PHOTOISOMERIZATION AND THERMOISOMERIZATION II: STERIC REQUIREMENTS FOR PHOTOCHROMISM AND THERMOCHROMISM OF *N,N'*-BIS(SALICYLIDENE)DIAMINES

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Summary

We have investigated the photochemical and thermal isomerization of Schiff bases derived from *o*-hydroxybenzaldehydes and aromatic or aliphatic diamines. First-order rate constants of the thermal back reaction of the photoinduced isomerization were measured. From the steric requirement for the molecular rearrangement in the isomerization processes, the structure of the photoisomer was assigned to an *o*-quinoid amine form, while the thermo-induced colour was related to the yield of a zwitterion.

1. Introduction

Although numerous studies have already been reported on the photochromism and thermochromism of salicylideneamines, there is neither conclusive proof of the structure of the coloured species nor any example of utilization of such crystals [1, 2]. This is probably due to the fact that very little direct structural information concerning the transient species is obtainable by ordinary laboratory techniques. Furthermore, the Schiff bases chosen for detailed discussion are limited to *N*-salicylideneaniline (1) and a small number of very closely related derivatives.
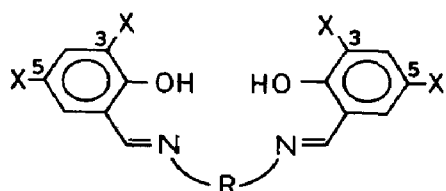
In our preceding paper [1] we showed that the introduction of bulky *tert*-butyl groups as the ring substituent of 1 and its derivatives is a very effective method of producing various stable photochromic crystals and we proposed a reasonable mechanism for the photoinduced colouration and fading processes of this class of compounds. The clarification of the mechanism of the colour change processes and the development of new compounds with such properties continue to be of interest in the search for practical utilization of these phenomena. In this present ·study we used diamines to prepare new photosensitive and thermosensitive Schiff bases and we measured the first-order rate constants k of the thermal fading of the

200

photocoloured species (photochromers) to elucidate the colour change processes of Schiff bases.

2. Experimental details

2.1. General comments

The general techniques used were the same as described in our preceding paper [1]. The compounds used were prepared by standard condensation of the appropriate amine and aldehyde, with elemental and spectral analyses as the check of the purity. The Schiff bases 2 [3], 5 [4], 7 [4], 8 [5], 11 [6], 13 [7], 15 [8], 16 [5], 17 [9], 18 [8] and 19 [10] are previously known compounds, while the others were first prepared in this study.

	X	R
2:	H	(CH$_2$)$_2$
3:	3-H, 5-t-Bu	(CH$_2$)$_2$
4:	t-Bu	(CH$_2$)$_2$
5:	H	o-Ph
6:	t-Bu	o-Ph
7:	H	m-Ph
8:	H	p-Ph
9:	t-Bu	p-Ph

	X	R
10:	H	(xylyl, CH$_3$)
11:	H	(CH$_2$ ... CH$_2$)
12:	t-Bu	(CH$_2$ ... CH$_2$)
13:	H	(pyridyl)

2.2. Product characterization data

The spectroscopic data for 3 (melting point, 168 - 169 °C) are as follows. IR (KBr): 1637 cm^{-1} (strong, C=N); 1589 cm^{-1} (medium, aromatic). Nuclear magnetic resonance (NMR) (CDCl$_3$): δ = 1.25 ppm (singlet (s), 18H, tert-butyl); δ = 3.89 ppm (s, 4H, CH$_2$); δ = 6.82 ppm (doublet (d), J = 8 Hz, 2H, 3(H)); δ = 7.14 ppm (d, J = 2 Hz, 2H, 6(H)); δ = 7.30 ppm (doublet of doublets, J = 8 Hz, J = 2 Hz, 2H, 4(H)); δ = 8.30 ppm (s, 2H, N=CH); δ = 12.9 ppm (broad singlet (bs), 2H, OH). C$_{24}$H$_{32}$N$_2$O$_2$ requires 75.75% C, 8.48% H and 7.36% N. The results of analysis were as follows: 75.61% C, 8.41% H and 7.31% N.

The spectroscopic data for **4** (melting point, 182 - 183 °C) are as follows. IR (KBr): 1633 cm^{-1} (strong, C=N); 1596 cm^{-1} (weak, aromatic). NMR (CDCl$_3$): δ = 1.27 ppm (s, 18H, *tert*-butyl); δ = 1.40 ppm (s, 18H, *tert*-butyl); δ = 3.90 ppm (s, 4H, CH$_2$); δ = 7.03 ppm (d, J = 2.5 Hz, 2H, 6(H)); δ = 7.33 ppm (d, J = 2.5 Hz, 2H, 4(H)); δ = 8.34 ppm (s, 2H, N=CH); δ = 13.5 ppm (bs, 2H, OH). C$_{32}$H$_{48}$N$_2$O$_2$ requires 78.00% C, 9.82% H and 5.69% N. The results of analysis were as follows: 77.96% C, 9.94% H and 5.74% N.

The spectroscopic data for **6** (melting point, 192 - 193 °C) are as follows. IR (KBr): 1619 cm^{-1} (strong, C=N); 1575 cm^{-1} (medium, aromatic). NMR (CDCl$_3$): δ = 1.33 ppm (s, 18H, *tert*-butyl); δ = 1.46 ppm (s, 18H, *tert*-butyl); δ = 7.20 ppm (d, J = 2 Hz, 2H, 6(H)); δ = 7.26 ppm (bs, 4H, aromatic H); δ = 7.45 ppm (d, J = 2 Hz, 2H, 4(H)); δ = 8.66 ppm (s, 2H, N=CH); δ = 13.50 ppm (s, 2H, OH). C$_{36}$H$_{48}$N$_2$O$_2$ requires 79.96% C, 8.95% H and 5.18% N. The results of analysis were as follows: 79.68% C, 8.97% H and 5.40% N.

The spectroscopic data for **9** (melting point, above 260 °C) are as follows. IR (KBr): 1613 cm^{-1} (strong, C=N); 1589 cm^{-1} (medium, aromatic). NMR (CDCl$_3$): δ = 1.32 ppm (s, 18H, *tert*-butyl); δ = 1.47 ppm (s, 18H, *tert*-butyl); δ = 7.22 ppm (d, J = 2.5 Hz, 2H, 6(H)); δ = 7.34 ppm (s, 4H, aromatic H). C$_{36}$H$_{48}$N$_2$O$_2$ requires 79.96% C, 8.95% H and 5.18% N. The results of analysis were as follows: 79.87% C, 8.97% H and 5.19% N.

The spectroscopic data for **10** (melting point, 133 - 134 °C) are as follows. IR (KBr): 1615 cm^{-1} (strong, C=N); 1565 cm^{-1} (medium, aromatic). NMR (CDCl$_3$): δ = 2.37 ppm (s, 3H, CH$_3$); δ = 6.75 - 7.5 ppm (multiplet (m), 11H, aromatic H); δ = 8.50 ppm (s, 2H, N=CH); δ = 13.16 ppm (s, 2H, OH). C$_{21}$H$_{18}$N$_2$O$_2$ requires 76.34% C, 5.49% H and 8.48% N. The results of analysis were as follows: 76.31% C, 5.52% H and 8.40% N.

The spectroscopic data for **12** (melting point, 149.5 - 150.5 °C) are as follows. IR (KBr): 1635 cm^{-1} (strong, C=N); 1605 cm^{-1} (weak, aromatic). NMR (CDCl$_3$): δ = 1.28 ppm (s, 18H, *tert*-butyl); δ = 1.40 ppm (s, 18H, *tert*-butyl); δ = 4.27 ppm (s, 4H, CH$_2$); δ = 7.08 ppm (d, J = 2 Hz, 2H, 6(H)); δ = 7.25 ppm (bs, 4H, aromatic H); δ = 7.36 ppm (d, J = 2 Hz, 2H, 4(H)); δ = 8.43 ppm (s, 2H, N=CH); δ = 13.64 ppm (s, 2H, OH). C$_{38}$H$_{52}$N$_2$O$_2$ requires 80.24% C, 9.21% H and 4.92% N. The results of analysis were as follows: 80.20% C, 9.25% H and 4.96% N.

The spectroscopic data for **14** (melting point, 103 - 105 °C) are as follows. IR (KBr): 1625 cm^{-1} (strong, C=N); 1580 cm^{-1} (medium, aromatic). NMR (CDCl$_3$): δ = 2.27 ppm (s, 3H, 5(CH$_3$)); δ = 2.37 ppm (s, 3H, N=CCH$_3$); δ = 4.76 ppm (s, 2H, CH$_2$); δ = 6.80 ppm (d, J = 8 Hz, 1H, 3(H)); δ = 7.01 ppm (bs, 1H, 6(H)); δ = 7.3 ppm (m, 1H, 4(H)); δ = 7.30 ppm (s, 5H, aromatic H); δ = 15.9 ppm (bs, 1H, OH). C$_{16}$H$_{17}$NO requires 80.30% C, 7.16% H and 5.85% N. The results of analysis were as follows: 80.16% C, 7.17% H and 5.79% N.

2.3. Photocolouration studies

Photocolouration studies were carried out by irradiating the crystalline Schiff-base powder, which was placed between two quartz plates, with 365

nm light. The progress of the thermal fading reaction of the resultant photochromers was followed spectrophotometrically at 25 °C in terms of the decrease in absorbance at around 480 nm. The detailed kinetic measurements and calculations of the rate constants k were described in our preceding paper [1].

3. Results and discussion

In general, interposing a methylene group between a nitrogen atom and an aromatic ring of the amine residues of N-salicylideneaminoaromatics is an effective method of producing photochromic Schiff bases [11, 12]. However, the rate constants for the Schiff bases derived from benzylamine are larger than those of the corresponding aniline derivatives [1]. This quantitative difference can be accounted for by the magnitude of the geometrical changes of the amine residue in the course of the thermal relaxation of the photochromer [1]. This observation also suggests that it is unnecessary for an aromatic ring to be present in the amine residue of the Schiff bases for the photochromism to occur. This is clearly demonstrated by the photochromic behaviour of crystalline 3 and 4. The rate constants k for the thermal fading reaction of the photochromers are summarized in Table 1, in which k_1 and k_2 show two-stage transient decay of the photochromers [1, 13, 14]. However, 2 does not exhibit photochromic character. In the case of 3 and 4, *tert*-butyl substituents do not produce an increase in the photochromer lifetime ($k_1^3 \approx k_1^4$; $k_2^3 = k_2^4$). Thus the non-photochromicity of 2 cannot be attributed to the possibility that photoinduced isomerization does occur but the reverse reaction is so rapid that no deepening of colour is observed. Similar behaviour was observed for 6 and 5; the former formed photochromic crystals while the latter did not. It is worth noting that crystalline 7 and 10 exhibit photochromism.

It has been confirmed that the appearance of the photochromic and thermochromic phenomena is accompanied by intramolecular proton transfer from the hydroxyl group to the imine nitrogen atom [11, 12]. It has also been suggested in the literature that the photochromism is associated with a non-planar structure for the starting molecules, in which the aminoaromatic group is out of the plane of the N-salicylideneamine moiety [15]. Pahor *et al.* [16] reported the crystal structure of non-photochromic 5, in which

TABLE 1

Rate constants k of thermal fading of photochromers

Compound	3	4	6	7	10	12
k_1 (s^{-1})	3.2×10^{-2}	6.3×10^{-2}	6.0×10^{-3}		1.5×10^{-3}	
k_2 (s^{-1})	1.7×10^{-3}	1.7×10^{-3}	7.0×10^{-5}	3.1×10^{-2}	1.0×10^{-4}	3.0×10^{-3}

one of two salicylidene groups is removed from the plane of all the other atoms of the molecule.

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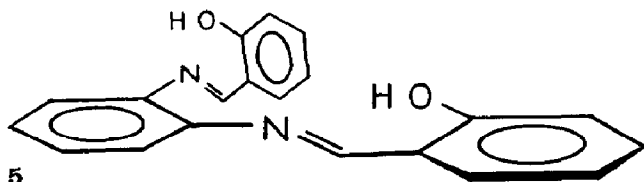
In contrast, a pair of salicylidene groups in each of the photochromic **6, 7** and **10** is thought to be out of the plane of the diaminophenyl moiety. From a consistent kinetic explanation of the thermal back reaction of photochromic *N*-salicylideneamines, we have previously suggested that a rotation around the C—N bond of the azomethine group is the key step in the stabilization of the photochromers [1]. With regard to the isomerization process of **6, 7** and **10**, a simple synchronous rotation of the two C=N bonds is impossible because of steric hindrance due to the resultant contact of the two planar benzylidene groups. Thus, a zwitterion [17] which involves a protonated sp^2-hybrid nitrogen atom and a phenolate oxygen atom is improbable for the photochromer of *N*-salicylideneanilines.

From these data, a possible mechanism of the photochromism of *N,N'*-bis(salicylidene)diamines can be suggested; the photoisomerization of **7** is illustrated:

7a   **7b**
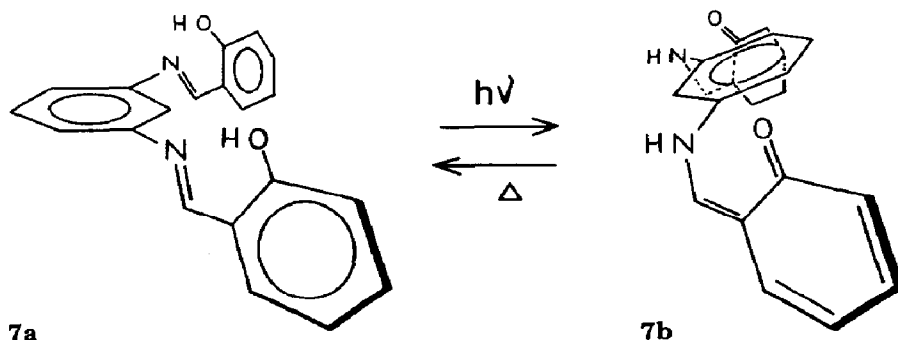
This mechanism is also supported by the fact that 2-(*N*-benzylacetimidoyl)-4-methylphenol (**14**)

14
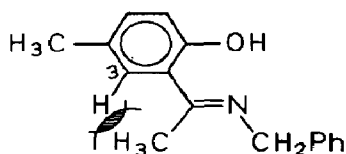
does not appear to be photochromic, in agreement with the observation of Mal *et al.* [18] who reported that the Schiff bases derived from *o*-hydroxy-acetophenone are not photochromic. The predominant factor determining the lack of photochromic behaviour for this type of compound could be the

steric inhibition to the coplanarity of the acetimidoyl group and the *o*-oxyphenyl group, owing to the contact of C(3)—H of the phenyl ring with the methyl protons [19]. This steric repulsion disturbs the formation of a quinoid form. In view of the inability of a simple C=N rotation model to account for the complex photoisomerization processes, we have proposed a change of hybridization of the imine nitrogen atom from sp^2 to sp^3 in the course of photochromism [1]. Our previous assignment [1] of the photochromer is consistent with the photocolouration mechanism in this study.

According to this mechanism, the methyl substituent between the two imine groups of **10** does not seem to interact repulsively with any other groups in the photoisomerization process. The quantitative difference between the rate constants of **7** and **10** is ascribed to the difference in mobility of the aminoaromatics in the crystal lattice. However, crystalline **11** is not photochromic. This is probably due to the increased difficulty of geometrical changes for the large amine moiety in the limited space in the crystal lattice. This problem was solved by the introduction of bulky groups into the salicylidene moieties to increase the molecular volume and thus allow partial movement of the amine residue for the photoisomerization: **12** forms photochromic crystals. In the case of **13**, which is not photochromic, the explanation given earlier with respect to the Schiff bases derived from 2-aminopyridine is also applicable [1, 11, 12]. The assumption of the tendency of **13** to take a planar conformation is supported by the planar structure of *N*-salicylidene-2-aminopyridine [11, 12]. There seems to be no room for photoinduced motion of the pyridine ring in the crystal lattice of the planar compound **13**. The diamine residues of all the photochromic Schiff bases in this study would change their position in the crystal lattice on irradiation with UV light, in a manner similar to that of **7**. Thus, the bulky *tert*-butyl groups might serve not only as space-openers which increase the molecular volume but also as anchor groups which fix the molecular conformation and diminish the mobility of the whole molecule. At the present stage, however, the origin of two-stage transient decay of the photochromers is not shown schematically.

For **8** and **9**, the situation is very different. As reported by Senier *et al.* [5], **8** can be obtained as either pale yellow or orange crystals. The pure yellow isomer can be isolated when **8** is freshly prepared, but care should be taken since the sample is easily contaminated with the orange isomer. The orange isomer can be obtained by recrystallization of the yellow isomer from common organic solvents or by heating the yellow form to above 101 °C. Microanalytical data obtained for both isomers agreed with the theoretical values; the two forms gave identical NMR spectra and produced a single spot in thin-layer chromatography on silica gel using a variety of solvents. They exhibited a small but significant difference in their IR spectra, in which the ν(C=N) absorptions of the yellow and the orange forms appeared at 1620 cm^{-1} and 1612 cm^{-1} respectively. Figure 1 shows reflectance spectra of both isomers. As could be expected from the mechanism of the photochromism of *N,N'*-bis(salicylidene)diamines, no photochromism
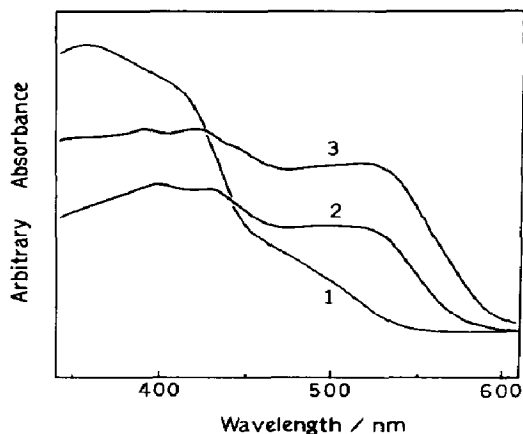
Fig. 1. Reflectance spectra of **8**: curve 1, the yellow isomer at 25 °C; curve 2, the orange isomer at 25 °C; curve 3, the orange isomer at 70 °C.

could be detected for either isomer of **8**. Upon being heated, the orange isomer acquired a deeper reddish colour and melted at 212 - 214 °C. However, such a thermal colour change could not be observed for the yellow isomer below 101 °C, at which temperature thermal rearrangement to the orange form occurred and the colour of the compound became deeper. Compound **9** was obtained as orange crystals and was thermochromic; however, we could not obtain a yellow isomer as for **8**.

From a survey of the reported thermochromic Schiff bases an important condition for the appearance of thermocolouration was found to be the existence of an aromatic ring or a similar conjugating system bound directly to the imine nitrogen. This is in striking contrast to the structural requirement of photochromic Schiff bases, in which such an aromatic ring is not necessary. The X-ray crystal structures of N,N'-bis(4'-alkoxybenzylidene)-1,4-phenylenediamines have been determined [20, 21]; it is most probable that the Schiff bases derived from p-phenylenediamine are structurally similar to these compounds, which exhibit an E configuration in the azomethine moieties and are packed in crystal layers.

These observations imply one possible assignment for each isomer of **8**:

8a   **8b**   **8c**
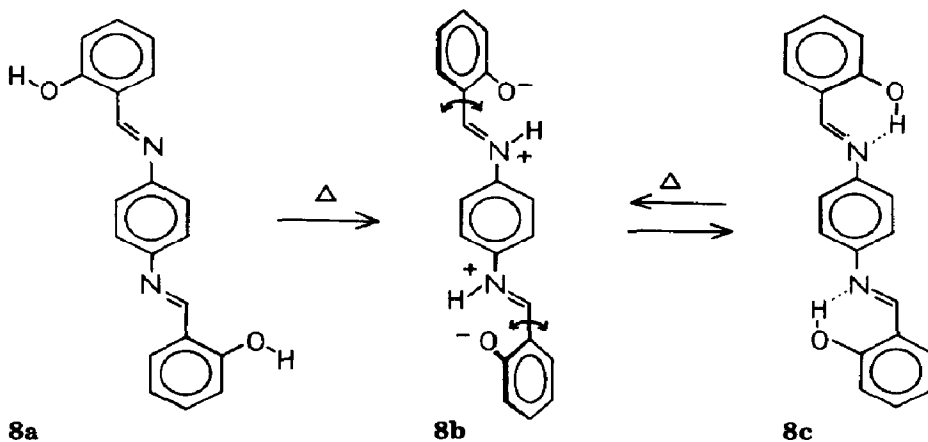
In the transformation of the yellow isomer (8a) to the orange isomer (8b), a rotation of the 2-hydroxyphenyl group is required around the aromatic carbon–methine carbon bond. Continued heating of 8 causes an ultrafast proton transfer from the hydroxyl group to the imine nitrogen followed by a vigorous torsional vibration around the imine carbon–aromatic carbon bond to stabilize the resultant zwitterion, in which the double bonds of the aromatic ring and the protonated imine residue are conjugated. The planar structure of the thermochromic molecules [22 - 25] is responsible for the ease with which such π orbitals overlap. It should be noted that there is neither proof nor any theoretical reason to support an o-quinoid form [26] as being the thermocoloured species (thermochromer). Hadjoudis [12] measured the proton–nitrogen ^{14}N nuclear quadrupole double-resonance (NQR) spectra of N-salicylideneanilines before and after the photoinduced or thermoinduced colouration. The characteristic difference between the NQR spectral pattern of the thermochromer and that of the photochromer can now be attributed to the quite different structure of the thermocoloured zwitterion with an sp^2 nitrogen compared with the photocoloured ketoamine form with an sp^3 nitrogen. The zwitterion mechanism for the thermochromism is rationalized by the drastic changes in the UV–visible absorption spectra of benzylideneanilines when the solvent is changed from non-polar to one that is polar and hydrogen bonding [27, 28]. The reddish colour of the Schiff bases in acidic solvents can be assigned to the N-protonated forms of the bases.

The thermoisomer 8c was completely converted to the original orange isomer 8b but not to the yellow isomer 8a when it was cooled to room temperature. For compounds 15, 16, 17 and 18
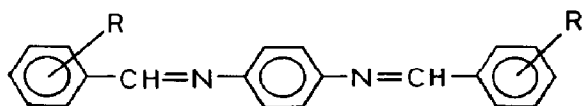

15: R = H   17: R = m-OH
16: R = o-OCH3   18 R = p-OH

we could not isolate isomers corresponding to 8a and 8b in spite of careful experimentation monitored by IR spectroscopy. Therefore, the driving force for the isolation of 8a is attributable to the favourable formation of hydrogen bonds between the oxygen atoms of one molecule and the nitrogen atoms of the other. This intermolecular hydrogen bond, which is indicated by the low frequency C=N band, would give these molecules a pseudopolymeric structure leading to ready precipitation when they are prepared in solution. In the case of 9, such an intermolecular hydrogen bonding is made impossible by the distance separating the neighbouring molecules owing to the bulky tert-butyl substituents. The interpretation of these findings is consistent with the properties previously reported for isomers of Schiff bases

[13]. This interpretation could not be proved, however, by attempts to isolate similar isomers of Schiff base **19** derived from terephtalaldehyde and o-aminophenol. It turned out that the condensation product exhibited a different type of photoisomerization and thermoisomerization [29]:

19a   19b   19c
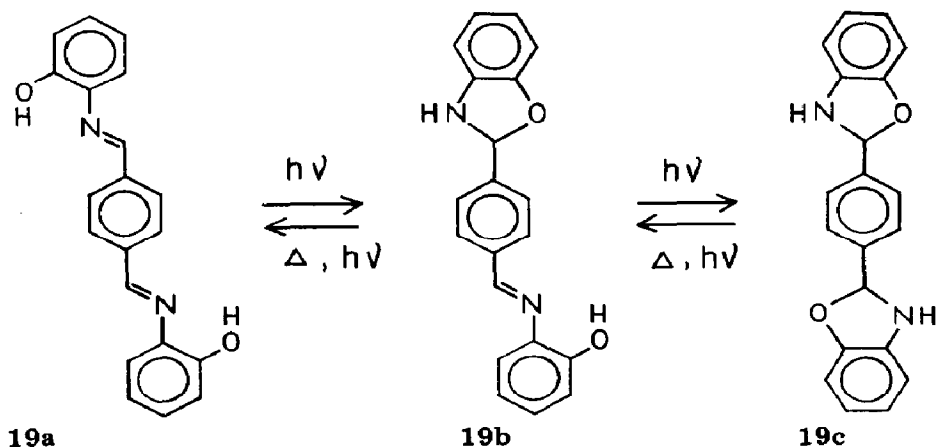
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