Expressions (14) and (15) indicate the behavior of spiropyran (I) at –100°C (cf. Fig. 1, curve 5).

CONCLUSIONS

1. The spectral and kinetic properties of the photoinduced colored species in a solution of 6-nitrospiropyrans in hexane are determined by associates of colored and colorless species.

2. The spectral bands at 580 and 615 nm belong to associates of the monomeric colored and colorless state of type BB and AB, the band at 520-540 nm belongs to the associate of the dimer of the colorless state of type ABA_2, and the state with charge transfer $(A^+B^-)A_n$, formed in the reaction of ABA_2 with the colorless state, is responsible for the absorption band at 670 nm.

3. The highly polar state $(A^+B^-)A_n$, which takes up other states, forms high-molecular associates.

4. The thermal decolorization of states AB, BB, and ABA_2 takes place one order of magnitude more rapidly than that of state $(A^+B^-)A_n$.

5. The bulky alkyl substituent on the nitrogen atom in spiropyran hinders association of the colorless form and the formation of associate ABA_2 and creates additional hindrances to the reaction of decolorization in the state of isomerization and cyclization.

LITERATURE CITED

1. V. A. Barachevskii, G. I. Lashkov, and V. A. Tsekhomskii, Photochromism and Its Use [in Russian], Khimiya, Moscow (1977).
2. T. Bercovici, R. Heiligman-Rim, and E. Fischer, Mol. Photochem., 1, 23 (1969).
3. C. Balny, R. Donzou, T. Bercovici, and E. Fischer, Mol. Photochem., 1, 225 (1969).
4. A. A. Parshutkin and V. A. Krongauz, Mol. Photochem., 6, 437 (1974).
5. K. G. Dzhaparidze, Spirochromenes [in Russian], Metsniereba, Tbilisi (1979), pp. 12, 63.
6. V. Krongauz, J. Kiwi, and M. Gratzel, J. Photochem., 13, 89 (1980).
7. J. Gruda and R. M. Leblanc, Can. J. Chem., 54, 576 (1976).

COMPLEXATION OF THE THERMALLY INDUCED COLORED FORM OF 6-NITROSPIROPYRANS IN A POLAR SOLVENT

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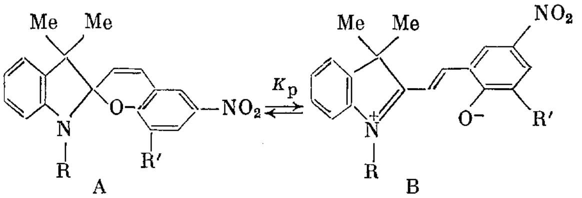
UDC 541.11:541.49:547.816

The photoinduced colored form of 6-nitrospiropyrans in aliphatic and weakly polar solvents is a complex of the colored state [1]



Complexes in a dilute solution consist of type AB and BB dimers which absorb at 615 and 580 nm. The effect of dimers of the colorless form A_2, which form complexes of the ABA_2 type with absorption at 520-540 nm in the reaction with dimers AB, becomes marked in a concentrated solution. In the reaction with the colorless state, the latter generate a highly polar state $(A^+B^-)A_n$ with $\lambda_{max} = 670$ nm, capable of taking up other colored states with the formation of high-molecular aggregates.

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0568-5230/84/3309-1806$08.50

TABLE 1. Properties of 6-Nitroindolinospiropyrans

Compound	R	R′	Mp, °C	State	Color
(I)	CH_2CH_2OH	OMe	195–196 (Ia) 80–81 (Ib)	Crystalline Amorphous	Dark green Violet
(II)	$CH_2CH_2OCOC(Me){=}CH_2$	OMe	45–46	»	Blue
(III)	CH_2CH_2OH	H	170–171	Crystalline	Cherry-red

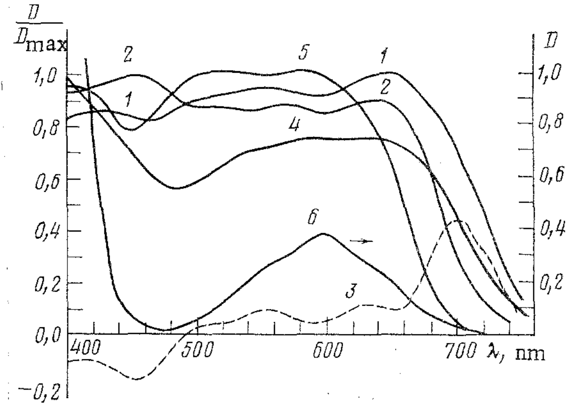

Fig. 1. Spectra of the diffuse reflection of 6-nitro-8-methoxyspiropyran (I) in the amorphous (1) and crystalline (2) states; 3) difference in spectra 1 and 2; 4, 5) spectra of 6-nitro-8-methoxyspiropyran (II) and spiropyran (III); 6) absorption spectrum of a solution of amorphous (I) in THF immediately after dissolution, $5 \cdot 10^{-3}$ M.

The nature of the thermally induced colored form of 6-nitrospiropyrans was studied in the present article in order to determine the possibility of complexing of form B in a polar solvent (THF, MeOH) and to obtain further details of this event.

EXPERIMENTAL

6-Nitroindolinospiropyrans of the formula reported above (Table 1) in concentrated solutions in THF, methyl ethyl ketone, and MeOH, and in the solid state, prepared by crystallization or concentration of solutions in the dark at 0-30°C were studied.

Spiropyrans (I) and (III) were synthesized by boiling equimolar quantities of the corresponding 2-methylindolines and salicylaldehydes in MeOH or methyl ethyl ketone for 3 h with subsequent crystallization from MeOH (EtOH) or separation on Al_2O_3 (benzene:acetone = 5:1) with a yield of 60-70%. (II) was prepared by acylation of (Ib) at −40°C according to [2] (Al_2O_3, benzene:acetone = 4:1) (55%).

Spiropyran (I) was prepared in the crystalline (Ia) and amorphous (Ib) modifications, and their identity was confirmed by elemental analysis and TLC (R_f 0.56, benzene:acetone = 5:1, Silufol UV-254). Modification (Ia) was formed in crystallization from MeOH (EtOH), while (Ib) was formed on separation of the spiropyran on Al_2O_3 or on dissolution of (Ia) in THF or methyl ethyl ketone with subsequent rapid evaporation of the solvent.

The spectra of the broad bands of the spiropyran powders were recorded by reflection on an SF-14 spectrophotometer, and the UV spectra of the solutions were recorded on a Specord UV-VIS spectrometer at ∿20°C.

DISCUSSION OF RESULTS

The spectra of the diffuse reflection of the colored form of 6-nitrospiropyran (I)-(III) in the solid state are shown in Fig. 1. The spectra of the spiropyrans in which the solid samples were prepared from concentrated solutions in THF, methyl ethyl ketone, and EtOH in the dark (the colored and colorless forms in these solutions are in thermodynamic equilibrium) have a complex structure and are dependent on the type of substituents and the method of separation of the compound from the solution.

The complex structure of the spectrum of 6-nitro-8-methoxyspiropyrans (I) and (II) appears in the presence of bands at 500-520, 560-580, 620-640, and 700 nm (cf. Fig. 1, spectra 1-4). The position of the bands coincides with the position of the band of complexes of merocyanine state B in aliphatic solvents, and according to [1], the 500-520-, 560-580-, 620-640-, and 700-nm reflections can be respectively assigned to complexes of types ABA_2, BB, AB, and $(A^+B^-)A_n$.

As a consequence, the process of complexing of 6-nitrospiropyrans takes place in a polar solvent (THF, methyl ethyl ketone, EtOH), and as the data reported indicate, no marked thermal activation energy is required, and the process can take place without photoactivation. The latter indicates a certain effect of the concentration of the solution on the reaction of form B of the 6-nitrospiropyrans, which consists of the fact that complexes ABA_2 and $(A^+B^-)A_n$ are formed in a certain concentration range above 0.01 M. This finding confirms the existence and necessity of dimers A_2 for the appearance of ABA_2 [1]. With a decrease in the concentration of the solution, complexes ABA_2 and $(A^+B^-)A_n$ dissociate into dimers BB, AB, and monomers B with absorption at 560, 630, and 600 nm (cf. Fig. 1, spectrum 6), and these complexes are again formed on concentration of the solution (spectrum 1). This process can be conducted repeatedly.

In addition, the capacity to form complex $(A^+B^-)A_n$ with $\lambda_{max} = 700$ nm in a polar solvent is dependent on the substituents of the benzopyran fragment, which determines the activity of the colored molecules in the reaction. The low polarity of the merocyanine molecules of 6-nitrospiropyran (III), in contrast to 6-nitro-8-methoxyspiropyrans (I) and (II), hinders the appearance of the 700-nm state (cf. Fig. 1, spectrum 5) and also increases the energy barrier of the reaction of formation of the complex in a polar solvent, which requires a certain activation energy [3].

The presence of complex $(A^+B^-)A_n$ is a necessary condition for the formation of the other highly polar state which has a 450-nm band in the spectrum and is only found in the crystalline samples of (Ia) (spectrum 2). Similar absorption at 460 nm, assigned to the second band of the spectrum of $(A^+B^-)A_n$, was observed in [3] in crystallization of 6-nitro-8-methoxyspiropyran in an electric field. In addition, a comparison of amorphous and crystalline samples of (I) shows that the highly polar state is formed from complex $(A^+B^-)A_n$ (spectrum 3), and the appearance of the state with absorption at 450 nm results in an increase in the melting point of crystals (Ia) by 115°C (see Table 1) and their poor solubility in most organic solvents. The bulky substituent on the N atom prevents the appearance of the state with absorption at 450 nm, and 6-nitro-8-methoxyspiropyran (II) is thus only obtained in the amorphous state with a low melting point. The crystalline and amorphous samples of (I) are capable of interconversion. Dissolution of (Ia) on boiling in THF or MeOH with subsequent rapid evaporation of the solvent results in amorphous (Ib), and vice versa, slow crystallization of (Ib) from MeOH yields (Ia). These transitions of (Ia) and (Ib) are accompanied by the corresponding spectral changes (spectra 1-3).

The process of the formation of the amorphous and crystalline states of (I) in a polar solvent is thus as follows. Concentration of the solution results in complexes of spiropyran and merocyanine molecules which form high-molecular aggregates. These aggregates consist of a nucleus, complex $(A^+B^-)A_n$, and an amorphous environment which consists of dimers AB and BB and tetramers ABA_2. When the spiropyran is rapidly separated from the solution, the aggregates are chaotically arranged and create loose packing. Prolonged holding of the aggregated solution results in transformation of the nuclei of the high-molecular formations into another state, apparently a polar state of the colorless form $(A^+A^-)A_n$. The polar aggregates formed combine in a subsequent reaction and create structures with a high packing density.

CONCLUSIONS

Thermally induced formation of colored complexes which result in the amorphous and crystalline states of solid compounds takes place in a concentrated solution of 6-nitrospiropyrans in a polar solvent.

LITERATURE CITED

1. V. D. Arsenov, A. A. Parshutkin, V. S. Marevtsev, and M. I. Cherkashin, Izv. Akad. Nauk SSSR, Ser. Khim., 1976 (1984).
2. V. D. Arsenov, V. D. Ermakova, M. I. Cherkashin, and P. P. Kisilitsa, Izv. Akad. Nauk SSSR, Ser. Khim., 452 (1975).
3. A. A. Parshutkin and V. A. Krongauz, Mol. Photochem., 6, 437 (1974).