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ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Pressure Effects on the Radical–Radical Recombination Reaction of Photochromic Bridged Imidazole Dimers

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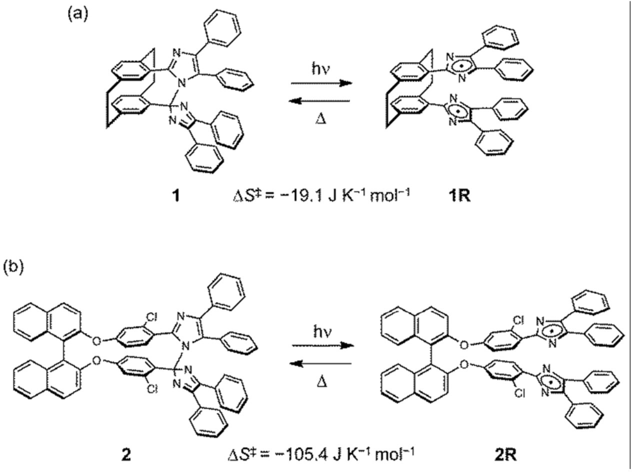
The bridged imidazole dimers are one of the attractive fast photochromic compounds which have potential applications to the ophthalmic lenses, real-time hologram and molecular machines. The strategy for expanding their photochromic properties such as the colour variation and tuning the decolouration rates have been vigorously investigated, but the insight about the structural changes along the photochromic reactions has not been demonstrated in detail. Here, we demonstrated the pressure dependence of the radical–radical recombination reaction of the bridged imidazole dimers. The radical–radical interaction can be controlled by applying high pressure. Our results give fundamental information about the molecular dynamics of the bridged imidazole dimers, leading to the development of new functional photochromic machines and pressure-sensitive photochromic materials.

Introduction

High pressure effects on chemical reactions are essential to understand the behaviour of biological functions and the origin of life in the deep sea. The interest has inspired many researchers and the pressure effects on the various chemical reactions and photochemical properties have been reported, such as cycloadditions,[1–5] *Z–E* isomerizations,[6–9] intermolecular interactions,[10–12] asymmetric photoreactions,[13,14] photochromic reactions[15–19] and so on.[20–22] Since the effects of pressure on chemical reaction rates are generally correlated to the difference in the partial molar volumes between the reactant and transition state, these studies have revealed that not only enthalpy but also entropy are important factor to control chemical reactions. Pressure can easily change the distance between molecules and viscosity of solvent which enable to control weak interactions such as supramolecular interactions. Moreover, the investigation of the pressure dependence of reaction rates provides the important information about the structural changes along the chemical reactions.

Scheme 1 Photochromic reactions of (a) **1** and (b) **2**.



Hexaarylbiimidazole (HABI) is the T-type photochromic compound in which two imidazole rings are connected by the C–N bond.[23] Upon UV light irradiation, the C–N bond cleaves to form the coloured imidazolyl radicals. However, the slow thermal back reaction caused by the intermolecular radical recombination reaction needs to be improved for the application to ophthalmic lenses. To overcome the requirements, we have designed and investigated the bridged imidazole dimers in which two imidazolyl radicals are tethered together by a linker. [2.2]Paracyclophane ([2.2]PC)-bridged imidazole dimer (**1**) is one of the attractive photochromic compounds which show a fast thermal back reaction (Scheme 1).[24] The thermal back reaction is attributed to the intramolecular recombination reaction between the photogenerated radicals (**1R**). The fast structural change accompanied by the photochromic reaction of the bridged imidazole dimer has a potential application in light-driven molecular machines,[25,26] but we have little quantitative information about the structural changes for them. The photochromism of the bridged imidazole dimers depends on the bridging moiety because it strongly effects on the distance between the imidazolyl radicals and stabilities of imidazole dimers.[27,28] 1,1'-Bi-2-naphthol (BINOL)-bridged imidazole dimer (**2**) also shows the fast radical–radical recombination reaction.[29] Although HABI have some structural isomers which show not only photochromism but also piezochromism,[30,31] 1 and 2 form only photochromic 1,2'-

isomer. The activation entropy ($\Delta S^{\ddagger}$) of the thermal recombination reaction of the biradical **2R**, $\Delta S^{\ddagger} = -105.4$ J K^{-1} mol^{-1} in benzene, is much smaller than that of **1R**, $\Delta S^{\ddagger} = -19.1$ J K^{-1} mol^{-1} in benzene. It suggests that both **1R** and **2R** go from the disordered biradical states to the ordered transition states during the thermal back reaction, but the structural change in going from the biradical state to the transition state of **2R** is larger than that of **1R**. Hence, the flexible bridging moiety would increase the degree of freedom of the biradical and increase the difference of the entropy between the biradical and transition states. In this study, we investigated the pressure effects on the thermal back reactions of **1R** and **2R** to understand the structure–entropy relationship.

Experimental Details

Sample preparation

Compound **1** was purchased from Kanto Chemical Co., Inc. and used without further purification. Compound **2** was synthesized according to a literature procedure.[29] These compounds were dissolved in spectroscopic grade toluene for all measurements.

Laser Flash Photolysis Measurement

The laser flash photolysis experiments were carried out with a TSP-1000 time resolved spectrophotometer (Unisoku). A 10 Hz Q-switched Nd:YAG (Continuum Minilite II) laser with the third harmonic at 355 nm (ca. 4 mJ per 5 ns pulse) was employed for the excitation light. The probe beam from a halogen lamp (OSRAM HLX64623) was guided with an optical fiber scope to be arranged in an orientation perpendicular to the exciting laser beam. The probe beam was monitored with a photomultiplier tube (Hamamatsu R2949) through a spectrometer (Unisoku MD200) for the decay profile of **1R** and **2R** and the transient absorption spectroscopy of **2R**, and monitored with a multi-channel spectrophotometer (Unisoku MSP-1000-V1) for the transient absorption spectroscopy of **1R**. The inner-cell type high pressure optical measurement cell (light pass length, 4 mm; Syn Corporation Ltd. PCI-500) and high pressure hand pump (Syn Corporation Ltd. HP-500) were used for all measurements.

Results and Discussion

Pressure Effects on the photochromism of 1

Fig. 1a shows the transient absorption spectra of **1** in toluene at the pressure range from 0.1 MPa (atmosphere) to 400 MPa. The sharp absorption band at 400 nm and the broad absorption bands in the visible light region were observed upon UV light irradiation. The absorption band around 750 nm attributable to the intramolecular radical–radical interaction is a characteristic band for **1R** in which two imidazolyl radicals are closely spaced due to the [2.2]PC bridging unit.[32] This absorption band provides the information about the degree of the radical–radical interaction. Although the relative intensities of the absorption bands in the visible light region slightly increase, almost no changes were observed by applying pressure. The thermal radical recombination reaction rates also show no pressure dependence (Fig. 1b). These results indicate that the [2.2]PC moiety strongly binds the two imidazole rings and the structural change during the thermal back reaction is small. The $\Delta S^{\ddagger}$ value for the thermal back reaction indicates the difference of the degree of freedom between the initial state and the transition state. The small $\Delta S^{\ddagger}$ value for the thermal back reaction of **1R** shows good agreement with those results.

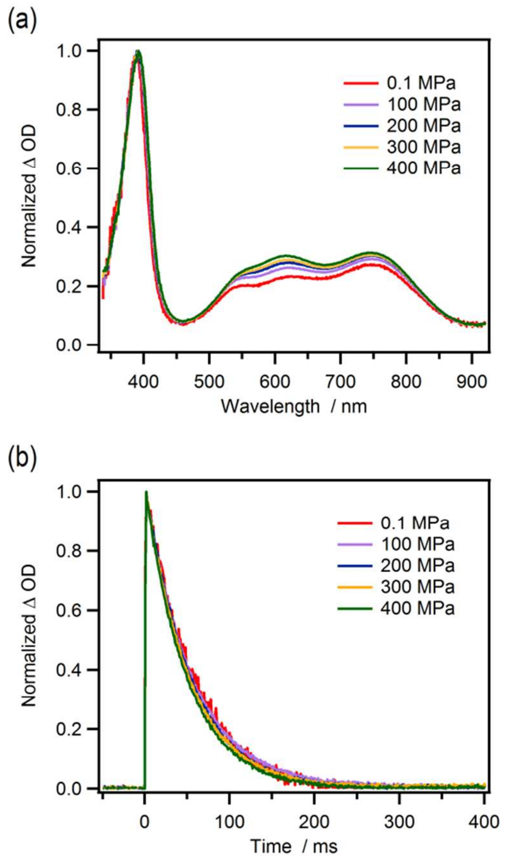


Fig. 1 (a) Transient absorption spectra at 2 ms after laser excitation of **1** in toluene at 298 K (6.7×10^{-5} M; 4 mm light path length; excitation wavelength, 355 nm; pulse width, 5 ns; power, 4 mJ/pulse). Each spectrum was recorded at 0.1, 100, 200, 300 and 400 MPa. (b) Decay profiles of the absorbance of the coloured species of **1**, monitored at 400 nm in toluene (6.7×10^{-5} M) at 298 K.

Pressure Effects on the photochromism of 2

Fig. 2 shows the transient absorption spectra of **2** in toluene at 0.1, 200 and 400 MPa. The absorption band at 800 nm of **2R** is small compared with that of **1R**. It indicates that the radical–radical interaction of **2R** is smaller than that of **1R** which is also expected from the TDDFT calculation in our previous report. The weak radial–radical interaction would be derived from the structural flexibility of the BINOL moiety which increases the distance between the imidazolyl radicals and reduces the overlap integral of the wave function between the imidazolyl radical moieties. **2R** shows weak absorption band around 800 nm at 0.1 MPa. The ΔOD value around 800 nm increases and the maximum wavelength of the absorption band blueshifts with increasing the pressure. High pressure induces the reduction in the distance between the photogenerated radicals because **2** has the structural flexibility derived from the BINOL moiety. Our previous report demonstrated the control of the radical–radical interaction by flipping the imidazole rings.[33] As the interaction becomes weak, the ΔOD and maximum wavelength of the absorption band decreases and shifts to the longer wavelength, respectively. Therefore, the spectral change around 800 nm of the transient absorption spectra of **2** can be described as the increase in the intramolecular radical–radical interaction, reflecting the restricted conformation of **2R** under high pressure.

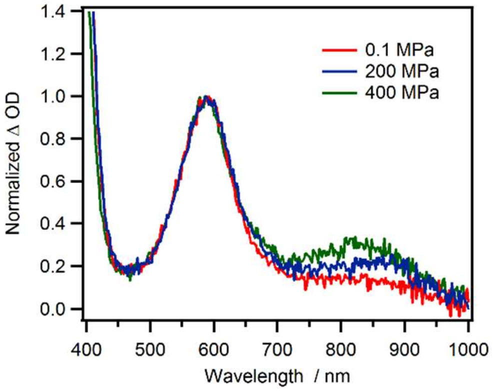


Fig. 2 Transient absorption spectra at 2 ms after laser excitation of **2** in toluene at 298 K (6.2×10^{-5} M; 4 mm light path length; excitation wavelength, 355 nm; pulse width, 5 ns; power, 4 mJ/pulse). Each spectrum was recorded at 0.1, 200 and 400 MPa.

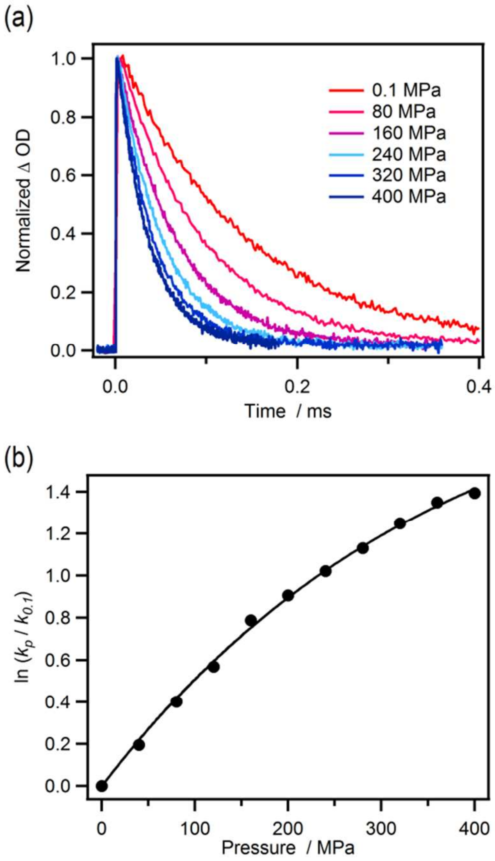


Fig. 3 (a) Decay profiles of the absorbance of the coloured species of **2**, monitored at 400 nm in toluene (6.2×10^{-5} M) at 298 K. (b) Pressure effects on the thermal back reaction rate of **2R** in toluene.

This result indicates that the radical–radical interaction can be controlled by applying pressure.

Since difference of the entropy between the initial biradical state and the transition state for the thermal back reaction of **2R** is large, the effects of pressure were observed clearly in the photochromism of **2**. The thermal radical recombination reaction rate of **2R** also depends on pressure in contrast to that of **1R**. Fig. 3a shows pressure dependence of the decay profiles of **2R** at 298 K, monitored at 400 nm. The radical recombination reaction is accelerated with increasing the pressure which suppresses the large conformational change during the thermal recombination expected from the large negative $\Delta S^{\ddagger}$ value. The activation volume $\Delta V^{\ddagger}$ brings out the effective information to elucidate the structural changes. The $\Delta V^{\ddagger}$ is given by eq. 1,

$$\Delta V^{\ddagger} = -RT\left(\frac{\partial \ln k_p}{\partial P}\right)_T \tag{1}$$

where k_p is the rate constant at pressure P. However, as integration of eq. 1 is not possible, some mathematical approximations have been described. In this study, we applied the eqs. 2 and 3 for the analysis of the pressure dependence of the thermal radical recombination reaction rates (Fig. 3b).[8]

$$\ln(k_p / k_{0.1}) = aP + b\ln(1 + cP) \tag{2}$$

$$\Delta V^{\ddagger} = -(a + bc)RT \tag{3}$$

As a result, the $\Delta V^{\ddagger}$ was estimated to be −14.4 $\mathrm{cm^3\ mol^{-1}}$ at 298.15 K. The reported $\Delta V^{\ddagger}$ values for the cyclization of naphthopyran and the *cis–trans* isomerization of azobenzene are from −3.7 to −8.6 $\mathrm{cm^3\ mol^{-1}}$ and −25.1 $\mathrm{cm^3\ mol^{-1}}$, respectively.[8,18] Thus, the photochromism of **2** accompanies the relatively large structural change between those of naphthopyran and azobenzene. We also investigated the pressure dependence of the activation enthalpy ($\Delta H^{\ddagger}$) and $\Delta S^{\ddagger}$ for the thermal recombination reaction. The activation parameters were estimated from Eyring analysis at 0.1, 200 and 400 MPa (Table 1, ESI†).

Table 1 Activation parameters for the thermal recombination reaction of **2R** in toluene

Pressure / MPa	$\Delta H^{\ddagger}$ / kJ $\mathrm{mol^{-1}}$	$\Delta S^{\ddagger}$ / J $\mathrm{K^{-1}\ mol^{-1}}$	$\Delta G^{\ddagger}$ / kJ $\mathrm{mol^{-1}}$
0.1	19.1	−107.8	51.3
200	22.3	−89.3	48.9
400	28.5	−64.4	47.7

The pressure dependence of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values show inverse tendency. The $\Delta S^{\ddagger}$ value increases and shifts to the direction which tends to reduce the activation free energy ($\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$) under high pressure. The $\Delta H^{\ddagger}$ value also increase by applying pressure but the increase of $\Delta H^{\ddagger}$ value leads to the increment of the $\Delta G^{\ddagger}$ because enthalpy and entropy complement each other, which is known as the enthalpy–entropy compensation.[14] The decrease of the absolute value of $\Delta S^{\ddagger}$ suggests the small structural change between the biradical and transition states due to the high viscosity of solvent under high pressure. This result is relative to the pressure dependence of the transient absorption spectra and thermal recombination rates. Thus, the $\Delta S^{\ddagger}$ estimated from Eyring analysis gives an efficient scale to predict the distance between the photogenerated radicals.

Conclusions

We investigated the pressure effects on the thermal radical recombination reaction of bridged imidazole dimers. The colour and thermal back reaction rate for the photochromism of a flexible bridged imidazole dimer changes in response to pressure. The geometry of **2R** is restricted under high pressure due to the flexibility of BINOL moiety although that of **1R** is affected by pressure because [2.2]PC moiety strongly connects imidazole rings. The $\Delta S^{\ddagger}$ shows good agreement with the structural flexibility of the bridging moiety and the degree of structural changes during the reaction. Therefore, we can predict the pressure dependence of the photochromic properties from the $\Delta S^{\ddagger}$ value. Moreover, we found that the radical–radical interaction can be controlled by applying high pressure. It offers the effectivity of pressure to investigate the weak intermolecular interactions. These results lead to the development of pressure-sensitive photochromic compounds and give fundamental information about the molecular dynamics of the bridged imidazole dimers, leading to the development of new functional photochromic compounds.

Acknowledgements

This work was supported partly by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency (JST) and a Grant-in-Aid for Scientific Research (A) (22245025) from Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Notes and references

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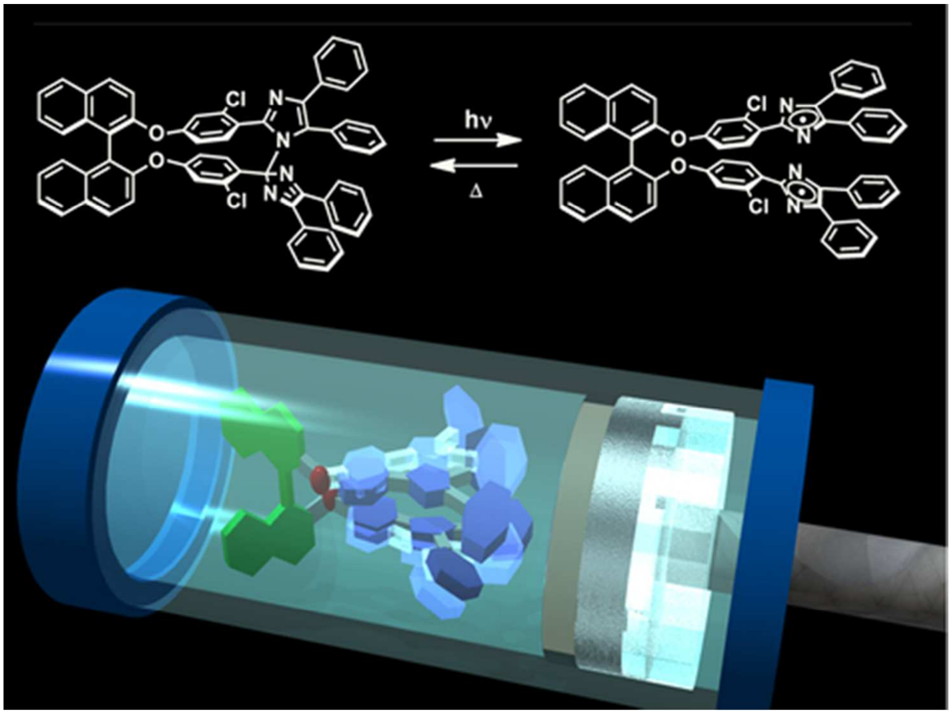
† Electronic Supplementary Information (ESI) available: UV–vis absorption spectra and Kinetics for the thermal back-reaction. See DOI: 10.1039/c000000x/

1 R. A. Grieger and C. A. Eckert, *J. Am. Chem. Soc.*, 1970, **92**, 2918.
2 R. A. Grieger and C. A. Eckert, *J. Am. Chem. Soc.*, 1970, **92**, 7149.
3 W. J. le Noble and B. A. Ojosipe, *J. Am. Chem. Soc.*, 1975, **97**, 5939.
4 W. Jarre, D. Bieniek and F. Korte, *Angew. Chem. Int. Ed. Engl.*, 1975, **14**, 181.
5 W. H. Pirkle, C. A. Eckert, W. V. Turner, B. A. Scott and L. H. McKendry, *J. Org. Chem.*, 1976, **41**, 2495.
6 T. Asano, *J. Am. Chem. Soc.*, 1980, **102**, 1205.
7 T. Asano, T. Yano and T. Okada, *J. Am. Chem. Soc.*, 1982, **104**, 4900.
8 T. Asano and T. Okada, *J. Phys. Chem.*, 1984, **88**, 238.
9 K. Hara, N. Ito and O. Kajimoto, *J. Phys. Chem. A*, 1997, **101**, 2240.
10 M. Okamoto, F. Tanaka and H. Teranishi, *J. Phys. Chem.*, 1986, **90**, 1055.
11 N. J. Turro, M. Okamoto and P.-L. Kuo, *J. Phys. Chem.*, 1987, **91**, 1819.
12 M. Rekharsky and Y. Inoue, *J. Am. Chem. Soc.*, 2000, **122**, 4418.
13 Y. Inoue, E. Matsushima and T. Wada, *J. Am. Chem. Soc.*, 1998, **120**, 10687.
14 Y. Inoue, H. Ikeda, M. Kaneda, T. Sumimura, S. R. L. Everitt and T. Wada, *J. Am. Chem. Soc.*, 2000, **122**, 406.
15 Y. Sueishi, M. Ohcho and N. Nishimura, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2608.
16 Y. Kimura, Y. Takebayashi and N. Hirota, *J. Phys. Chem.*, 1996, **100**, 11009.
17 Y. Goto, T. Takahashi, Y. Ohga, T. Asano, M. Hildebrand and N. Weinberg, *Phys. Chem. Chem. Phys.*, 2003, **5**, 1825.
18 Y. Goto, K. Sugita, T. Takahashi, Y. Ohga and T. Asano, *Chem. Lett.*, 2003, **32**, 618.
19 S. Tomotsune and T. Sekiya, *Eur. Phys. J. B*, 2013, **86**, 218.
20 T. Asano and W. J. le Noble, *Chem. Rev.*, 1978, **78**, 407.
21 R. van Eldik, T. Asano and W. J. le Noble, *Chem. Rev.*, 1989, **88**, 549.
22 A. Drljaca, C. D. Hubbard, R. van Eldik, T. Asano, M. V. Basilevsky and W. J. le Noble, *Chem. Rev.*, 1998, **98**, 2167.
23 T. Hayashi and K. Maeda, *Bull. Chem. Soc. Jpn.* 1960, **33**, 565.
24 Y. Kishimoto and J. Abe, *J. Am. Chem. Soc.*, 2009, **131**, 4227.
25 K. Kinbara and T. Aida, *Chem. Rev.*, 2005, **105**, 1377.
26 W. R. Browne and B. L. Feringa, *Nature Nanotech.*, 2006, **1**, 25.
27 S. Hatano, T. Horino, A. Tokita, T. Oshima and J. Abe, *J. Am. Chem. Soc.*, 2013, **135**, 3164.
28 T. Yamaguchi, S. Hatano and J. Abe, *J. Phys. Chem. A*, 2014, **118**, 134.
29 T. Iwasaki, T. Kato, Y. Kobayashi and J. Abe, *Chem. Commun.* 2014, **50**, 7481.
30 D. M. White and J. Sonnenberg, *J. Am. Chem. Soc.* 1966, **88**, 3825.
31 S. Delbaere, M. Olio, J. Berthet, M. Sliwa, S. Hatano and J. Abe, *Chem. Commun.* 2013, **49**, 5841.
32 K. Mutoh, E. Nakano and J. Abe, *J. Phys. Chem. A*, 2012, **116**, 6792.
33 K. Shima, K. Mutoh, Y. Kobayashi and J. Abe, *J. Am. Chem. Soc.*, 2014, **136**, 3796.



We revealed the structure–entropy relationship of the photochromism of bridged imidazole dimers and the radical–radical interaction could be controlled by applying high pressure.
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