

## Peculiarities of Photochromism and Luminescence of Dinitrosubstituted Hydroxyazomethinespiropyran

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**Abstract**—Photochromic and luminescent properties of a novel spiroopyran modified by attachment of the nitroazomethine moiety in the 5'-position have been studied by laser photolysis and spectral and luminescent methods. Intermediate products have been detected and their decay rate constants have been determined during laser photolysis in toluene and a poly(methyl methacrylate) film. In alcohol solutions reverse photochromism is observed: coloration of the solution in the dark and its discoloration under exposure to light. The reasons for the appearance of reverse photochromism and the peculiarities of luminescence in alcohol solutions are discussed in comparison with the model nitrospiroopyran.

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Preparation and study of novel compounds of the spiroopyran class are of interest due to widespread application of spiroopyrans as optical labels, photo-switches, in photochemical sensor systems [1–3].

In this work, the spectral and luminescent properties of novel hydroxyazomethinespiropyran **I** with nitro groups in the spiro and azomethine moieties were studied in organic solvent solutions and the polymer matrix of poly(methyl methacrylate) (PMMA) at 293 K. In compound **I**, the azomethine moiety is attached to the indoline moiety of spiroopyran, as in azomethinespiropyrans studied earlier [4–6]. By analogy with model nitrospiroopyrans [1, 7, 8] and nitrohydroxyazomethines [9], the presence of the nitro group as a substituent in the spiroopyran and azomethine moieties can substantially change the photochemical behavior of the compound under study.

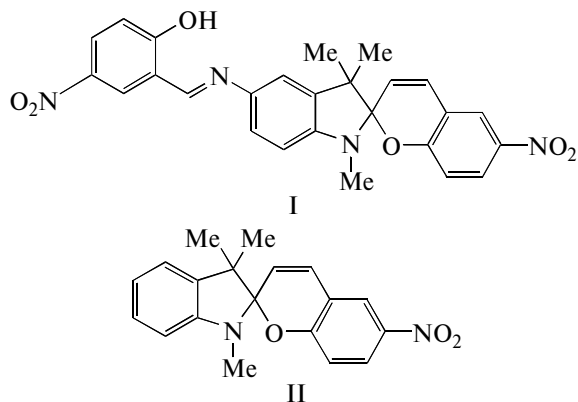
1',3'-Dihydro-5'-(2-hydroxy-5-nitrobenzylideneimino)-1',3',3'-trimethyl-6-nitrospiro[(1)-benzopyran-2,2'-(2H)-indole] (**I**) was synthesized according to the procedure described in [10]. In studies of the photochromic properties of **I**, model nitrospiroopyran **II** was used for comparison. Purity of the compounds was controlled by thin-layer chromatography, melting points, NMR spectroscopy, and elemental analysis. The spectral studies were performed in solutions of organic solvents (ethanol, acetonitrile, toluene) at 293 K. The solutions were prepared both at room light and under dark conditions. Concentrations of the compounds in solutions were  $5 \times 10^{-6}$ – $5 \times 10^{-4}$  mol L<sup>-1</sup>. The introduction of **I** and **II** into a PMMA film (60 μm thick) was performed by joint dissolution in methylene chloride of the polymer and the test compounds, with subsequent casting the solutions on a horizontal glass surface.

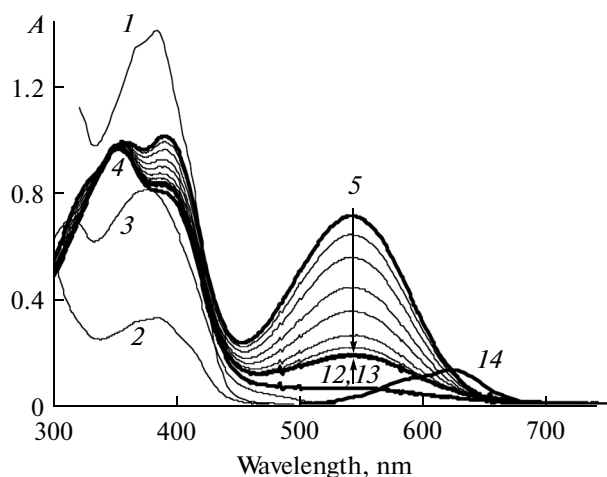
Stationary electronic UV/VIS absorption spectra were measured on a MultiSpec-1501 spectrophotometer, and luminescence spectra were recorded on a CaryEclipse spectrofluorimeter.

The absorption spectra and the formation and decay kinetics of the intermediate products were measured on a nanosecond laser photolysis apparatus. A nitrogen laser (PRA LN 1000, with 1 ns pulse duration and 337 nm radiation wavelength), operating in the 10 Hz frequency regime was used as an excitation source. The measurements were carried out at room temperature in the presence and absence of atmospheric oxygen.

Stationary irradiation of the solutions and the film was performed by light of DRS-1000 or Fluotest-6w

### EXPERIMENTAL





**Fig. 1.** Absorption spectra of **I** in (1) toluene, (2) acetonitrile, (3) PMMA film, and (4–13) ethanol; the solution in ethanol was prepared (4) at room light and (5) in the dark; spectra 6–12 and 13 were recorded after irradiation of solutions 5 and 4, respectively, with light of  $\lambda = 365$  nm; 14 after irradiation of the solution in toluene with light of  $\lambda = 365$  nm at 275 K.

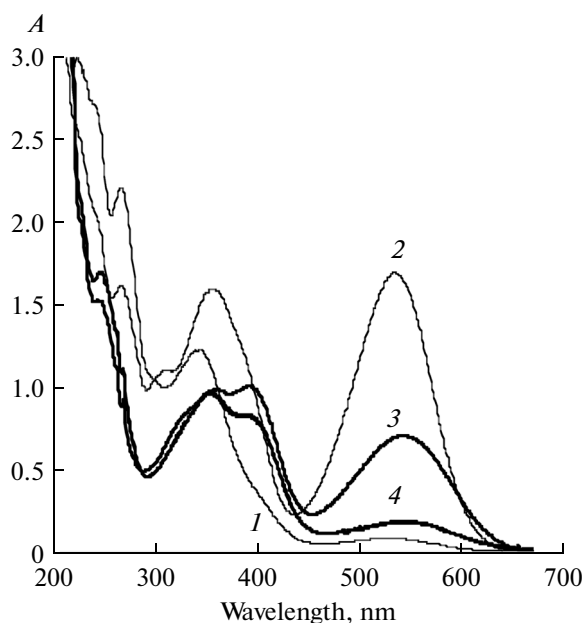
lamps with isolation of the spectral line with  $\lambda = 365$  nm.

The absorption spectra of compound **I** in weakly polar toluene, in polar solvents (acetonitrile, ethanol), and in the PMMA film are shown in Fig. 1. In an alcohol solution of **I** prepared in the light, as in toluene, acetonitrile, and PMMA, the spiropyran moiety of the compound exists in the cyclic form (Fig. 1). Preparation in the dark or keeping of the alcohol solution prepared in the light further under dark conditions leads to its coloration due to the formation of compound **I** with the merocyanine form of the spiropyran moiety.

In the concentration range of  $5 \times 10^{-6}$ – $6 \times 10^{-5}$  mol L $^{-1}$ , the absorbance at the maximum of the absorption band of the colored product at thermal equilibrium depends linearly on the concentration of **I** in ethanol. The position of the absorption band of the colored product ( $\lambda_{\text{max}} = 550$  nm) is close to that observed in a solution of the model nitrospiropyran with the thermo- or photoinitiated merocyanine form (MC); however, the extent of coloration of the solution of **I** under dark conditions is much greater (Fig. 2).

Upon stationary UV light (DRSh-1000) irradiation with cooling (275 K) of a solution of **I** in toluene, it is possible to detect a colored metastable product with an absorption maximum at 630 nm and a bend at  $\lambda = 580$  nm, which, on the basis of coincidence with the absorption spectrum of the open form (OF) of nitrospiropyran [7, 11], can be attributed to **I** with the merocyanine form of the spiropyran moiety of the molecule (Fig. 1, spectrum 14).

During laser photolysis of **I** in toluene and the PMMA film, intermediate products are detected with



**Fig. 2.** Absorption spectra of solutions of (1, 2) **I** and (3, 4) **II** in ethanol prepared in the dark (1, 3) before and (2, 4) after their irradiation with light of  $\lambda = 365$  nm.

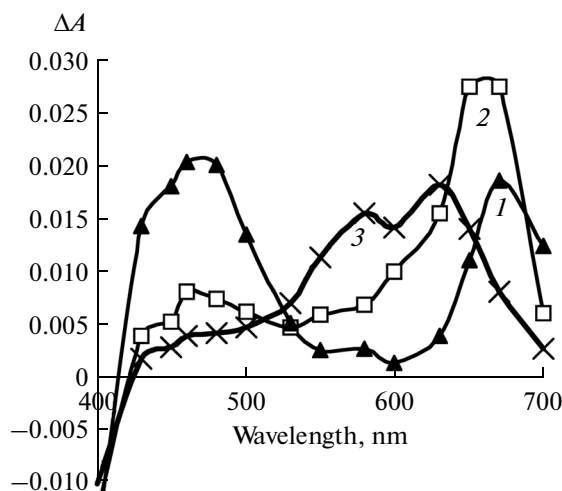
significantly different lifetimes. Figure 3 shows the absorption spectra of the intermediate products in a toluene solution in the absence of atmospheric oxygen at observation times of (1) 50 ns, (2) 100  $\mu$ s, and (3) 1 ms.

At a time of 50 ns after the laser pulse, two absorption bands are detected with maximums at 460 and 670 nm, analogous to those observed upon laser photolysis of solutions of nitrosubstituted spiropyran **II** [12–14]. The decay of both of these absorption bands is described by the first-order rate law with the same value of the rate constant  $k = 3.9 \times 10^4$  s $^{-1}$ , on the basis of which they can be assigned to the same product, and they can be attributed to the triplet state of the open form of **I** on the basis of data on quenching by atmospheric oxygen (decay rate constant  $k = 3.2 \times 10^6$  s $^{-1}$ ).

At 100  $\mu$ s, an absorption spectrum due to the short-lived isomer of OF is detected, which can be one of the intermediate isomers TTT or CTT [15]. By the time 1 ms, it isomerizes to the OF isomer with longest lifetime (TTC), the merocyanine (MC) form with the characteristic absorption spectrum similar to that observed upon stationary irradiation ( $\lambda_{\text{max}} = 580$  and 630 nm).

The decay kinetics of the intermediate products observed, the triplet, the intermediate OF, and the MC form, obey the first-order rate law with decay rate constants of  $k = 3.9 \times 10^4$ ,  $1.3 \times 10^3$ , and  $0.08$  s $^{-1}$ , respectively.

In contrast to azomethinespiropyrans studied earlier [6, 16], the products of breaking the spiro bond prevail in the absorption spectrum of the intermediate

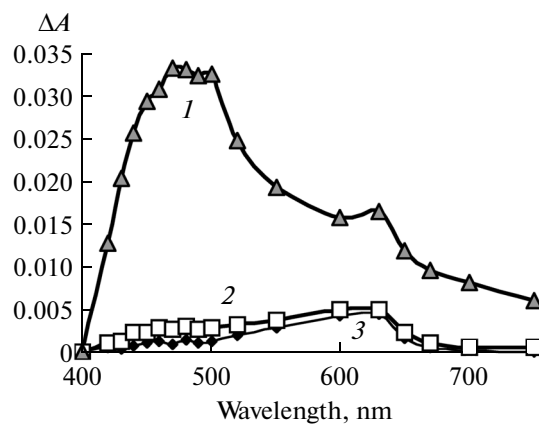


**Fig. 3.** Absorption spectra of intermediate products obtained upon laser photolysis of **I** in toluene with light of  $\lambda = 337$  nm in the absence of atmospheric oxygen within (1) 1  $\mu$ s, (2) 100  $\mu$ s, and (3) 1 ms after the laser pulse.

products of laser photolysis of **I** and the product of proton transfer in the azomethine moiety is not observed. It is possibly due to the decrease in the lifetime of the form with transferred proton in the azomethine moiety, which is caused by the presence of the electronegative substituent  $\text{NO}_2$ , analogous to that observed in [17] for nitrosubstituted azomethinespirooxazines.

Laser excitation of compound **I** in PMMA (Fig. 4) gives rise just after the laser pulse to a product with an absorption spectrum other than that of the product detected in the toluene solution. The relatively short-lived intermediate product with an absorption spectrum having a maximum at about 500 nm decays following the one-exponential law with a rate constant of  $k = 1.5 \times 10^4 \text{ s}^{-1}$ . The spectrum observed can be a superposition of the absorption spectra of the product of photoinduced proton transfer in the azomethine moiety (450–500 nm) and the short-lived photoisomer of OF (about 600 nm). The possibility that the proton transfer product can be observed in PMMA is consistent with the increase in its lifetime in a polymer matrix for azomethinespiroopyrans studied earlier [18].

Within 500  $\mu$ s and 3 ms after the laser pulse, products with similar absorption spectra, but different lifetimes are detected (Fig. 4, spectra 2, 3), which, as in the toluene solution, are supposed to be the OF isomers. Their decay kinetics are described by the first-order law with rate constants of  $1.7 \times 10^3$  and  $140 \text{ s}^{-1}$ , respectively. It is important to note that the decay rate constant of the product with the longest lifetime (Fig. 4, spectrum 3) is much higher than the decay rate constant of the MC form of the model nitrospiropyran in the PMMA film. In contrast to the model nitrospiropyran, passing from the solutions of **I** to the solid polymer is accompanied by acceleration of the decay



**Fig. 4.** Absorption spectra of intermediate products obtained upon laser photolysis of **I** in a PMMA film with light of  $\lambda = 337$  nm within (1) 20 ns, (2) 500  $\mu$ s, and (3) 3 ms after the laser pulse.

of the open form of **I** [1, 19, 20], rather than increase in its lifetime. It is possible that the presence of the nitrosubstituted azomethine moiety in **I** does not favor stabilization of the MC form, and the photoisomer of OF detected in the experiment has a shorter lifetime than that in the model nitrospiropyran. The same effect of the lack of stabilization of the MC form and detection of mainly short-lived *trans*-keto isomer formed as a result of proton transfer and the subsequent *cis*–*trans* isomerization in the azomethine moiety was observed earlier in [18] for naphtho- and bromosubstituted hydroxyazomethinespiroopyrans in PMMA.

The photochromic behavior of **I** in alcohol solutions differs from that in toluene and acetonitrile solutions and from an alcohol solution of the model nitrospiropyran, which is characterized by direct photochromism: coloration by the action of UV irradiation and discoloration in the dark (Figs. 1, 2).

Irradiation with UV light ( $\lambda = 365$  nm) of an alcohol solution of **I** colored in the dark leads to weakening the color and establishment of photoequilibrium between the open (OF) and closed forms (Fig. 1, spectrum 12). The action of visible light shifts the equilibrium toward the closed form and discolors the solution to the level of absorbance of the starting solution prepared in the light (Fig. 1, spectrum 4). The so-called reverse (negative) photochromism is observed: coloration of the solution under dark conditions and discoloration under exposure to light. At photoequilibrium, under the action of 365-nm light, the absorbances at the absorption maximum of OF (550 nm) upon discoloration of the solution colored in the dark and upon coloration of the solution prepared at room light coincide (Fig. 1, spectra 12, 13).

The fact of formation and accumulation for a rather long time (hours) of the colored form in the alcohol solution only (dark coloration is not observed

in polar acetonitrile) can indicate a substantial role of hydrogen bonds in the protic polar solvent ethanol. This can result from conformational rearrangements involving solvent molecules, in particular, the formation of a complex with solvent molecules.

The extent of coloration under dark conditions of an alcohol solution of **I** at equilibrium is much higher than for the solution of the model nitrospiropyran (Fig. 2). Hence, attachment of the nitrohydroxyazomethine moiety to spiropyran increases the OF content at thermal equilibrium, and the extent of coloration by the action of UV light at photoequilibrium is smaller than at thermal equilibrium and much smaller than for the model spiropyran (Fig. 2).

The increase in the extent of dark coloration in alcohol solutions of 6-nitrospiropyrans was observed earlier upon introduction of additional substituents, such as nitro group, bromine, and OMe, into the 8-position of the chromene moiety of spiropyran [1, 8].

For compound **I**, the shift of thermal equilibrium toward OF and the appearance of reverse photochromism is associated with attachment of the substituent to the indoline moiety of the photochrome molecule.

Upon repetition of the photochromic cycles, a decrease in the extent of dark coloration of alcohol solutions of **I** is observed, which can be caused by degradation processes of **I** typical of spiropyrans, in particular, nitrospiropyrans [8]. It will be shown below that a decrease in the extent of dark coloration in an alcohol solution by aging the solution is accompanied by changes in luminescence of the solution.

Compound **I** exhibits luminescence in the crystal state and in solutions of organic solvents. For solutions of **I** in toluene and acetonitrile, regardless of the excitation wavelength, luminescence (green) with a band maximum at 530–550 nm is observed (Fig. 4), which is due to the formation of a product of proton transfer in the azomethine moiety, a process that is typical of hydroxyazomethines [9] and hydroxyazomethinespiropyrans [4, 5]. Green luminescence is observed for **I** in the PMMA matrix as well, whereas blue coloration of the film and luminescence at longer wavelengths—red luminescence due to the formation of the stabilized merocyanine form [7]—are observed for model spiropyran **II** in PMMA under the same irradiation conditions. The lack of red luminescence is consistent with the laser photolysis data showing that there is no buildup of the MC form because of a high cyclization rate constant in PMMA for the MC precursor, the shorter-lived isomer of OF of **I**.

The excitation spectrum of **I** in an ethanol solution prepared in the light exhibits two excitation bands, the band at 360–390 nm as in toluene and acetonitrile solutions and additionally the weaker band at 430–450 nm. Excitation at both of these bands leads to an emission band with a maximum at 530 nm analogous to the luminescence band in toluene and acetonitrile

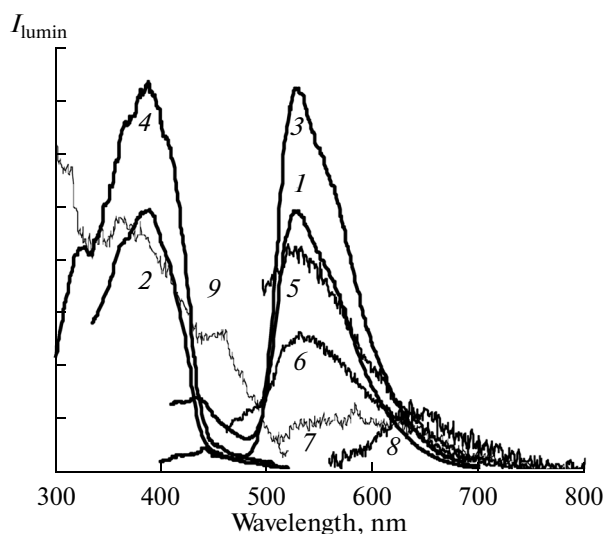


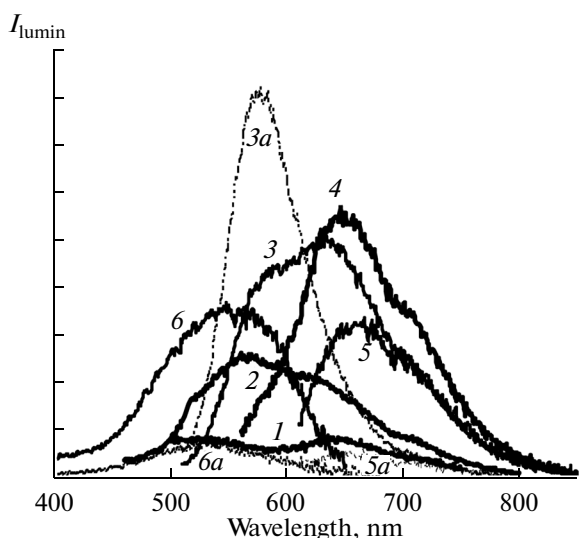
Fig. 5. Luminescence spectra of **I** in (1, 2) toluene, (3, 4) acetonitrile, and (5–9) ethanol solution prepared at room light. Emission: in (1) toluene ( $\lambda_{\text{ex}} = 390$  nm), (3) acetonitrile ( $\lambda_{\text{ex}} = 390$  nm), and (5–8) ethanol ( $\lambda_{\text{ex}} =$  (5) 390, (6) 450, (7) 500, and (8) 550 nm). Excitation: in (2) toluene, (4) acetonitrile, and (9) ethanol ( $\lambda_{\text{det}} = 530$  nm).

(Fig. 5). For a solution of **I** in alcohol, the intensity of the luminescence band with  $\lambda_{\text{max}} = 530$  nm is more than an order of magnitude lower than in toluene and acetonitrile. Only upon long-wavelength excitation ( $\lambda_{\text{ex}} = 550$  nm) of an alcohol solution of **I**, very weak luminescence is detected at  $\lambda_{\text{max}} = 640$  nm due to the presence of small amounts of OF undetectable in the absorption spectra (Fig. 5, spectrum 8).

As an alcohol solution of **I** takes a color in the dark, it is possible to detect dual luminescence (Fig. 6) with emission bands in the region of 540–560 nm.

The position of the maximums of the luminescence bands of the colored alcohol solution depends on the excitation wavelength (Fig. 6), which indicates the presence of several luminescing products with overlapping absorption spectra.

In the observed emission spectrum with two maximums, the short-wavelength component (550–600 nm) corresponds to the excitation band at 450–500 nm. The long-wavelength component in the emission spectrum (in the region of 600–650 nm) is due to luminescence of OF; in the excitation spectrum, it corresponds to the band with a maximum at 530–550 nm, which coincides with the long-wavelength absorption band of OF. This emission band disappears during discoloration of the colored solution by the action of UV or visible light. The disappearance of the long-wavelength component is accompanied by a simultaneous enhancement of the short-wavelength component of the emission spectrum. Figure 6 (spectra 3, 3a) demonstrates the enhancement of the short-



**Fig. 6.** Luminescence spectra of *I* in ethanol solution prepared in the dark (1–6) before and (3a, 5a, 6a) after photodiscoloration. Emission:  $\lambda_{\text{ex}} =$  (1) 390, (2) 450, (3, 3a) 500, (4) 550, and (5, 5a) 600 nm. Excitation:  $\lambda_{\text{det}} =$  (6, 6a) 700 nm.

wavelength component and the disappearance of the long-wavelength component in the emission spectrum at excitation  $\lambda_{\text{ex}} = 500$  nm upon photoinduced discoloration of the solution. The same figure shows the decrease in the intensity of the emission band (curves 5, 5a) at an excitation wavelength of  $\lambda = 600$  nm and the excitation band (curves 6, 6a) with detection at  $\lambda = 700$  nm, which were due to the decrease in the OF content during irradiation.

During the course of photochromic cycling, the changes in the intensity of the short-wavelength band depend inversely on the changes in the intensity of the long-wavelength component, which, on the basis of the data of the absorption and excitation spectra, may indicate competition for absorption of light between the luminescing products with the absorption maximums of 450–500 and 530–550 nm. As the number of photochromic cycles increases, the efficiency of short-wavelength luminescence in the absence of OF increases, thereby indicating the accumulation of the luminescing product from cycle to cycle. The enhancement of luminescence can be due to the formation of products associated with the disappearance of OF ( $\lambda_{\text{max}}$ ) the absorption spectrum in the region of 400–450 nm corresponding to the excitation range of short-wavelength luminescence suggests the formation of the product with a high luminescence quantum yield.

In summary, the photochemical behavior of highly polar compound **I** has a number of features due to combination of the spiro pyran and azomethine moieties and the presence of nitro groups as substituents in these moieties: (1) During laser photolysis of **I** in tolu-

ene, the formation of intermediate products involves the triplet state of **I** with the open form of the spiro moiety, a process that is typical of nitrospiropyran [12–14]. (2) In contrast to model spiropyran **II**, stabilization of the MC form is not observed and a shorter-lived isomer of OF is detected upon laser photolysis of **I** in the polymer. (3) In alcohol solutions of **I**, the thermal equilibrium is shifted toward OF to a greater extent than in model nitrospiropyran **II**. At the same time, attachment of the azomethine moiety steeply decreases the photochromic properties (extent of coloration) of the spiropyran moiety of the molecule, thereby causing reverse photochromism. (4) Luminescence of colored solutions of **I** in alcohol is characterized by dual luminescence due to luminescence of **I** with the merocyanine form of the spiropyran moiety and the product of proton transfer in the azomethine moiety. With repetition of the photochromic cycles, the contribution of the strongly luminescing degradation product, which is formed with participation of the MC form, increases and begins to prevail.

#### ACKNOWLEDGMENTS

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