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In-situ illumination with inelastic neutron scattering: A study of the photochromic material cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (CMTE)[†]Hamish Cavaye^{*a} and Maksim Schastny^a

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For the first time we successfully demonstrate *in-situ* illumination of a photochromic material during an inelastic neutron scattering (INS) experiment at cryogenic temperatures. cis-1,2-Dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (CMTE) is a well-studied and commercially available photochromic compound that undergoes a cyclisation reaction when exposed to light with a wavelength of around 400 nm. CMTE was therefore used as a proof of concept material to demonstrate the new sample environment used on the TOSCA indirect geometry spectrometer. When combined with simulated INS spectra from DFT calculations, the resulting difference spectra were interrogated to obtain insight into how the photoisomerisation affects the vibrational modes of the material. It was found that rigidification of the molecule after illumination, caused by the cyclisation of the central six-membered ring in CMTE, led to a blue-shifting in the methyl group torsion modes as well as methyl group scissor modes.

1 Introduction

Photoisomerisation is a form of isomerisation induced by photoexcitation.¹ This process is usually, but not always, reversible and compounds which undergo photoisomerisation are widely studied for use as molecular switches,^{2,3} molecular motors,⁴ or in molecular memory and electronics.^{5,6} Photochromic materials undergo a reversible photoisomerisation between two forms each having a different absorption spectrum, thus leading to a change in colour.⁷

One such photochromic material is cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (CMTE, Figure 1), first reported by Irie and Mohri in 1988.⁸ Upon UV or blue-light excitation the pale yellow open form of CMTE (oCMTE) undergoes a reversible photocyclisation reaction to the deep red closed isomer (cCMTE). Illumination at 405 nm leads to a photostationary state (PSS) with 60% of the sample being in the closed form, which is stable at elevated temperatures, remaining in the same ratio of oCMTE:cCMTE for at least 12 h in solution at 80°C. The stability is attributed to the low aromatic stabilization energy of the thiophene rings.^{9,10}

Since its first report in the literature, CMTE has been well studied by a number of groups. It has been used to successfully form optical patterns,¹¹ to reversibly affect photoconduction and pho-

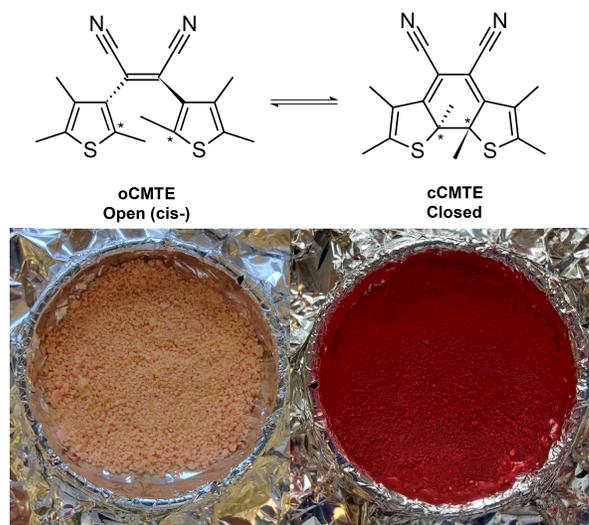


Fig. 1 Top - the photoisomerisation reaction of cis-CMTE. Bottom - photographs of CMTE before (left) and after (right) undergoing photoisomerisation.

toluminescence in conducting polymers,¹² in photomemory applications,^{13,14} in doped polymer films,¹⁵⁻¹⁷ and as anisotropic nanoparticles.^{18,19}

One vital aspect for characterisation of photoisomeric materials such as CMTE is the study of their vibrational properties, which have been linked to the mechanism for the isomerisations they undergo.⁸ The obvious techniques for this include both infrared

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and Raman spectroscopies as ubiquitous methods for studying vibrational spectra. CMTE was used in a case study to examine the link between UV-visible and IR absorption spectra.²⁰ However, inelastic neutron scattering (INS) offers an important route to highly complementary vibrational information, particularly for hydrogen-containing materials.^{21–23} Unfortunately, the vast majority of vibrational spectroscopy using INS requires cryogenic temperatures. With this comes a challenge for performing *in-situ* illumination of photoswitching materials and *ex-situ* photoisomerisation is required, which can lead to difficulty with mass-normalisation of the resulting spectra and uncertainty that the material being studied has indeed simply undergone photoisomerisation and not some other process. This study introduces a new capability for performing illumination simultaneously with INS, opening up the technique to use with this important class of compounds.

2 Experimental Methods

2.1 Materials

Cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (CMTE) was purchased from Tokyo Chemical Industry (TCI) Co. Ltd. (Oxfordshire, UK) and used as received. The pale yellow powder was handled in low light conditions when not under illumination to reduce unintentional photoisomerisation. For samples illuminated *ex-situ* (see below), the CMTE was scattered in a petri dish before illuminating for a number of hours using an LED (385 nm), with periodic grinding and mixing to ensure a maximum level of light penetration. These samples were seen to undergo a stark colour change from pale yellow to deep red after photoisomerisation (Figure 1).

2.2 FTIR Spectroscopy

Attenuated total reflection (ATR) FTIR spectra were recorded on a Bruker Vertex 70 Fourier transform infrared spectrometer using a Bruker Diamond attenuated total internal reflection accessory at room temperature. All measurements were performed on the sample in the solid state. Each spectrum was an average of 64 scans with a resolution of 2 cm^{-1} and recorded in the range of $50\text{--}4000\text{ cm}^{-1}$.

2.3 Inelastic neutron scattering

INS spectra were recorded on the indirect geometry spectrometer TOSCA at the ISIS Neutron and Muon Source (Chilton, Oxfordshire, UK).^{24,25} The resolution is approximately 1.25% of the energy transfer, affording sufficient resolution in the energy range of interest, $0\text{--}2000\text{ cm}^{-1}$. Before measurement, *ex-situ* illuminated samples were placed in standard TOSCA aluminium sample holders and sealed with indium wire. Samples for *in-situ* illumination were placed in the sample environment detailed below. All samples were cooled to below 60 K using a closed-cycle refrigerator (CCR) before data were collected.

2.4 Photoisomerisation and sample environment

The *ex-situ* illumination of CMTE was undertaken using a LUX-EON FlipChip 1 PowerStar UV LED connected to a custom built mains power supply. This LED had a peak emission wavelength of 385 nm and an emission divergence of 180° .

A new capability to enable illumination of the sample *in-situ*, inside a CCR vacuum bin, during an inelastic neutron scattering experiment was designed and built. The sample environment comprised two main parts; a transparent sample holder, and an LED light source. A photo can be seen in figure 4.

The transparent sample holder consisted of three off-the-shelf quartz cuvettes held in a custom-built aluminium frame, which could be attached to the end of a standard TOSCA CCR stick. The cuvettes used in this study were Suprasil quartz, spectral range $200\text{--}2500\text{ nm}$, pathlength 1 mm , chamber volume $350\text{ }\mu\text{L}$ from Hellma. The dimensions of these three cuvettes side-by-side allowed the full $40\text{ x }40\text{ mm}$ neutron beam spot to be utilised, could contain approximately 0.5 g of powdered CMTE sample, and afforded a large surface area available for illumination.

The *in-situ* LED light source consisted of two SZN05A0B LEDs from Seoul Semiconductor mounted to a bracket, 3-D printed from acrylonitrile styrene acrylate (figure S1). Each LED had a peak emission wavelength of 405 nm at room temperature and an emission divergence of 120° . The bracket was angled to allow maximum illumination of the sample without impinging on the incident or scattered neutron pathways and one LED was placed on each side of the sample to allow illumination of both sides. The LEDs were connected through wiring in the CCR stick to a Keithley 2401 Source Meter power supply external to the TOSCA instrument and were driven at approximately 9 V with a current limit of 700 mA (figure S2). Due to working outside of the standard operational temperature limits, offline tests examined any possible changes in the LED emission wavelength at low temperature by recording the LED spectrum at room temperature and at 77 K in liquid nitrogen (figure S3). Only a small shift of wavelength from 406 nm to 404 nm was observed at low temperature, which remained suitable for the desired photoisomerisation reaction.²⁰

2.5 Theoretical spectra calculations

Simulated FTIR and INS spectra for both the cis- and trans- open forms of CMTE as well as the photoisomerised closed form were calculated. Biovia Materials Studio (2017 R2) was used with corresponding literature crystal structures²⁶ to generate input files for the calculations. Periodic density functional theory (DFT) calculations were performed using the CASTEP code (version 17.21) on the SCARF supercomputing cluster.^{27–33} Initially a geometry optimisation was completed, followed by a Γ -point phonon and optical frequency dielectric field task (PHONON+EFIELD). Calculations used a Perdew-Burke-Ernzerhof (PBE) functional with optimised norm-conserving pseudopotentials with a plane-wave cut-off energy of 990 eV.

The resulting CASTEP outputs were visualised with Materials Studio to generate theoretical FTIR spectra and to aid in assignment of the modes. Except where specified in the text, theoretic-

cal INS spectra were then produced using the AbINS³⁴ code for Mantid^{35,36} using "QuantumOrderEvents"=2 and were rebinned to match the resolution of the experimental data from TOSCA.

3 Results and Discussion

In this study samples of CMTE were subjected to photoisomerisation both *ex-situ* and *in-situ*. Initial tests were performed using FTIR spectroscopy to ensure that changes were occurring before INS was employed to test the novel sample environment hardware.

3.1 FTIR spectroscopy

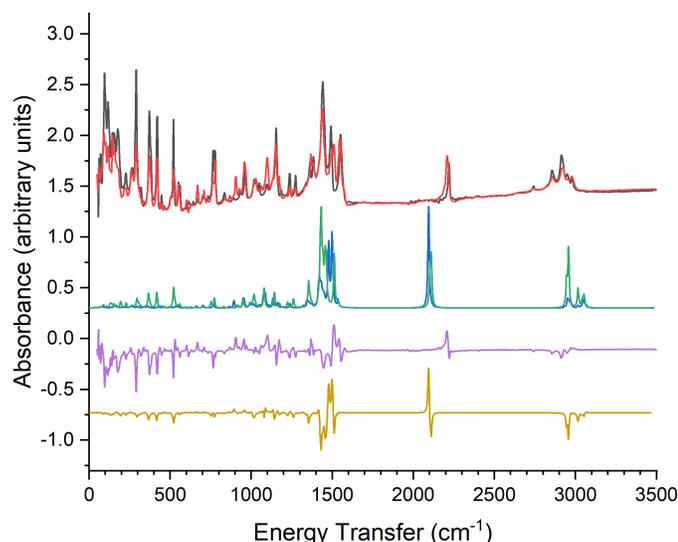


Fig. 2 Experimental ATR-FTIR spectra of fresh (black) and *ex-situ* illuminated (red) CMTE and the calculated FTIR spectra for oCMTE (green) and cCMTE (blue). Also shown are the experimental (purple) and calculated (orange) difference spectra. Spectra are normalised and offset on the y-axis for clarity.

Figure 2 shows the FTIR spectrum of the pale yellow CMTE sample as received from the supplier (black line). This is expected to be the open, *cis*-form of the material, henceforth referred to as oCMTE. Obvious features of the spectrum include the expected nitrile stretch at 2200 cm^{-1} and C-H stretches in the region of $2850\text{--}3050\text{ cm}^{-1}$. Despite the technical difficulties in accurately simulating IR spectra, the comparison of the experimental spectrum (black line) and the simulated spectrum for oCMTE (green line) show good agreement.

Also shown in figure 2 is the experimental spectrum of the *ex-situ* illuminated CMTE sample (red line), which had become a deep red in colour indicating photoisomerisation had occurred. Comparing this spectrum with either the fresh CMTE spectrum or the simulated spectrum of the closed form of CMTE (blue line), large changes are not seen and so it can be asserted that only the very superficial layers of the sample effectively underwent photoisomerisation. This is not unexpected because the UV light used to isomerise the sample is not likely to penetrate very deeply into the solid particles, thus a significant portion of the CMTE is left in the open form.

A more informative result comes when we examine the difference spectrum of the fresh and illuminated CMTE spectra. This difference spectrum is also shown in figure 2 (purple line). We can compare this difference spectrum with the simulated difference spectrum shown in orange. There is significant agreement between the experimental and theoretical difference spectra, affording confidence that the simulations are accurate and we are indeed able to observe the photoisomerisation occurring by FTIR.

Some obvious points of difference can be observed. Firstly, at the highest energies, the intensity of all the C-H stretches are somewhat reduced after illumination. Secondly, the nitrile stretch peak is red-shifted by approximately 15 cm^{-1} , and the intensity of the peak appears enhanced after illumination. Interrogation of the simulation suggests it is the symmetric nitrile stretches that have primarily been enhanced more so than the antisymmetric. The last major observation is that the energy of the methyl deformation modes around $1400\text{--}1550\text{ cm}^{-1}$ look to have been blue-shifted slightly, which may not be surprising with the rigidification of the whole molecule.

These *ex-situ* results afforded confidence that the fresh sample as received was indeed in the open *cis*-form and that illumination was promoting at least partial photoisomerisation to occur.

3.2 Inelastic neutron scattering

Vibrational spectroscopy using INS is directly analogous to that which is measured using photons, such as IR and Raman spectroscopies. A neutron with energy E_i collides with the sample, transferring some of its energy to excite vibrational modes before being scattered with an energy E_f . The transferred energy $E_i - E_f$ is equal to the energy of the excited mode and thus a spectrum can be recorded. Unlike photon-based techniques, optical selection rules do not apply to INS and so it is sensitive to all vibrational modes. However, the intensities of the modes in an INS spectrum are directly proportional to the neutron scattering powers of the nuclei involved in that mode. Due to the very high scattering power of ^1H (approximately 82 barn), which is approximately two orders of magnitude larger than that of any other nucleus, INS spectra of organic materials are usually dominated by signal arising from modes involving hydrogen.

Firstly we examine the INS spectrum of an unilluminated, pale yellow sample of CMTE and compare it with the simulated spectrum calculated for the *cis*-form of oCMTE, both shown in figure 3 between $0\text{--}2000\text{ cm}^{-1}$. There is very good correlation between the measured and calculated spectra across most of the plotted energy range, particularly between $100\text{--}1500\text{ cm}^{-1}$. Below 100 cm^{-1} the simulated spectrum shows a number of modes that are not present in the experimental data. The modes at these low energies are primarily phonon modes caused by collective motion of the molecules in a crystal. The absence of these peaks in the measured spectrum has two main possible explanations. Firstly, it may suggest that the CMTE used in this study is actually quite amorphous and not microcrystalline. Secondly, the simulated spectrum was generated from the output of a gamma-point only calculation. It is likely that these lower energy modes could therefore have some unmodelled dispersion, which is not included in

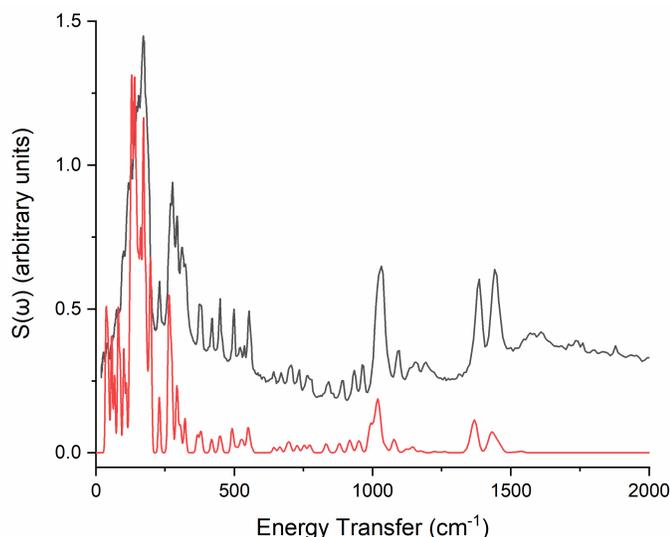


Fig. 3 Experimental INS spectrum of the un-illuminated CMTE sample (black) and the simulated INS spectrum of oCMTE (red). This theoretical spectrum has had combination and overtone modes omitted, i.e. fundamental modes only, and both spectra are normalised and offset on the y-axis for clarity.

the simulated spectrum displayed here. The other main difference between the spectra can be seen above 1500 cm^{-1} where intensity present in the experimental spectrum is missing from the simulated one. These modes correspond to various vibrational combinations and first overtones. In order to avoid complication caused by combinations of the low energy phonon modes the simulated spectrum in figure 3 only includes fundamental modes and thus we do not expect to see these higher energy peaks.

A spectrum was also calculated for the trans- form of oCMTE (figure S4) but it did not have the same level of agreement with the experimental spectrum, thus we can again be confident that the unilluminated CMTE sample is indeed in the cis- form.

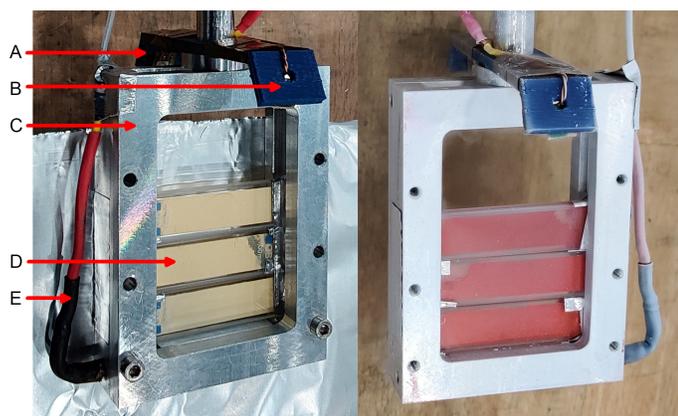


Fig. 4 Photograph of the CMTE sample environment with CMTE before (left) and after (right) *in-situ* illumination during the INS experiment on TOSCA. A) 3-D printed LED mounting bracket, B) LED attachment point, C) aluminium cuvette holder frame, D) quartz cuvettes containing the powdered sample, E) thermocouple for sample temperature logging. Slight discolouration and misting of the right-hand image is caused by a thin layer of ice forming after the sample was removed from the CCR.

Having confirmed the morphology and form of the CMTE sample as received, we moved on to testing the novel *in-situ* illumination capability. Figure 4 shows the CMTE sample and sample environment before and after the INS measurement with illumination. The photochromic effect is very obvious to see, with the fresh CMTE showing the typical pale yellow colour, which changes to a deep red after illumination.

Figure 5 shows the INS data from the measurements with this new sample environment. The black and blue lines show the spectra of the CMTE before and after illumination respectively. While there are some clear changes, the sample has only undergone partial photoisomerisation. As with the FTIR experiment, above, this is perhaps not unexpected; the wavelength of incident light (405 nm) was chosen because the closed form has a lower absorption coefficient than the open form at this wavelength, however it is still non-zero and so the incident light can only penetrate so far into the solid sample and thus only the surface layers of the sample are illuminated. Additionally, the INS data were recorded as a series of short duration (approximately 1 h) runs. It was noted that within the uncertainty of the statistics from such short data collection times the photoisomerisation appeared to be complete within the first 1 h of illumination. As such the data presented represents the PSS achieved within the limitations of the penetration depth of the incident light. With this in mind it becomes informative to interrogate the difference spectrum again, which is plotted in orange.

Without a fully photoisomerised sample to compare with, the simulated spectrum of pure cCMTE is uninformative, however a simulated difference spectrum could also be obtained by simple subtraction of the simulated spectrum of oCMTE from that of cCMTE. This simulated difference spectrum is plotted in figure 5 in purple. Despite the relatively high level of noise in the measured data, the correlation between the experimental and calculated difference spectra is very good. We can therefore be confident that the sample has indeed undergone the expected photoisomerisation reaction and that our simulated INS spectrum for cCMTE is also accurate.

Having successfully performed *in-situ* illumination during the INS experiment, one can subsequently interrogate the difference spectrum to identify which vibrational modes are affected by the photo-reaction in a similar manner to that done with FTIR, above. After illumination, a significant decrease in intensity of the modes between $160\text{-}180\text{ cm}^{-1}$ can be seen, as well as an increase in intensity of the modes between $190\text{-}270\text{ cm}^{-1}$ and around 315 cm^{-1} . These changes can be explained by a blue-shifting of the methyl torsional modes, particularly for those methyl groups marked with an asterisk in figure 1, i.e. those closest to the newly formed bond, as well as methyl group scissoring of the other two methyl groups on each 5-membered ring. These observations are consistent with the formation of the bridging C-C bond and subsequent rigidification of the molecule, which affects the energies of these modes.

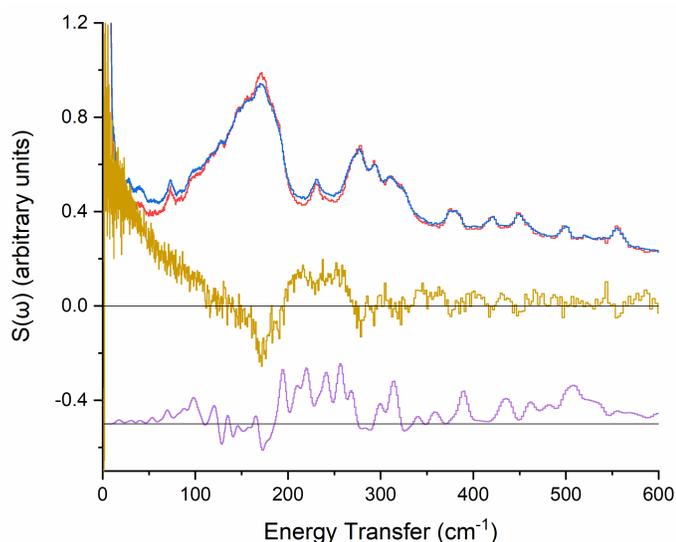


Fig. 5 INS spectra of CMTE before (red) and after (blue) illumination *in-situ*. The difference spectrum of the two (orange) is shown and compared with the calculated difference spectrum expected for oCMTE and cCMTE (purple). The difference spectra have been rescaled and offset on the y-axis for clarity.

3.3 Limitations of the technique

While potentially very useful for studying photoisomeric systems by INS, it is important to note the limitations of this new *in-situ* illumination technique and where future improvements may be focused.

Firstly, when compared to IR and Raman spectroscopies, a significantly longer data collection time is required for INS, that is a number of hours vs a few minutes. This issue is somewhat exacerbated by the use of a difference spectrum, which involves the subtraction of one dataset from another, thus compounding uncertainty in the data. For TOSCA, the uncertainty of the signal increases with increasing energy transfer, and so interrogation of higher energy modes would require longer experiments to improve signal to noise as much as possible. In the future, instrument and neutron target upgrades will lead to shorter measurement times and improved statistics.

Additionally, INS experiments commonly require large sample sizes and a balance must be struck between having sufficient sample for a strong signal, but with as much of the sample available for illumination as possible, therefore maximising the difference between the fresh and illuminated sample spectra.

Lastly, INS experiments of organic materials such as CMTE are almost always performed at cryogenic temperatures in order to reduce the effect of the Debye-Waller factor.²¹ This typically equates to sample temperatures below 20 K. However, the use of powerful LEDs to illuminate the sample within the CCR during the INS measurement meant the lowest achievable temperature was limited to approximately 50 K. This issue could be mitigated with the use of more powerful cooling hardware or by improvements to further thermally isolate the LEDs from the sample itself.

4 Conclusions

We have, for the first time, demonstrated the successful measurement of an INS vibrational spectrum with *in-situ* illumination. The commercially available photochromic material CMTE was used in this proof of concept study and changes in the vibrational spectrum of the molecule were clearly observed. Use of simulated difference spectra confirmed the expected photoisomerisation had occurred and allowed the identification of energy shifts for various vibrational modes upon illumination.

Previously, study of photoisomeric materials by INS would have required *ex-situ* illumination methods, which are generally expected to take longer and require more careful data analysis, particularly in terms of normalisation to sample mass. This new sample environment adds a valuable tool to the arsenal of those studying materials that undergo photochemical changes.

Author Contributions

HC was responsible for the initial design of the experiment and sample environment, sample preparation, recording the FTIR and INS spectra, performing the theoretical calculations, and the analysis of the data. MS was responsible for the prototyping, construction, and testing of the illumination hardware.

Conflicts of interest

There are no conflicts to declare.

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