the wavelength of irradiation λ_i (405, 366, and 313 nm) according to the relative absorbance of the two isomers at λ_i, as usual in photoreversible systems. No irreversible photoreactions were observed under these conditions. The spectra are shown in the *Figure:* curves *a* and *b* are those before and after establishment of PSS at 313 nm, while curves *c* describe the extrapolated spectra of the pure (*Z*)-isomer, assuming a 'reasonable' value for the composition at PSS [1]. The range of uncertainty is small, since the minimum of the spectra *b* at *ca.* 310 nm is in all cases not far from zero. We assumed in each case an absorbance of the (*Z*)-isomer at this minimum midway between zero and the value in curve *b*. The resulting values for the composition at PSS indicate 80–90% (*Z*)-isomer. In the *Table* the wavelengths of the absorption peaks and the isosbestic points at −80 °C (−116 °C for *2b*) are summarized. In all cases the absorbance of the (*Z*)-isomer beyond 360–380 nm is larger than that of the (*E*)-isomer. This makes flash-photolytic kinetic studies easier by measuring the decay of absorbance around 400 nm. It also results in extensive (*Z*)→(*E*) photoconversion with light at 405 nm. Experiments at −170 °C yielded essentially similar results. For molar extinction coefficients of the (*E*)-isomers at room temperature, see *Exper. Part.* At temperatures above −80 °C thermal reversion to the original spectra takes place at rates varying with the temperature.

Sensitized (E)→(Z) Photoconversion. Since the photoconversion was measured by means of optical absorption spectroscopy, we could only use sensitizers not absorbing in the range 300–370 nm, while direct photoconversion was prevented by using sensitizers absorbing above 410 nm. Only biacetyl, $E_T = 231\ \mathrm{kJ \cdot mol^{-1}}$, was used, employing irradiation at 436 nm, which led to PSS's containing 70–80% (*Z*)-isomer at −80 °C. Compound **2b** could not be measured. Solutions were flushed with Ar. Biacetyl phosphorescence at −40 °C was efficiently quenched by all five compounds.

Table. *Position of Absorption Peaks and (E)/(Z) Isosbestic Points of Solutions in Methylcyclohexane at −80°* (Compound **2b** at −116°). Values in parentheses denote shoulders.

	Compound	Absorption peaks (nm)					Isosbestic points (nm)
1a	(*E*)	226	(232)	260		325	379, 242
	(*Z*)		230	270		355	
1b	(*E*)	(228)	236	250.5	(280)	322	376, 247
	(*Z*)	237	(265)		360		
1c	(*E*)	(230)	236	(260)	267	320	379, 246
	(*Z*)		235		270	340	
2a	(*E*)				270	(320)	359, 251, 220
	(*Z*)		245			332	
2b	(*E*)				267	(316)	363, 257
	(*Z*)	(234)	253	(270)	(288)	314	

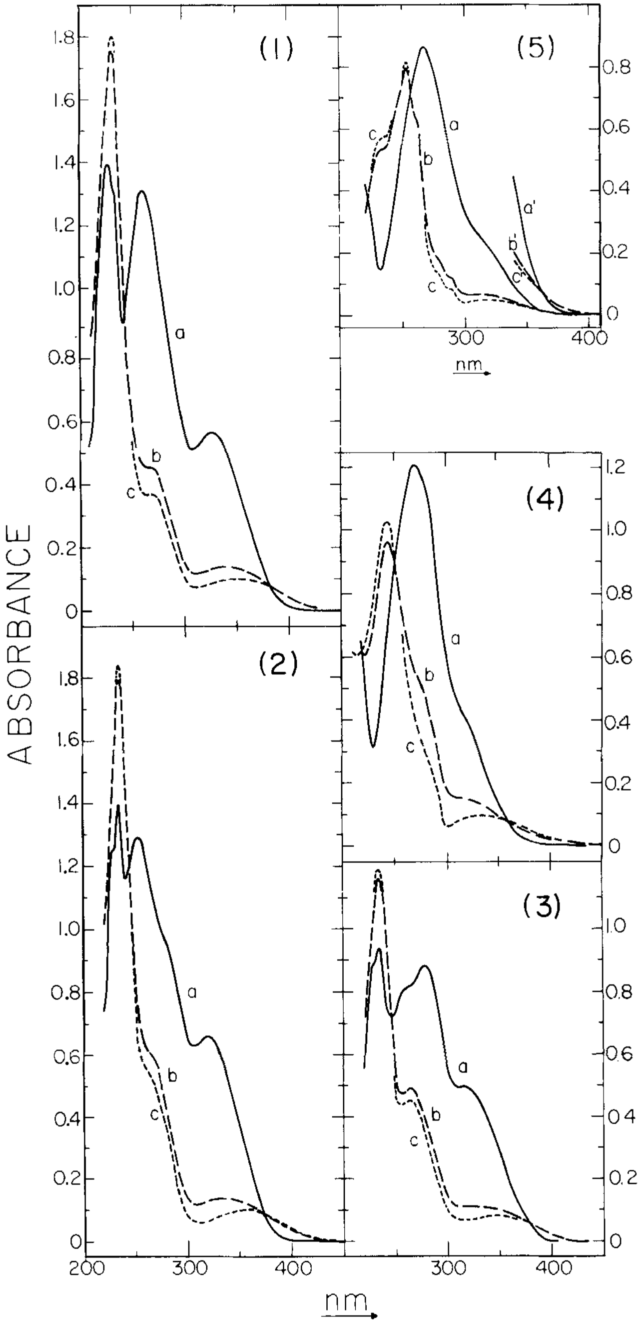

Figure. *Absorption spectra before (a) and after (b) photoequilibration with 313 nm irradiation at –80°.* Curves *c* are extrapolated spectra of the (*Z*)-isomers, as described in the text. Solutions in methylcyclohexane. Compounds were as follows: (1): **1a**, (2): **1b**, (3): **1c**, (4): **2a**, (5): **2b**. In **5**, spectra were taken at – 116°. Curves *a'* and *b'* were taken at a five-fold concentration.

Relative Efficiencies of (E) → (Z) *Photoconversion* vs. *the Temperature.* The rates of photoconversion at – 80 and – 170 °C were virtually identical, as observed in all arylazomethines studied hitherto.

Thermal (Z) → (E) *Reversion.* The rate of reversion was measured spectrophotometrically as a function of the temperature in a flash photolysis set-up, making use of the fact that above about 380 nm the (*Z*)-isomer absorbs much more strongly. The temperature range was from – 10° to + 60 °C. With compound **2a**, the (*Z*) → (*E*) reversion rates were measured with the *Cary* spectrophotometer, in the range – 80° to – 50 °C. The *Arrhenius* plots yielded activation energies of 55–60 kJ · mol^{-1} for compounds **1a**–**1c** and **2a**. Compound **2b** was not measured. At – 120 °C it has an estimated half-life of several hours, which decreases relatively slowly at higher temperatures. We believe that solutions of this compound contain an impurity which catalyses the thermal reversion.

Fluorescence. None was observed ($Q_F < 10^{-3}$) in solutions down to – 180 °C.

3. Experimental. – 3.1. *Materials.* All compounds mentioned have been described, though with few details, by *Perkampus & Behjati* [4] and were synthesized accordingly. The corrected melting points were as follows: **1a**: 72°, **1b**: 21.5°, **1c**: 22–26°, **2a**: 16–17°, **2b**: 59–60°. The low m.p.'s were measured in a 12° cold chamber. MS were all as expected, though we obviously could not purify **1c** sufficiently by fractional distillation and recrystallization. UV (positions in nm, abs. coeff. × 10^{-4} in parentheses): **1a**: 226 (1.42), 232 (sh), 260 (1.11), 325 (0.48); **1b**: 228 (sh), 236 (1.45), 254 (1.26), 280 (sh), 322 (0.60); **1c**: 228 (1.06), 235 (1.12), 257 (0.93), 277 (1.00); **2a**: 268 (1.37); **2b**: 261 (1.30).

3.2. *Methods.* Our low-temperature photochemical absorption (*Cary 14* and *Cary 2200*) and flash-photolytic techniques were essentially as described in [2]. Thermostatted pyrex cells with light paths of 70 mm and a cross section of 4 × 12 mm were used in the flash work below and above r.t. The monitoring light passed through an interference filter before entering the measuring cell, to prevent photoconversion by this light. Excitation was through *Corning 7-54* filters.

4. Discussion. – The photoinduced changes in the UV absorption spectra of the title compounds are qualitatively similar to those reported by us for benzylidene aniline and its homologues. We therefore assign them, by analogy, to (*E*) → (*Z*)-isomerization. As in stilbene and its unhindered derivatives, the (*Z*)-isomers have a much less intense and red-shifted longest absorption band compared with the (*E*)-isomers. In **2a** and **2b** the long-wavelength peak of the (*E*)-isomer is shifted, relative to the compounds **1a**–**1c**, to shorter wavelengths, and appears only as a shoulder. The shortest peak corresponding to the (*E*)-isomers of **1a**–**1c** is missing in **2a** and **2b**, while the (*Z*)-isomers all possess peaks in the range 230–250 nm. The activation energies for the (*Z*) → (*E*) reversion are slightly smaller than for the homocyclic compounds [1]. The photosensitized isomerization indicates that isomerization in the triplet manifold is feasible, but does not allow inferences concerning the direct photoisomerization. Biacetyl (BA) seems to act as a 'high-energy sensitizer', *i.e.* $E^T_{BA} > E^T_{(Z)}$. Accordingly, the triplet energy of both isomers is less than 230 kJ · mol^{-1}.

On the whole, the spectroscopy, reversible photochemistry and *cis* → *trans* kinetics of the pyridylazomethines are thus rather similar to that of the homocyclic compounds.

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REFERENCES

[1] *K. Maeda & E. Fischer,* Molec. Photochem. *9*, 309 (1979).
[2] *K. Maeda & E. Fischer,* Israel J. Chem. *16*, 294 (1977).
[3] *E. Fischer,* J. Phys. Chem. *71*, 3704 (1967).
[4] *H.-H. Perkampus & B. Behjati,* J. Heterocyclic Chem. *11*, 511 (1974).