FROZEN-IN NON-EQUILIBRIUM ROTAMER MIXTURES IN 1,2-DIARYLETHYLENES OBTAINED BY LOW-TEMPERATURE IRRADIATION*

NELLY CASTEL and ERNST FISCHER

Department of Structural Chemistry, The Weizmann Institute of Science, Rehovot (Israel)

(Received 28 June 1984)

ABSTRACT

trans-1,2-Di(2-naphthyl)-ethylene, formed in rigid media by UV irradiation of its cis isomer, comprises a mixture of three modifications, not in equilibrium with each other, that are tentatively assigned to the three possible rotamers. At somewhat lower viscosities, in the range 10^{6} - 10^{9} cP, equilibrium is established. Detection is by emission-spectroscopic methods. Three other related compounds showed only slight effects of the same kind.

INTRODUCTION

In an earlier publication in this journal [1] and elsewhere [2] the emission-spectroscopic evidence was summarized for the existence of mixtures of two rotamers in solutions of suitable compounds related to 1-phenyl-2-(2naphthylethylene, I. For 1,2-di(2-naphthyl)ethylene, II, three rotamers are expected, and have indeed been observed by the present authors [2, 3].

The rate of spontaneous thermal interconversion of the postulated rotamers depends inter-alia on the potential barrier separating these rotamers from each other, estimated to be 4-5 kcal mol⁻¹ [4, 5] at very low viscosities of the medium. Much higher barriers are expected in very viscous media. On cooling such solutions, therefore, one may expect that thermal equilibrium among the rotamers will be established until certain viscosity values are reached at which the rate of equilibration falls off sufficiently to freeze-in the rotameric composition. The equilibrium composition is itself a function of the temperature, since the enthalpies of the rotamers A, B and C, though similar, are not identical. On cooling, a change in favour of the rotamer possessing the lower enthalpy is observed in the emission spectra, as long as the viscosity is low enough. This is shown in Fig. 1 for a solution of II in ethanol. Indeed, this was the explanation given by the present authors [6] for the observation at very low temperatures of only two of the three

0022-2850/85/\$03.30 © 1985 Elsevier Science Publishers B.V.

^{*}A preliminary account of part of this investigation was presented as a poster at the 10th IUPAC Symposium on Photochemistry, Interlaken, July 1984.

160



rotamers in II. Thus, in ethanol solutions of II at -100° C, the emission can be assigned to three different modifications, (Fig. 2b) whereas at -160° and below, the contribution of the modification emitting at the longest wavelength, "LL", diminishes to almost zero, while that emitting at medium wavelength, "L", contributes much less (Fig. 1). The same variation in rotamer composition with temperature is observed in decalin solutions, but to a lesser extent.

Another relevant observation is that the photostationary state attained by UV irradiation of stilbene [7, 8] and of its unhindered derivatives, including I and II, at temperatures approaching 90 K, contains predominantly the respective *trans* isomers, [9, 10]. This is because on cooling, the quantum yield of the *trans* \rightarrow *cis* photoconversion drops much more sharply than that of the reverse reaction. It should be possible, in principle, to create *trans* from *cis* at viscosities at which thermal equilibration among the rotamers is slowed down sufficiently to permit their individual detection. Rotamer composition is then governed by its equilibrium value in the *cis* form, which may differ from that in the *trans* form. (No rotamer equilibration is expected in the excited state [6, 11].)



Fig. 1. Temperature dependence of the emission spectrum of *trans*-II in ethanol, 10^{-5} M, excited at 362 nm (2 nm slits). Note the shift of the S = L equilibrium in favour of S on cooling.



Fig. 2. Emission spectra of solutions as in Fig. 1, excited at the wavelengths indicated: (a) following $cis \rightarrow trans$ photoconversion at -175° C; (b) heated to -100° C (equilibrium mixture). The three modifications S, L and LL are each characterized by a set of three peaks, as indicated by the arrows. Excitation and emission slits 2 nm.

In a recent publication [12], Scheck and co-workers suggested the use of this method of low-temperature irradiation to create non-equilibrium mixtures of rotamers, and reported results obtained with I, II and 1,2-di(1-naphthyl)ethylene in ethanol at 77 K. However, in the light of the present experience, their reported spectra seem badly distorted, possibly because of the use of high concentrations and only partial $cis \rightarrow trans$ conversion.

Somewhat similar experiments were therefore carried out in the present work, but under much better defined conditions of the viscosity, and at concentrations below 10^{-5} M, where complete photoconversion and negligible resorption of emitted light are assured.

EXPERIMENTAL

Materials

The compounds used have all been described in previous publications.

The solvents used were as follows: ethanol was 96% "analytical" (Frutarom). Decalin (cis + trans mixture) was a Merck product, used after passage through a column of basic active Alumina (Woelm).

Spectrophotometry

Absorption spectra were measured on a Varian-Cary 2200 instrument, while a Perkin-Elmer MPF-44 fluorescence spectrophotometer was used for emission measurements. Both instruments were equipped with our usual in situ cooling and irradiation arrangements [14]. The cell was immersed in a copper block cooled by a stream of liquid air controlled by a thermostat. A mercury lamp (Mazda, 125 W medium pressure, in a Wild illuminator) served as the light source for the low-temperature photoconversion. For the present purpose it was not necessary to filter the light, which was just passed through a water-filled Pyrex container. After each experiment on the emission spectrophotometer, the absorption spectra were taken at room temperature in order to check the isomeric composition. Solutions were flushed with Argon throughout. Emission spectra are uncorrected but in the spectral range used, corrections are small.

RESULTS

General results

The cis isomers available were those of I, II and 1-(1-naphthyl-2-(2-naphthylethylene, III. With 1-(2-naphthyl)-2-(3-phenanthryl)ethylene, IV, a 30-50% conversion into cis was achieved by UV irradiation at 0°C. All four compounds had previously been shown to exhibit the emission anomalies ascribed to their existence as rotamer mixtures [1, 2]. Solutions of the cis

isomers of up to 10^{-5} M in either decalin or ethanol were cooled to -145° C (decalin) or -170° C (ethano!) and irradiated at these temperatures with light from a 125 W mercury arc passed through a water-filled Pyrex vessel. Irradiation for 30-90 min sufficed to reach the photostationary state. After recording the absorption or emission spectra (the latter in a wide range of excitation wavelengths), the solutions were warmed up to -100° C, recooled to the low temperature at which irradiation had been carried out, and the spectra recorded again. These two sets of spectra will be referred to as "before" and "after". Only for compound Π were extensive differences between the "before" and "after" spectra observed. These results will be described in detail in the following section. In the three other compounds the differences were almost within the limits of experimental uncertainty, with the exception of compounds III and IV, where a decrease of the longest absorption peak was observed after defreezing, somewhat similar but much less pronounced than in the spectrum of Π (Fig. 3). In order to ensure that the negative results were not due to carrying out the experiments at -170° C (instead of at 77 K, as was done by Scheck), experiments were repeated at -185°C with ethanolic solutions of I, III and IV. $Cis \rightarrow trans$ photoconversion takes much longer at these extremely high viscosities and low temperatures. Again, the differences between the "before" and "after" spectra were tiny compared with those observed for II.



Fig. 3. Absorption and emission spectra of *trans*-II in ethanol, 10^{-5} M, at -170° C, formed by UV irradiation of *cis*-II. (--) "Before": (--) "after" heating and recooling (= unfreezing). Note the disappearance of the absorption peak at 368 nm, and of the L set of emission peaks, after unfreezing. Excitation at 362 nm, 2 nm slits.

Compound II

As reported earlier [2, 3], excitation at suitable wavelengths provides evidence for the existence of three modifications, S, L and LL, which were assigned here to the three postulated rotamers A—C. In both decalin and ethanol (Fig. 2b) the emission spectra show this quite distinctly at -100° C: 354, 368 and 376 nm excitation yields emission spectra assignable to a rotamer mixture in which S, L and LL, respectively, predominate, while excitation at 362 nm yields an emission consisting mainly of a superposition of the S and L spectra. This makes it a particularly useful excitation wavelength for detecting changes in rotamer composition.

Trans-II, formed by UV irradiation at -170°C (Fig. 2a) presents essentially the same picture as at -100° C, except that the spectral definition is much better. Figure 3 describes the absorption spectrum, as well as the emission spectrum excited at 362 nm, before and after heating. All spectra were taken at -170° C. The absorption spectrum of S and the emission spectrum of L overlap strongly. Beneath the shortest emission band, marked S₁, one can see the longest absorption peak, which almost disappears after heating. The emission spectrum "before' (Fig. 3), is clearly a superposition of the S and L spectra, characterized by sets of three peaks marked S_1-S_3 and $L_1 - L_3$, which contribute about equally to the observed spectrum. Equilibration by heating and recooling causes the equilibrium to shift sharply in favour of S. This is shown even more clearly in Fig. 4, which describes the emission spectra obtained by exciting with a 20 nm(!) slit in order to reduce photoselective excitation. On going from Fig. 4a to 4c, the spectra "before" reflect an increasing contribution of the L modification, which predominates in Fig. 4c. The spectra "after" (dashed curves) indicate almost pure S in Fig. 4a and 4b, with some contribution of L in Fig. 4c. There is almost no contribution of the LL modification "after". The differences between "before" and "after" spectra were less pronounced in decalin solutions, probably because in the latter, at about -135° C, the equilibrium rotamer mixture is more in favour of the L and LL modifications.

No effort was made at this stage to follow the kinetics of the thermal equilibration during the unfreezing process. However, in ethanol at -160° , and in decalin at -140° , it is estimated that the change from the spectra "before" to "after" takes place within minutes, and can be followed at intermediate temperatures. A flash-induced *cis* \rightarrow *trans* photoisomerization, followed by measurement of the decay of the L emission excited at 362 nm or of the absorption at the longest absorption peak, is feasible in principle at suitable temperatures, but may be hampered by the low quantum yield of photoisomerization at very high viscosities (about 10^8-10^9 cP at -160° C for ethanol and -140° C for decalin [13]). Quantitative kinetic experiments are planned, using both slow and fast methods.



Fig. 4. Emission spectra of solution as in Fig. 3, at -170° C, (-) before and (-) after unfreezing, excited with 20 nm(!) slits. Emission slits 1 nm. Excitation at (a) 360; (b) 370; (c) 380 nm. Note the decrease in the contribution of "L" after unfreezing.

DISCUSSION

In earlier work [2] attempts were made to find factors which affect the rotameric composition: change of solvent, incorporation in stretched films, and aggregation in poor solvents were some of the factors investigated. Only by aggregation was it found possible to move the equilibrium almost completely to the S modification [15], but this is obviously not a "clean" method. Varying the temperature undoubtedly moves the equilibrium, but at the same time the spectra change their shape. The method described above permits the detection of a non-equilibrium composition, and moreover the measurement of the kinetics of the subsequent thermal equilibration, as a function of the temperature and viscosity. It also opens up new possibilities of detecting differences between other physical properties of the postulated rotamers.

The experimental results raise several questions. First, what determines the non-equilibrium rotameric composition resulting from the $cis \rightarrow trans$ photoconversion, and secondly, why are positive observations restricted to compound II? Regarding the first point, it has been assumed throughout [1, 2], in accordance with the empirical rule first put forward by Havinga for the photocyclization of trienes to cyclodienes [11], that in the excited state no change of rotameric composition takes place*. Accordingly, the composition of the *cis* isomer in the ground state should determine that of the *trans* isomer produced from the *cis* isomer via the singlet excited state. However, this assumption may not always hold, i.e. during the *cis* \rightarrow *trans* transformation in the excited state equilibration may take place for some compounds. Another explanation could be that in the other compounds the rotamer equilibrium in the *cis* and *trans* isomers happens to be similar.

^{*}Momicchioli and co-workers [5] estimate the energy barriers to interconversion of rotamers in the excited state to be at least four times higher than in the ground state.

REFERENCES

- 1 E. Fischer, J. Mol. Struct., 84 (1982) 219.
- 2 For a review, see E. Fischer, J. Photochem., 17 (1981) 331.
- 3 G. Fischer and E. Fischer, J. Phys. Chem., 85 (1981) 2611.
- 4 F. Momicchioli, I. Baraldi and M. C. Bruni, Chem. Phys., 70 (1982) 161; 82 (1983) 229.
- 5 L Baraldi, F. Momicchioli and G. Ponterini, J. Mol. Struct., Theochem, (1984) in press. In this paper the energy differences between rotamer A and rotamers B and C are estimated to be 0.3 and 0.6 kcal mol⁻¹, respectively, taking into account the actual bend lengths in the naphthyl groups.
- 6 E. Haas, G. Fischer and E. Fischer, J. Phys. Chem., 82 (1978) 1638.
- 7 S. Malkin and E. Fischer, J. Phys. Chem., 18 (1964) 1153.
- 8 R. H. Dyck and D. S. McClure, J. Chem. Phys., 36 (1962) 2326.
- 9 T. Wismontski, G. Fischer and E. Fischer, J. Chem. Soc., Perkin Trans. 2, (1974) 1930. 10 E. Fischer, J. Phys. Chem., 77 (1973) 859.
- 11 H. J. C. Jacobs and E. Havinga, Adv. Photochem., 11 (1979) 305.
- 12 M. V. Alfimov, V. F. Razumov, A. G. Rachinski, V. N. Listvan and Yu. B. Scheck, Chem. Phys. Lett., 101 (1983) 593.
- 13 G. Fischer and E. Fischer, Mol. Photochem., 8 (1977) 279.
- 14 E. Fischer, Mol. Photochem., 2 (1970) 99.
- 15 E. Fischer, J. Phys. Chem., 84 (1980) 403.