

Fluorescence of α,ω -Diphenylpolyenyl Carbocations

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Abstract: The fluorescence lifetimes of the α,ω -diphenylpolyenyl carbocations in CH_2Cl_2 solution increase with decreasing temperature toward limiting values. This behavior is very similar to that of the corresponding α,ω -diphenylpolyenyl carbanions, and the quantitative differences are surprisingly small. By analogy with the anions, it is proposed that deactivation of the excited state occurs by fluorescence, internal conversion, and by skeletal twisting of these conformationally labile ions. This last method of deactivation is an activated process and becomes negligible at low temperatures.

Introduction

We have been making a systematic study of the spectroscopic properties, especially the fluorescence, of the alkali metal salts of diphenylpolyenyl carbanions. In the solvents usually employed for the preparation of such species—ethers or amines—these salts exist as mixtures of tight and loose ion pairs.^{1,2} Photolysis of solutions of 1,3-diphenylallyl carbanion (DP3^-) with white light results in photoisomerization from the preferred trans,trans conformation into the cis,trans to an extent that is strongly temperature dependent.³ There is a close resemblance to the excited state behavior of stilbene,⁴ and it is likely that the twisting of the carbanion in the excited state proceeds to the perpendicular state from which descent to the ground state of either the trans,trans or cis,trans conformation can occur (Figure 1) without the emission of radiation.⁵ Twisting of the trans,trans form is an activated process. Return from the excited to the ground state also occurs by fluorescence and by internal conversion; the fluorescence lifetime, τ , is given by

$$1/\tau = k_f + k_{ic} + A \exp(-E/RT) \quad (1)$$

where k_f and k_{ic} are the corresponding rate constants and A and E are the Arrhenius preexponential factor and activation energy for skeletal twisting. The fluorescence lifetimes of a wide range of ion pairs, not only of DP3^- ⁵⁻⁷ but also of its vinyllogs,⁸ have been found to conform to this equation. In contrast, the cis,trans form of DP3^- does not fluoresce; as in the case of cis-stilbene, the barrier to twisting is negligible.

Sondermann and Kuhn described the preparation of the α,ω -diphenylpolyenyl carbocations by treatment of the corresponding carbinols with BF_3 etherate in CH_2Cl_2 solution and recorded their absorption maxima.⁹ They concluded that the wide variation in the values of the absorption maxima reported in earlier literature can be attributed to the failure of many previous workers to employ conditions under which these carbocations are stable. Pivnenko et al. were unable to interpret the ^1H NMR spectrum of a solution

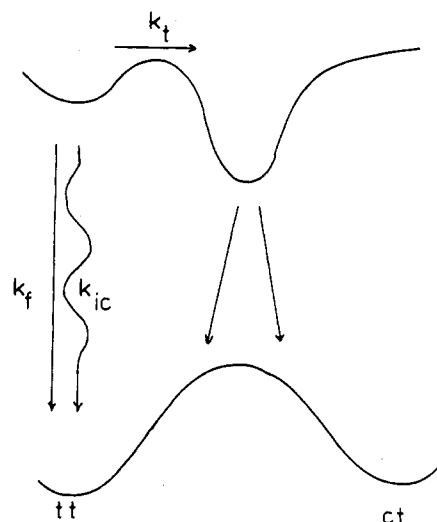


Figure 1. Potential energy diagram for trans,trans and cis,trans DP3^- showing the competition between fluorescence, internal conversion, and skeletal twisting to deactivate the excited state.

of diphenylallyl carbocation (DP3^+) in sulfuric acid because the inequivalence of the methine protons is too small¹⁰ Olah and Spear¹¹ prepared DP3^+ in the superacid mixture $\text{SbF}_5/\text{FSO}_3\text{H}/\text{SO}_2$; the solution was stable up to -15°C . The spectrum showed that only the trans,trans conformation is adopted and that, whereas the barrier to rotation about the phenyl-allyl bond is low, the barrier to cis-trans interconversion is much greater. The NMR spectra of the 1,5-diphenylpentadienyl cation (DP5^+) and the higher vinyllogs do not appear to have been examined. Hafner and Pelster mentioned that these species fluoresce at low temperature, but gave no details.¹² Indeed, the literature contains very little data on the fluorescence or fluorescence lifetime of any carbocation—with the notable exception of certain substituted xanthyliums which can be formed thermally¹³ or photochemically^{14,15} from the parent 9-xanthenols; the fluorescence of dibenzosuberonyl cation has been studied under similar condi-

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(1) Burley, J. W.; Young, R. N. *J. Chem. Soc., Chem. Commun.* **1969**, 1127.

(2) Burley, J. W.; Young, R. N. *J. Chem. Soc., Perkin Trans. II* **1972**, 835.

(3) Young, R. N.; Parkes, H. M.; Brocklehurst, B. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 65.

(4) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415.

(5) Parmar, S. S.; Brocklehurst, B.; Young, R. N. *J. Photochem.* **1987**, *40*, 121.

(6) Brocklehurst, B.; Young, R. N.; Parmar, S. S. *J. Photochem.* **1988**, *41*, 167.

(7) Oliver, C. E.; Young, R. N.; Brocklehurst, B. *J. Photochem. Photobiol. A.* **1993**, *70*, 17.

(8) Oliver, C. E.; Brocklehurst, B.; Young, R. N. Unpublished results.

(9) Sondermann, J.; Kuhn, H. *Chem. Ber.* **1966**, *99*, 2491.

(10) Pivnenko, N. S.; Grin, L. M.; Lavrushina, O. V.; Pedchenko, N. F.; Labrushin, V. F. *Teor. Eksp. Khim.* **1975**, *11*, 625.

(11) Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 1539.

(12) Hafner, K.; Pelster, H. *Angew. Chem.* **1961**, *73*, 342.

(13) Boyd, M. K.; Lai, H. Y.; Yates, K. *J. Am. Chem. Soc.* **1991**, *113*, 7294.

(14) Wan, P.; Yates, K.; Boyd, M. K. *J. Org. Chem.* **1984**, *50*, 2881.

(15) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929.

tions¹⁶ However, we have been unable to locate any study of the temperature dependence of the fluorescence lifetime of any carbocation.

At the simplest level, quantum mechanics predicts that the electronic spectra of alternant species such as the polyenylic anions should be identical to their carbocationic counterparts. More sophisticated considerations, of course, only predict similarity. Fabian and Zahradnik¹⁷ have reported the results of their PPP calculations which predict absorption maxima in excellent agreement with the experimental data of Sondermann and Kuhn⁹ for the carbocations. The corresponding comparisons they drew with the carbanion data of Hafner and Goliash¹⁸ are less meaningful since the latter authors studied the sodium salts in ether. These form tight ion pairs resulting in spectra that are blue-shifted with respect to the free anions (or loose ion pairs) to extents that increase with increasing chain length.

Since solutions of both the carbanions and the carbocations fluoresce, it is clearly of great interest to investigate whether their fluorescence lifetimes exhibit similar temperature dependences. It has been suggested that DP3⁻ may photoisomerize by the initial loss of an electron to yield the ground state diphenylallyl radical which, being conformationally very labile, could isomerize before recapturing the electron.^{19,20} "Even weakly stabilizing solvent molecules can act as acceptors for electron transfer reactions from photoexcited carbanions, since the addition of antibonding interactions to already significant electron-electron repulsion may be sufficient to overcome nuclear attraction terms".²⁰ However, we have found no evidence for this process occurring with any of the diphenylpolyenylic carbanions—even in highly polar solvating solvents such as methylamine and 1,2-dimethylethylenediamine.⁵⁻⁸ The likelihood of the photochemically induced loss of an electron from a carbocation to create a dipositive transient is slight. However, a much more plausible event is the transfer of an electron to DP3⁺ from its counteranion thereby generating the diphenylallyl radical as a transient which would ultimately return the electron. Alternatively, the polyenylic cations could twist in their excited states in a manner entirely analogous to that proposed for their anionic counterparts. The present work seeks to obtain the data necessary to test these hypotheses.

Results

In order to increase the stability of the solutions it was found necessary to use an excess of BF₃ etherate in CH₂Cl₂ over that required for stoichiometry; lower concentrations led to the formation of cloudy solutions as did solutions with ether contents below that specified in the Experimental Section—particularly at very low temperatures. The stabilities of the carbocations increase with increasing chain length and with decreasing temperature. Solutions of DP3⁺ had to be maintained below -50 °C to survive long enough to permit measurements to be made. (The 1,3-diphenylbutenyl cation and several of its derivatives have been reported to show similar instability in SO₂/FSO₃H solution undergoing rapid cyclization to the corresponding indanyl ions.^{21,22}) Study of the longer chain α,ω -polyenylic cations was easier—the more so the greater the chain length—and it was readily possible to work with the diphenylnonatetraenyl cation (DP9⁺) at -10 °C. Since the decomposition products were all found to absorb at much shorter wavelengths, their presence in small concentrations in fact caused no problems in either absorption or fluorescence measurements.

(16) Johnson, L. J.; Lobaugh, J.; Wintgens, V. *J. Phys. Chem.* **1989**, *93*, 7370.

(17) Fabian, J.; Zahradnik, R. *Wiss. Zeit. Tech. Univ. Dresden* **1977**, *26*, 315.

(18) Hafner, K.; Goliash, K. *Angew. Chem.* **1962**, *74*, 1189.

(19) Tolbert, L. M. *Acc. Chem. Res.* **1986**, *19*, 268.

(20) Tolbert, L. *Org. Photochem.* **1983**, *6*, 177.

(21) Pittman, C. U., Jr.; Miller, W. G. *J. Am. Chem. Soc.* **1973**, *95*, 2947.

(22) Miller, W. G.; Pittman, C. U., Jr. *J. Org. Chem.* **1974**, *39*, 1955.

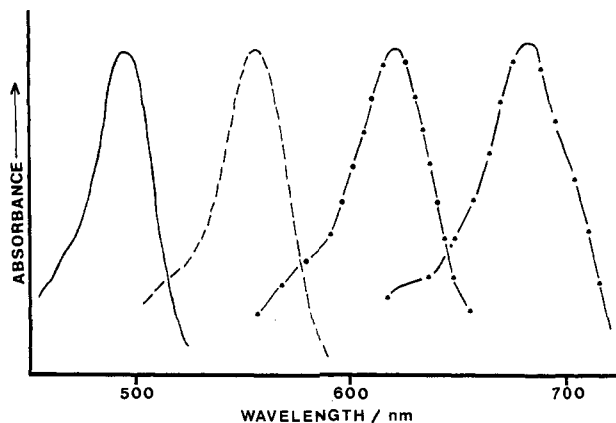


Figure 2. The absorption spectra of DP3⁺, DP5⁺, DP7⁺, and DP9⁺ in CH₂Cl₂.

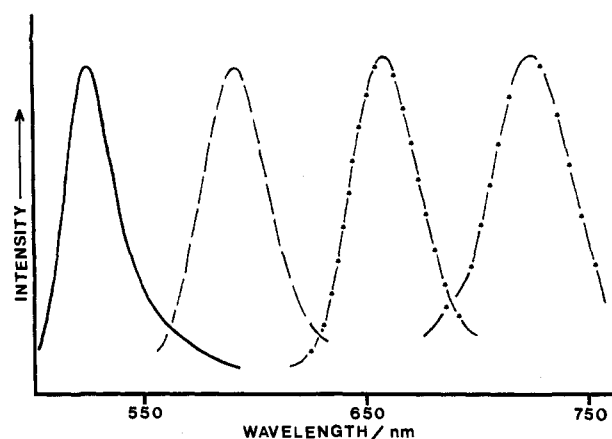


Figure 3. The emission spectra of DP3⁺, DP5⁺, DP7⁺, and DP9⁺.

The absorption spectra (Figure 2) of the α,ω -diphenylpolyenyl carbocations all consist of a single band with absorption maxima that agree well with the values reported by Sondermann and Kuhn.⁹ The position and bandshape of the emission spectra (Figure 3) are independent of excitation wavelength and solution temperature. The absorption spectra of DP5⁺, DP7⁺, and DP9⁺ were measured at several temperatures over the range -20 to -85 °C. No changes in the positions of their absorption maxima were detected. The band shapes were similarly invariant, and the absorbances increased with decreasing temperature to extents compatible with the solvent contraction. The spectra of the corresponding carbanions⁸ are similar to those of the cations but are shifted to somewhat longer wavelengths: the absorption maxima for the loose ion pairs (and free anions) of DP3⁻, DP5⁻, DP7⁻, and DP9⁻ are at 565, 595, 647, and 709 nm, respectively.

An interesting observation is that the absorption maximum of 1,5-di-*p*-tolyl-pentadienyl cation (DT5⁺) located at 595 nm is very markedly red-shifted with respect to that of the closely related DP5⁺ (560 nm); the emission spectrum exhibits a corresponding shift (to 624 from 588 nm). In contrast, the absorption spectra of the polyenyl carbanions shift to the red by only 1–2 nm on the introduction of methyl groups to the rings.²³ The spectra of solutions of DT5⁺ formed in CH₂Cl₂ using BF₃ etherate are indistinguishable from those formed using TiCl₄. Tests were also made to determine if the absorption spectrum was sensitive to the proportions of Et₂O and CH₂Cl₂ in the solution. It was found that the absorption maximum of the ditolylpentadienyl cation moved from 591 to 587 nm on increasing the volume fraction of Et₂O to 50% and to 583 nm at 100%—these changes being temperature independent. Other cations behaved analogously, and this modest dependence on solvent composition was regarded

(23) Parkes, H. M.; Young, R. N. *J. Chem. Soc., Perkin Trans. II* **1980**, 1137.

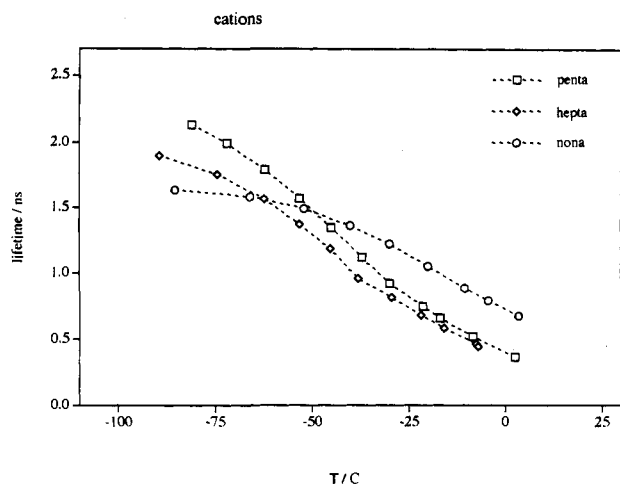


Figure 4. The temperature dependence of the fluorescence lifetimes of DP5⁺, DP7⁺, and DP9⁺.

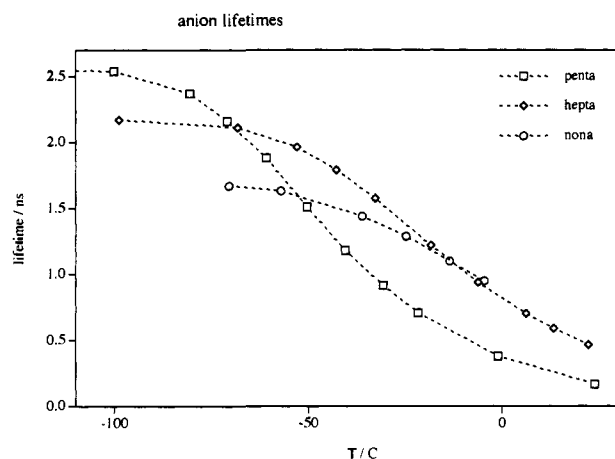


Figure 5. The temperature dependence of the fluorescence lifetimes of loose ion pairs of DP5⁻, DP7⁻, and DP9⁻.

as inconsequential; all subsequent solutions were prepared as described in the Experimental Section.

The fluorescence lifetimes of the carbocations were determined as a function of temperature. The excitation wavelengths (nm) used and the cut-off wavelength of the filter placed in front of the photomultiplier were, respectively, as follows: DT5⁺ (570, 630), DP7⁺ (620, 645), and DP9⁺ (670, 695). In every case the fluorescence decay was well fitted by a single exponential. The lifetimes increase with decreasing temperature in a sigmoidal manner as shown in Figure 4. It would be expected that these would each reach a ceiling value at a sufficiently low temperature but the rather high freezing point of CH₂Cl₂ (-95 °C) precluded direct observation of this. For comparison, Figure 5 shows the temperature dependences of the fluorescence lifetimes of the analogous DP5⁻, DP7⁻, and DP9⁻ anions as the Li⁺ or Na⁺ salts in MTHF[8]—in which solutions only the loose ion pair is present. These results also conform to eq 1 and the τ_0 and Arrhenius parameters are listed in Table 1.

Experiments were conducted to investigate whether photoisomerization of DP3⁺ was observable using an absorption spectrophotometer as in the case of the corresponding carbanion.⁴ No change was in fact detected with this nor with the DP5⁺—the only other cation investigated. However, the accessible temperature range was severely limited by the instability of these cations, and study was only possible between -50 and -80 °C.

Discussion

The absorption maxima shift to the red with increasing chain length as expected; the positions of the maxima correspond quite

Table 1. Arrhenius Parameters and Low Temperature Limiting Fluorescence Lifetimes

cation	E_a , kJ mol ⁻¹	$10^{13} A$, s ⁻¹	τ_0 , ns	anion	E_a , kJ mol ⁻¹	$10^{13} A$, s ⁻¹	τ_0 , ns
DT5 ⁺	21.5	2.6	2.3	DP5 ⁻	22.6	5.1	3.3
DP7 ⁺	21.2	2.6	2.0	DP7 ⁻	23.9	2.7	2.2
DP9 ⁺	23.6	2.5	1.7	DP9 ⁻	23.1	1.5	2.1

closely to the formula $\lambda_{\max}/\text{nm} = 433 + 62n$ where n is the number of olefinic double bonds in the parent polyene. The emission maxima show a similar regularity and conform to the formula $\lambda_{\max} = 458 + 66n$. In a solvent such as dichloromethane, which has quite a small permittivity, it is to be expected that the carbocations are present as ion pairs with little dissociation into free ions. From the insensitivity of the absorption spectra to temperature it seems that the type of ion pair does not change. Since the counterion is polyatomic (HOBf₃⁻), the interionic separation must be quite large, and the ion pair is perhaps best regarded as a loose pair, i.e., there may be no counterpart to the tight ion pair formed between carbanions and their monoatomic alkali metal counterions. The observation that the fluorescence decays were well fitted by single exponentials is also in consonance with the presence of a single kind of ion pair. It seems likely that, by analogy with the corresponding carbanions, the all-*E* conformations are adopted.²⁴

The fluorescence lifetimes for the four carbocations and their related carbanions were found to fit well to eq 1 on the choice of appropriate values of τ_0 . These are listed in Table 1 together with the Arrhenius parameters deduced. The preexponential factors of about 10^{13} s^{-1} are in line with expectation for an intramolecular rotational process. The τ_0 values systematically decrease with increasing chain length. The Arrhenius activation energies are so similar to each other that detailed comparison is not justified. The close parallel between the results obtained for these related carbocations and carbanions is very striking and strongly suggests that their excited states deactivate by a common mechanism involving competing pathways of fluorescence and skeletal twisting.

The failure to observe photoisomerization of DP3⁺ can be attributed to the limited temperature range accessible. The activation energy barrier for ground state cis,trans to trans,trans isomerisation is unknown and may well be small enough to permit thermal relaxation before conventional spectrophotometry can be carried out. Photoisomerization of the analogous carbanion proceeds to a photostationary state that progressively favors the thermodynamically more stable trans,trans conformation as the temperature is lowered—even when ground state relaxation is frozen out. It may be that the window of temperature accessed in the present study of DP3⁺ is inappropriate on analogous grounds. Future work is planned using flash photolysis and solvents having lower freezing points.

Experimental Section

1,3-Diphenylpropen-1-ol was prepared by reacting phenyl magnesium bromide with cinnamaldehyde;²⁵ the crude product was purified by HPLC: ¹H NMR $\delta = 7.2\text{--}7.4$ (m, 10 H), 6.71 (d, $J = 16$ Hz, 1 H, H(3)), 6.38 (dd, $J = 16, 6.7$ Hz, 1 H, H(2)), 5.38 (d, $J = 6.7$ Hz, 1 H, H(1)).

1,5-Diphenylpenta-1,4-dien-3-ol was prepared by reduction of dibenzalacetone with NaBH₄ in ethanol²⁶ with a little sodium methoxide as catalyst. During the workup considerable isomerization took place because the pH was inadvertently allowed to fall: HPLC provided the pure (*E,E*)-1,5-diphenyl-2,4-pentadien-1-ol compound: ¹H NMR (CDCl₃) δ 7.1–7.4 (m, 10 H), 6.73 (dd, $J = 16, 10.5$ Hz, 1 H, H(4)), 6.51 (d, 16 Hz, 1 H, H(5)), 6.37 (ddd, $J = 15, 10.5, 1$ Hz, 1 H, H(3)), 5.89 (dd, $J = 15, 7$ Hz, 1 H, H(2)), 4.81 (dd, $J = 7, 1$ Hz, 1 H, H(1)).

(24) Tolbert, L. M.; Ogle, M. E. *J. Am. Chem. Soc.*, **1990**, *112*, 9519.

(25) Nomura, H. *Bull. Soc. Chim. France* **1925**, *37*, 1245.

(26) Shoppee, C. W.; Henderson, G. N. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1028.

1,5-Di-(*p*-tolylpenta-1,4-dien-3-ol) was similarly prepared by NaBH₄ reduction of bis(*p*-methylstyryl) ketone (Aldrich).

1,7-Diphenylhepta-1,4,6-trien-3-ol was similarly prepared from benzal cinnamal acetone; careful control of pH prevented isomerization, and the pure compound was obtained by HPLC: δ 7.1–7.4 (m, 10 H), 6.8 (dd, $J = 15, 10.5$ Hz, 1 H, H(6)), 6.65 (d, 16 Hz, 1 H, H(1)), 6.55 (d, $J = 16$ Hz, 1 H, H(7)), 6.42 (dd, $J = 15, 10.5$ Hz, 1 H, H(5)), 6.20 (dd, 16, 6.5 Hz, 1 H, H(2)), 5.85 (dd, $J = 15, 6.5$ Hz, 1 H, H(4)), 4.85 (t, $J = 6.5$ Hz, 1 H, H(3)).

1,9-Diphenyl-nona-1,3,6,8-tetraen-5-ol was prepared from dicinnamal acetone. HPLC provided sufficient material to permit study of the carbocation, but scale-up to permit NMR spectroscopy was thwarted by rapid oxidation. The NMR spectrum of the unpurified reduction product gave the following: δ 7.2–7.5 (m, 10 H), 6.72 (dd, $J = 15, 10$ Hz 2H, H(2,8)), 6.51 (d, $J = 15$ Hz, 2H, H(1,9)), 6.37 (ddd, 15, 10, $J = 1$ Hz, 2 H, H(3,7)), 5.80 (dd, $J = 15, 6$ Hz, 1 H, H(4, 6)), 4.76 (t, $J = 6$ Hz, 1 H, H(5)).

All the above alcohols were found to be air and light sensitive unless sealed into ampules under vacuum and stored in a freezer.

A 30% solution of BF₃ etherate in diethyl ether was diluted with anhydrous CH₂Cl₂ to form a 0.1 molar solution. Carbocation solutions

were prepared for electronic spectroscopy by filling cuvettes with this solution and thermostating under a nitrogen atmosphere at 0 °C, or below, in an unsilvered dewar vessel mounted in the cell compartment of the spectrometer. The appropriate carbinol was introduced as a single drop of solution (ca. 10⁻⁴ molar) in the same solvent by means of a Pasteur pipette. After stoppering the cuvettes, absorption and emission spectra were recorded using Perkin-Elmer 554 and MPF44 instruments, respectively.

Carbanion solutions were prepared by the removal of a proton from the appropriate polyene precursor by the lithium salt of the dimer dianion of α -methylstyrene under high vacuum conditions as previously described.^{6,7}

Fluorescence lifetimes were measured at port HA12 of the synchrotron radiation source (SRS) at Daresbury using single photon counting. The experimental procedures and the method of data analysis have been described.^{6,7}

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