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Comparative Study on Properties, Structural Changes, and Isomerization of Cis/Trans-Stilbene under High Pressure

Jun Han, Qunfei Zheng, Cheng Jin, Shanmin Wang, Ying Liu,* Yusheng Zhao, and Jinlong Zhu*

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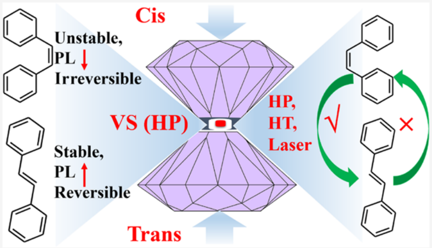

ABSTRACT: The comparison of different stereoisomeric organic compounds under high pressure has been less investigated. Here, we chose different stereochemical configurations of cis/trans-stilbene to study the luminescence properties, polymerization reaction, and structural changes at 0−20 GPa by spectroscopy and XRD. No fluorescence enhancement occurred in cis-stilbene due to $\pi-\pi$ stacking. At 16 GPa, the IR, UV−vis, and sample color changes show that it undergoes an irreversible polymerization, that $C(sp^2)-H$ changes to $C(sp^2 + sp^3)-H$. However, trans-stilbene undergoes fluorescence enhancement at 0−4 GPa due to the reduction of the torsion angle of the benzene ring and the C═C bond leading to the formation of rigid planar molecules, which is further confirmed by the IR and XRD results. At 8 GPa, the new peaks in UV−vis and XRD results show the formation of new substances by structural change. However, the structure of trans-stilbene is more stable, which leads to the return to the raw state after releasing the pressure, and a reversible transformation occurs at high pressure. The cis-trans isomerization under high pressure was also briefly investigated by combining heating and laser irradiation. The cis → trans-stilbene transition can only happen under a fixed-range light irradiation, and the trans → cis-stilbene transition could not happen even under irradiation with a 360 nm laser, which may provide a new idea for synthesizing trans isomers with a higher purity.

■ INTRODUCTION

Cis-trans isomerism is an important stereoisomerism in organic chemistry, which is very important to determine the specific structure of organic compounds.[1−7] Cis-trans isomerism generally occurs when atoms or functional groups cannot rotate freely due to the restriction of rotation in compound molecules, such as C═C, C═N, C═S, N═N, or benzene rings. These functional groups contain symmetric π bonds; as a result, the molecule cannot freely rotate and forms a cis-trans isomerism.[7,8] Cis-trans isomerism compounds often show different properties in physical, chemical, and biological aspects due to their different structures, such as melting point, solubility, and dipole distance.[1−7,9−12] For example, the melting point of maleic acid is ∼130 °C, while that of fumaric acid is ∼287 °C.[11] Again, for instance, the natural unsaturated fatty acids intrinsically are of cis-type, mainly found in vegetable oils, and are not harmful to human consumption. Since trans-fatty acids are obtained through the hydrogenation of cis-fatty acids in the industrialization process, excessive intake of artificial trans-fatty acids can increase the risk of cardiovascular disease.[12]

For such simple organic compounds based on functional groups containing symmetric π bonds, direct illumination can induce cis-trans isomerization, resulting in various optical response phenomena. Cis → trans conversion can be usually driven by light or heat, while trans → cis conversion is driven only by optical excitation.[13−18] Pressure, an important thermodynamic parameter for regulating the properties of materials, can effectively change the atomic spacing. This leads to a continuous and controlled adjustment of the band gap, which can change its luminescence properties and synthesize new materials with controllable properties. Due to the enhanced pressure-induced molecular $\pi-\pi$ stacking interaction, the fluorescence intensity of most organic molecules decreases.[19−23] Currently, only a few organic molecules show fluorescence enhancement under high pressure, which is mainly attributed to phase transitions, restricted molecular vibration, or weakened $\pi-\pi$ stacking. Examples include hydrogen-bond formation, increased viscosity, increased steric hindrance, and increased conjugation regions.[24−27] In short, high-pressure techniques provide an effective way to enrich the family of luminescent materials by enhancing luminescent properties and guiding the design of new functional luminescent materials. It is important to investigate the different properties of cis-trans isomeric compounds under high pressure and the possible cis-trans isomerization achieved by compression or with the assistance of light or heat.

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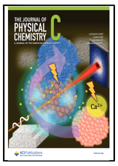

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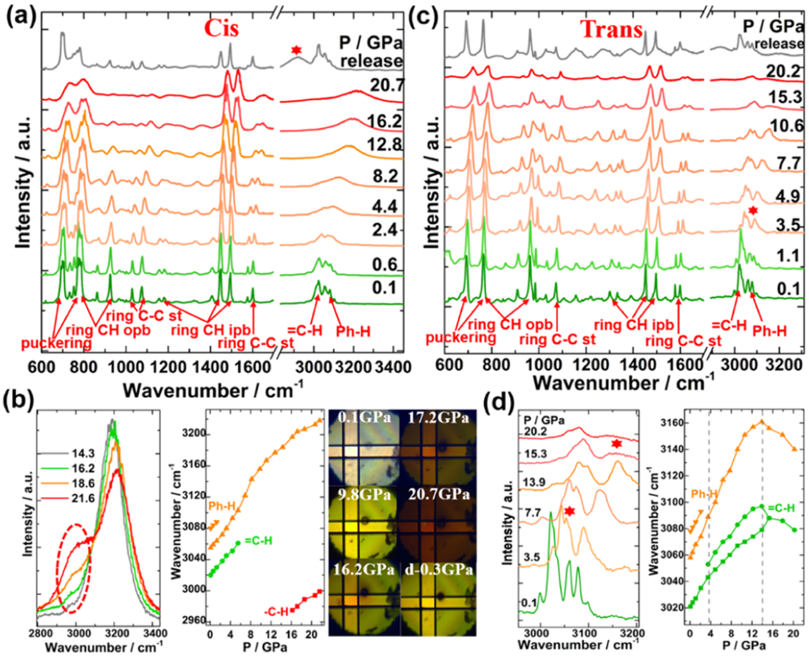

Figure 1. (a) Selected IR spectra of cis-stilbene under high pressure, (b) C−H stretching peak of cis-stilbene changes with pressure higher than 12.8 GPa (left panel), the peak position of the ═C−H stretching vibration changes at 0−20.7 GPa (middle), and there is a color change in the sample (right panel). (c) Selected IR spectra of trans-stilbene. (d) Details of the═C−H stretching peak and the peak position of trans-stilbene as a function of pressure.

In this work, stilbene formed by connecting a benzene ring on both sides of C═C is taken as the research object. The properties and structures of cis-trans-stilbene were studied by Raman spectroscopy, infrared (IR) spectroscopy, fluorescence spectroscopy, ultraviolet−visible (UV−vis) absorption spectroscopy, and X-ray diffraction (XRD). It is found that there are obvious differences and partial similarities in their performance under high pressure, and the conditions of cis-trans transformation under high pressure are preliminarily explored.

■ EXPERIMENTAL METHODS

Cis-stilbene (98%) was bought from the Shanghai Aladdin biochemical technology company, and trans-stilbene (97%) was bought from Alfa Aesar. The symmetric diamond Anvil Cell equipped with a pair of type-IIa diamond anvils with a culet size of 300 or 500 μm was used to generate high pressure. A T-301 stainless steel gasket was prepressed to a thickness of about 35−45 μm before a sample hole with a diameter of ~180 or 320 μm (for a culet size of 500 μm) was drilled in the center of the sample chamber. Finally, ruby balls were used to calibrate the pressure in all experiments.[28]

In situ IR spectra were collected on a Bruker VERTEX 70v system equipped with a HYPERION 2000 microscope and collected in the transmission mode using Globar as a conventional light source with a pressure transmission medium (PTM) of KBr in the range of 600−4000 cm^{-1}. *In situ* fluorescence spectra were collected using a 325 nm laser without PTM by a Renishaw micro-Raman spectroscopy system. *In situ* UV−vis spectra were collected in the wavelength range of 350−1000 nm using silicone oil as the PTM by an Andor spectroscopic system. An *in situ* high-pressure XRD experiment was performed at BL10XU undulator beamline at Japan's synchrotron radiation facility SPring-8. The wavelength of the incident X-ray beam was 0.413 Å, and argon gas was used as the PTM. Dioptas software was used to reduce the preliminary data.[29] All of the above decompression experiments were measured after 24 h. For the cis/trans-stilbene conversion, the Raman spectra were collected with laser wavelengths of 360 and 532 nm without a PTM. The Raman spectra were recorded with a back-scattering configuration, and a 1200 groove/mm grating was used. For the heating part, the whole cell was heated on a constant-temperature heating table, the thermocouple was placed on the seat of the anvil, and the temperature was maintained for more than 1 h each time.

■ RESULTS AND DISCUSSION

The vibration and rotation of different bonds of cis/trans-stilbene under high pressure were studied by *in situ* infrared spectra, as shown in Figure 1a−d. At 0.1 GPa, the spectral peaks of cis/trans-stilbene are very close. A blue shift occurs with the increase in pressure, indicating that vibration is strengthened under high pressure in both systems. For the whole spectrum, we found that the main changes in the sample came from the stretching vibrations of the C−H bond. Therefore, the ═C−H stretching vibration peaks of cis-stilbene and trans-stilbene at around 3100 cm^{-1} were enlarged and are plotted in Figure 1b,d, respectively.

For the cis-stilbene system (Figure 1a), after 2.4 GPa, some of the C−H vibrations on the benzene ring disappeared, mainly due to the solidification of the sample. At 16.2 GPa, some cis-stilbene samples' color changed from bright yellow to light red, representing the formation of a new substance. Simultaneously, the spectrum showed the C(sp^3)−H vibration emerges at ~2980 cm^{-1}, which responds to the color change of the samples. At 20.7 GPa, most of the samples changed to reddish-brown, and the C(sp^3)−H vibration peak was more obvious (Figure 1b). After releasing to ambient pressure, it can be seen that most of the vibration peaks reappear and the

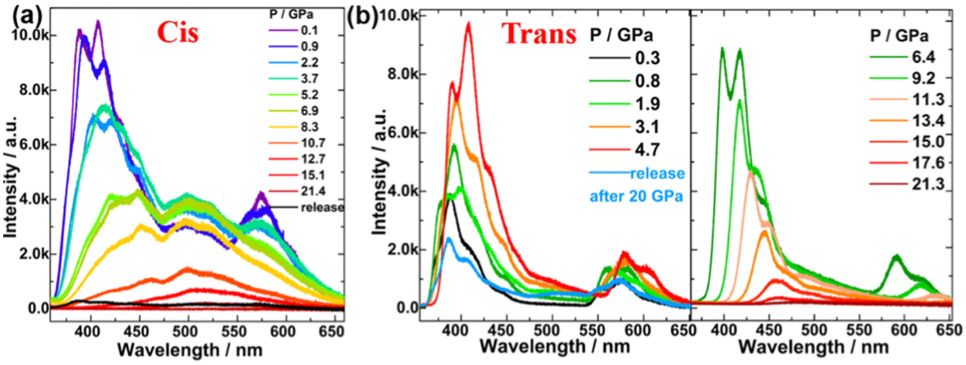

Figure 2. Selected fluorescence spectra of (a) cis-stilbene and (b) trans-stilbene under different pressures.

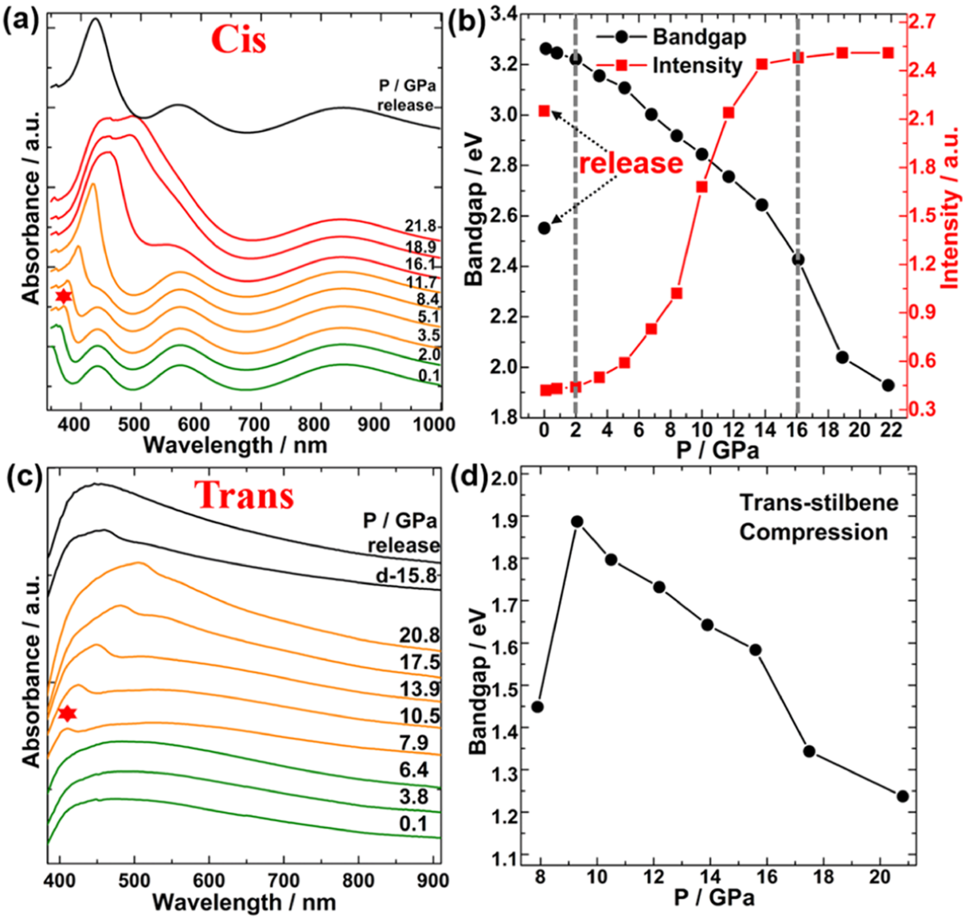

Figure 3. (a) Selected *in situ* UV−vis patterns of cis-stilbene under high pressure. (b) Variation of band gap and peak intensity of cis-stilbene with pressure, and these two isolated points at ambient pressure represent the band-gap value and the intensity value released to ambient pressure. (c) Selected *in situ* UV−vis patterns of trans-stilbene under high pressure. (d) Band gap of trans-stilbene under high pressure.

samples mostly returned to their original bright-yellow color. However, a very clear C(sp^3)−H vibration peak was preserved at ~2920 cm^{-1}, indicating that the C−H stretching from sp^2 transformed to sp^2 + sp^3. This means that the cis-stilbene undergoes an irreversible polymerization under high pressure.

The changes in trans-stilbene under high pressure have a certain similarity to those of cis-stilbene (Figure 1c). At 3.5 GPa, the =C−H vibrational peak split into two peaks, while the two Ph−H vibrational peaks merged into one peak, indicating that the benzene ring and the C=C bond changed simultaneously. It is presumed that trans-stilbene coplanarizes with the benzene ring and the C=C bond under high pressure, leading to the simultaneous polymerization. At 13.9 GPa, the intensity of the Ph−H vibration peak becomes weak and broadens, indicating that the sample gradually becomes amorphous. The trend of the peak position shift is the same as that of the =C−H vibration, both of which turned from a blue shift to a red shift (Figure 1d), suggesting that the benzene ring was easily disrupted in the molecule after pressure. After release, the majority of the spectral peaks reappeared, indicating that trans-stilbene undergoes a reversible transition and is more stable than cis-stilbene under high pressure.

This difference is related to the stability of the two structures themselves. The two benzene rings of cis-stilbene are on one side of the C═C bond, and the electron cloud density on the benzene ring is too large, and the resistance effect will lead to the formation of an angle between the two benzene ring planes, which is easy to transform into trans-stilbene under the action of external forces. For the trans-stilbene, two benzene rings are on both sides of the C═C bond, the electron cloud density of trans-stilbene is more evenly distributed, and it can be stable in a large plane. Therefore, trans-stilbene is more stable than cis-stilbene and is more resistant to polymerize.

To compare the different luminescence properties of cis-stilbenes and trans-stilbenes under high pressure, *in situ* fluorescence spectroscopy was performed, as shown in Figure 2a (cis-stilbene) and 2b (trans-stilbene). At ambient pressure, there are two main peaks for both samples, which are the $\pi^* \rightarrow \pi$ vibration transition in the stilbene molecule. The two peaks are very close, indicating that the benzene ring is strongly conjugated with the C═C bond. From 0 to 21 GPa, the peak position of cis/trans-stilbene is always red-shifted, which means that the long distance between intermolecular and intramolecular bonds of the sample under high pressure becomes shorter and the band gap decreases, resulting in the red shift of the spectrum peaks. The left peak of cis-stilbene moves roughly from 388 to 527 nm from ambient to 15.1 GPa and that of trans-stilbene moves from 388 to 458 nm. This suggests that trans-stilbene is more stable, while cis-stilbene is more easily regulated under high pressure, consistent with the infrared spectra results. In the pressure range of 0−15 GPa, the peak intensity of cis-stilbene gradually decreases, indicating that the $\pi-\pi$ stacking interaction in the stilbene molecule is enhanced under high pressure, leading to the enhancement of nonradiative transition, and thus, the fluorescence is weakened. The fluorescence peak intensity of trans-stilbene increases at 0−4.7 GPa and decreases at 4.7−15.1 GPa, whereas the fluorescence intensity did not change much at 0−1 GPa. According to the theoretical simulation of trans-stilbene under high pressure by Zou et al.,[30] the torsion angle change of the benzene ring and the C═C bond resulted in the change in fluorescence intensity. At 0−1 GPa, the torsion angle did not change much, which corresponds to little change in the fluorescence intensity. At 1−4 GPa, the torsion angle decreased all of the time corresponding to the increase in fluorescence intensity. The decrease in torsion angle tends to form rigid planar molecules, which would enhance the fluorescence intensity. At 15−20 GPa, the fluorescence peak intensity of cis/trans-stilbene is almost invisible, mainly from the gradual amorphization and $\pi-\pi$ stacking interaction of samples under high pressure. This pressure point is close to the pressure of 16 GPa, where the new C(sp^3)−H peak emerges and the color changes in the IR spectra results, confirming that the sample begins to undergo a process of simultaneous amorphization and polymerization after 15.1 GPa. At 21.4 GPa, the peaks of cis/trans-stilbene are almost invisible. After decompression to ambient pressure, the peak of cis-stilbene returned to the original position of 388 nm, while the fluorescence intensity did not recover. On the other hand, the peak position of trans-stilbene returned with a half intensity of its original intensity.

Summarily, consistent with the infrared results, trans-stilbene is more stable under high pressure, and a reversible fluorescence process of first enhancing and then decreasing will occur under high pressure. However, the fluorescence intensity of cis-stilbene under high pressure was always decreased due to the $\pi-\pi$ stacking interaction, accompanying the irreversible polymerization and an amorphous process.

In situ UV−vis spectra were performed to study the band-gap evolution as a function of pressure, as shown in Figure 3. The valence electron information of stilbene can be obtained by *in situ* high-pressure UV−vis spectra, and the variation trend of the optical band gap of the sample can be obtained by approximate fitting the peak wavelength according to the Kubelka−Munk function and the Tauc plot (Figure S1).[31−33] All of the peak position and intensity changes are dominated by the right-hand-side spectral peaks. Figure 3a shows the selected UV−vis spectra of cis-stilbene under high pressure, and the absorption peak comes from the $\pi \rightarrow \pi^*$ transition generated by the conjugation of the benzene ring and the C═C bond. Before 2.0 GPa, the sample was in a state of incomplete solidification, and the spectral peak at this time was mainly the peak of the diamond background, so the spectra showed that the peak intensity and band gap did not change much with pressure (Figure 3b). After 2.0 GPa, the sample was completely cured and the true UV−vis absorption peak appeared. The intensity of the spectral peak starts to increase rapidly, and the red shift of the spectral peak is slightly accelerated. This indicates that high pressure leads to a sharp enhancement of the $\pi-\pi$ stacking interaction, which leads to an enhanced absorption and wavelength increase (Figure 3b). At ∼9 GPa, the spectral peak intensity variation reaches its maximum. At 16.1 GPa, the change in peak intensity starts to slow down and does not change much until 21.8 GPa. After 16.1 GPa, the spectral peaks become broadened and finally split into two peaks, and the splitting of peaks becomes more obvious at 21.8 GPa. The appearance of the new peak in the UV−vis absorption spectrum is consistent with the sample turning red, as observed in the IR spectra at 16.2 GPa, proving that the cis-stilbene did polymerize at this pressure, resulting in a new $\pi \rightarrow \pi^*$ transition peak. The band gap changes from 3.2 eV at 2.0 GPa to 1.9 eV at 21.8 GPa, and the peak intensity changes from 0.4 to 2.5, an increase of nearly 6 times. After decreasing the pressure to ambient, the band gap decreased from 1.9 eV at 21.8 GPa to 2.5 eV at ambient, a decrease of 0.8 eV compared with the raw material band gap. The peak intensity returned from 2.5 to 2.1, which has a 5 times increase compared with the raw material with a value of 0.4. The new UV−vis absorption peak split at 16.1 GPa, and the failure to return to the initial state suggests that cis-stilbene undergoes irreversible polymerization under high pressure and that high pressure has a significant modifying effect on its band gap.

The UV−vis absorption spectra of trans-stilbene under high pressure are shown in Figure 3c. Before 7.9 GPa, the spectral peak is a large package, indicating that the optical band gap of the sample is too small to be detected and fitted. However, as the pressure increases to 7.9 GPa, a new $\pi \rightarrow \pi^*$ transition peak appears at 410 nm, corresponding to a band gap of 1.45 eV (Figure 3d). This pressure point corresponds to when the intensity of the Ph−H and ═C−H bond is nearly the same in the infrared spectrum. It indicates that a structural change has taken place in trans-stilbene at 7.9 GPa, leading to the sample transforming into a semiconductor and the band gap increasing. The speculations about the structural changes were confirmed by XRD experiments later. At 10.5 GPa, the band-gap energy reaches a maximum of 1.9 eV, and the corresponding structural change reaches a maximum. At 20.8 GPa, the band gap decreases to 1.25 eV, indicating that after 10.5 GPa, the continuous accumulation of electron cloud in

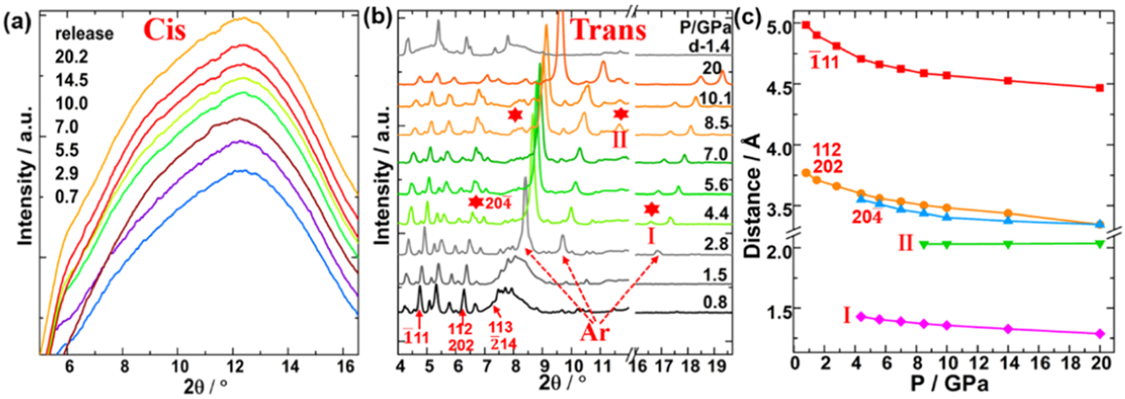

Figure 4. Selected *in situ* XRD patterns of cis-stilbene (a) and trans-stilbene (b) under high pressure. (c) The main XRD peaks of trans-stilbene vary with pressure.

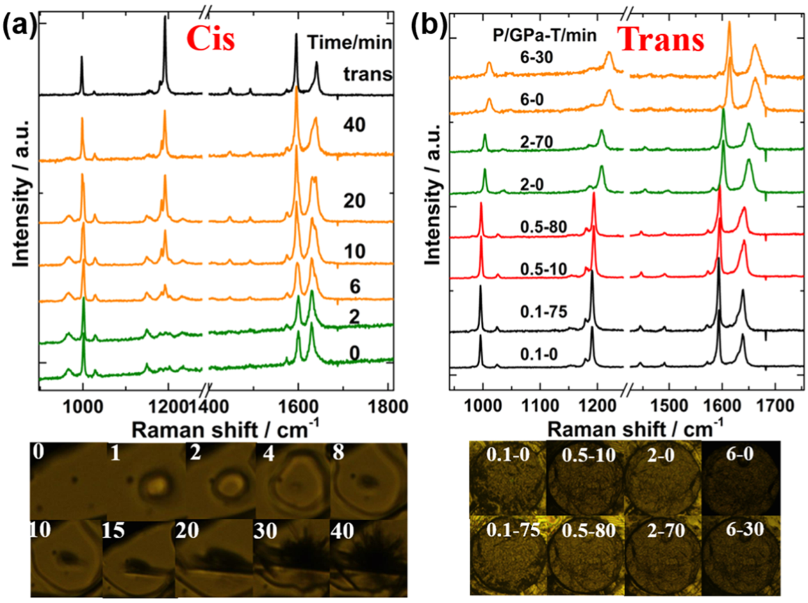

Figure 5. Selected *in situ* Raman patterns of (a) cis → trans-stilbene at 0.5 GPa by 532 nm laser irradiation, and (b) trans → cis-stilbene by 360 nm laser irradiation at different pressures; the pictures at the bottom correspond to the spectra at the top.

the molecule leads to the normal decrease of the band gap under high pressure. After 16 GPa, the changing trend of band gap with pressure also changed slightly, just like the change in the peak position in IR spectra, which was analyzed to be caused by the sample gradually becoming amorphous under high pressure. From 7.9 to 20.8 GPa, the peak of the spectrum was always red-shifted, indicating that the level of $\pi-\pi$ conjugation of trans-stilbenes was enhanced. After being released to ambient pressure, the peak returned to the initial position, which was consistent with the phenomenon observed in fluorescence and infrared spectra: trans-stilbene undergoing a reversible change process before 20.8 GPa.

In summary, a new UV−vis absorption peak emerges at 16 GPa of cis-stilbene, where an irreversible polymerization occurs, accompanied by the band gap dropping from 3.3 to 2.5 eV. The structural change of trans-stilbene at ~8 GPa leads to the formation of a new UV−vis absorption peak, and the band gap increases at first. After ~10 GPa, the pressure leads to the enhancement of $\pi-\pi$ conjugation, and the band gap decreases. Trans-stilbene undergoes a reversible change process before ~20 GPa.

To study the specific structural change information of cis/trans-stilbene under high pressure, *in situ* high-pressure XRD was performed, as shown in Figure 4a (cis-stilbene) and 4b (trans-stilbene). As cis-stilbene is an amorphous liquid at room temperature and pressure, the amorphous liquid has no diffraction peak. Samples solidified under high pressure but no crystallization showed up even up to 10 GPa.

The XRD spectra of trans-stilbene at high pressure are shown in Figure 4b, c, showing the major peak position changes with pressure after conversion to the distance of (*hkl*).[34] It can be seen that the main peaks at ambient pressure are concentrated at 4−7°, and the large peak envelope at ~8° is a mixture peak from the sample and argon. At 2.8 GPa, three new peaks appeared between 8 and 17°, which were analyzed and compared with the peaks of solid argon. At 4.4 GPa, the (204) peak on the shoulder of the (112) and (202) crystallographic indicator peaks gradually reveals itself,[34] while an unknown spectral I-peak appears around 17°. This pressure is close to the pressure point where both the fluorescence and IR spectra change around 4 GPa, indicating that trans-stilbene does have a structural transition at this pressure point. This is consistent with the pressure points in the theoretical simulation part of Zou et al.,[30] which corresponds to the twist angle variation of the benzene ring and the C═C bond in the crystal structure. At 8.5 GPa, the peaks of (113) and (214) are revealed, and the II-peak appears at ∼11.5°. This pressure corresponds to the appearance of a new absorption peak for trans-stilbene in the UV−vis absorption spectrum, both of which are new peaks from structural change, and this peak position is essentially unshifted under high pressure. At 20 GPa, most of the spectral peaks are present except for the influence of broadening and weakening that occurs due to amorphization. After 15 h of release to 1.4 GPa, the peaks at 4−8° were found to remain, indicating that the changes in trans-stilbene under high pressure are largely reversible, which is consistent with the results of the above-mentioned spectra studies.

To study the specific transformation of cis-trans isomerism under high pressure, we use Raman spectroscopy to perform a preliminary study on the specific transformation conditions of cis/trans-stilbene under low (<6 GPa) pressure. First, the stability of cis-stilbene was studied by increasing the irradiation time of the laser at a fixed pressure. A 532 nm, a laser with a power of 10 mW was used to irradiate at 0.5 GPa, and it was found that the cis-stilbene gradually changed into a trans-stilbene at about 6 min, as shown in the spectra in Figure 5a. The sample gradually changes from the original transparent solid to liquid droplets and then gradually expands. After 8 min, a dark solid sample was gradually formed in the center, and the sample gradually increased in size and a crystal with black color was formed after 40 min. The Raman peak of the black crystal is basically the same as that of trans-stilbene, indicating that cis-stilbene was completely transformed into trans-stilbene. At the same time, when the laser power is increased to more than 20 mW, cis-trans transition could not happen because the intensity is high enough to directly harm the sample. The size and pieces of trans-stilbene crystals can be controlled by changing the heating time and laser position. However, only the sample that becomes black at the center of the laser spot is trans-stilbene, and around the spot, the crystal formed by laser thermal radiation is still cis-stilbene. Alternatively, the cis-stilbene sample was then thermally heated by a heating plate to 125 °C keeping at 0.4 GPa; the sample melts into its original liquid state (melting point: 123−125 °C). After heating, the IR test showed that cis-stilbene did not change into trans-stilbene (Figure S2), and no trans-stilbene was detected. The above experiments show that cis-stilbene can be transformed into trans-stilbene at 0.4 GPa only under photoexcitation, while heating ($T \leq 125$°C) cannot change cis-stilbene into trans-stilbene.

In contrast, the conversion of trans → cis-stilbene is almost impossible for the experimental conditions we used. We tried a 360 nm and 8 mW laser (spot size ∼20 μm) irradiation for 80 min at 0.1, 0.5, 2, and 6 GPa, separately (Figure 5b), and other conditions such as heating or laser irradiation up to 125 °C. The trans-stilbene was also irradiated using a 532 nm laser at pressures and laser powers of 0.5 GPa and 10 mW (Figure S3a), 0.5 GPa and 65 mW (Figures S3b), 5 GPa and 20 mW (Figure S3c), and 5 GPa and 50 mW (Figure S3d), respectively. The Raman spectroscopy of both laser irradiations showed that none of them could achieve the conversion of trans → cis-stilbene. As shown in Figure 5b, a 360 nm laser irradiation was used at different pressures, and both spectra and pictures showed that no trans → cis-stilbene change occurred. After that, samples of trans-stilbene at 0.3 GPa (Figure S4a), 1.0 GPa (Figure S4b), and 5.3 GPa (Figure S5) were all heated to 125 °C, and the IR spectra results showed no spectral peak changing, which means no transformation of trans → cis-stilbene. The main reason is that the minimum temperature and activation energy required for trans → cis-stilbene conversion are 154 and 193 kJ/mol (≈212−440 °C) at ambient pressure.[35−39] In this experiment, the sum of the energy generated up to 125 °C (melting point: 123−125 °C) heating and the energy reduced by high pressure still failed to meet the minimum requirements for activation energy.

The reason for the absence of trans → cis-stilbene transition in this experiment is analyzed and understood mainly in terms of the molecular orbitals of the stilbene molecules. As stated in the introduction of the article, there is a C═C bond in the stilbene molecule, corresponding to a π-bond, and two parallel p-orbitals. Due to the requirement of π-bond (p-orbitals) symmetry, the olefin molecule cannot twist along the C═C bond, resulting in the inability of heating to convert trans → cis-stilbene. However, under the excitation of light, the π electrons produce a $\pi \rightarrow \pi^*$ leap and the π bond is weakened, leaving only the rotatable σ-bond. The cis-olefin is then converted to the ground state trans-olefin through the twisted intermediate of the excited state.[40−42] The 532 nm laser irradiation failed, mainly because the laser wavelength was too large to reach the minimum activation energy (energy barrier) required to overcome the σ-bond twisted after the π-electron leap in the C═C in the trans-stilbene molecule. For the 360 nm laser irradiation of the trans → cis-stilbene transition, the failure is mainly speculated from the following: first, the 360 nm laser spot is too large (spot size ∼20 μm), resulting in too low laser intensity to see the obvious conversion process; second, the 360 nm laser excitation also did not reach the minimum activation energy required to overcome the σ-bond twisted after the π-electron leap in C═C in the trans-stilbene molecule in the pressure range from 0.1 to 6 GPa.

Shortly summarized, the cis-stilbene can be basically converted into trans-stilbene at 0.5 GPa after irradiation by a 532 nm laser at 10 mW (<20 mW) and 40 min due to its instability, which provides a method for obtaining higher-purity trans-stilbene. However, it cannot be converted to trans-stilbene by heating to 125 °C, which assumed that the temperature does not meet the minimum temperature requirement for activation energy at 0.4 GPa. In contrast, the trans-stilbene could not overcome the activation energy under even 360 nm and 8 mW laser irradiation for 80 min to achieve the trans → cis-stilbene conversion. Further experiments, like using a shorter-wavelength laser irradiation, are worthy of testing. In conclusion, the cis-trans isomerization at high pressure is more likely to result in higher purity and better stability of trans compounds than at ambient pressure. The trans → cis transition will not occur under normal sunshine illumination and heating, and cis → trans will only occur in a fixed wavelength and intensity range, and cis → trans will not happen by heating.

■ CONCLUSIONS

In summary, we used *in situ* Raman, IR, fluorescence, and UV−vis spectroscopies to determine the luminescence properties, polymerization reactions, and structural changes of cis/trans-stilbene under high pressures of up to 20 GPa. First, for cis-stilbene, at 16 GPa, the changes in IR, UV−vis, and sample color indicate an irreversible polymerization occurred, and ═C(sp^2)−H changed to C−H(sp^2 + sp^3). However, trans-stilbene showed fluorescence enhancement at 0−4 GPa, which is consistent with the changes in IR and X-ray diffraction (XRD). At 8 GPa, the new peaks in UV−vis and XRD indicated the occurrence of structural change. However, the trans-stilbene is relatively more stable, which leads to the return of most of the substance to its original state after compression. Finally, the isomerization process of cis/trans-stilbene under high pressure combined with heating and laser irradiation was initially investigated. It was found that the cis → trans-stilbene only occurred under a fixed-range laser irradiation, while the trans → cis-stilbene could happen neither by heating nor by laser irradiation. Our study provides a reference for the cis-trans isomerization of other organic molecules under high pressure.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c04865.

> Method for intercepting calculations of the Eg at 8.4 GPa, Figure S1; heating of Cis-stilbene to 125 °C at 0.4 GPa, Figure S2; irradiation of Trans-stilbene under 532 nm laser at 0.5 GP and 10 mW, 0.5 GPa and 65 mW, 5 GPa and 20 mW, and 5 GPa and 50 mW, Figure S3; Trans-heating of stilbene to 125 °C at 0.3 and 1 GPa, Figure S4; and heating of Cis-stilbene to 125 °C at 5.3 GPa, Figure S5 (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Ying Liu − *Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China*; Email: liuy37@sustech.edu.cn

Jinlong Zhu − *Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China*; orcid.org/0000-0002-7314-8394; Email: zhujl@sustech.edu.cn

Authors

Jun Han − *Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China*

Qunfei Zheng − *Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China*

Cheng Jin − *Center for High Pressure Science and Technology Advanced Research (HPSTAR), Beijing 100094, China*

Shanmin Wang − *Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China*; orcid.org/0000-0001-7273-2786

Yusheng Zhao − *Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.2c04865

Author Contributions

The manuscript was written with contributions from all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Brandts, J. F.; Halvorson, H. R.; Brennan, M. Consideration of the Possibility that the slow step in protein denaturation reactions is due to cis-trans isomerism of proline residues. *Biochemistry* **1975**, *14*, 4953−4963.

(2) Hartley, G. S. The Cis-form of Azobenzene. *Nature* **1937**, *140*, 281.

(3) Hartley, G. S. 113. The cis-form of azobenzene and the velocity of the thermal cis→trans-conversion of azobenzene and some derivatives. *J. Chem. Soc.* **1938**, *0*, 633−642.

(4) Moss, G. P. Basic terminology of stereochemistry (IUPAC Recommendations 1996). *Pure Appl. Chem.* **1996**, *68*, 2193−2222.

(5) Stahl, W.; Schwarz, W.; Sundquist, A. R.; Sies, H. cis-trans isomers of lycopene and β-carotene in human serum and tissues. *Arch. Biochem. Biophys.* **1992**, *294*, 173−177.

(6) Bandara, H. M. D.; Burdette, S. C. Photoisomerization in different classes of azobenzene. *Chem. Soc. Rev.* **2012**, *41*, 1809−1825.

(7) Dugave, C.; Demange, L. Cis−Trans Isomerization of Organic Molecules and Biomolecules: Implications and Applications. *Chem. Rev.* **2003**, *103*, 2475−2532.

(8) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. pi.-Bond strengths in the second and third periods. *J. Am. Chem. Soc.* **1987**, *109*, 5217−5227.

(9) Strain, H. H. cis-trans Isomeric Carotenoids, Vitamins a and Arylpolyenes. *J. Am. Chem. Soc.* **1963**, *85*, 1025.

(10) Brown, E. V.; Granneman, G. R. Cis-trans isomerism in the pyridyl analogs of azobenzene. Kinetic and molecular orbital analysis. *J. Am. Chem. Soc.* **1975**, *97*, 621−627.

(11) Weiss, J. M.; Downs, C. R. The Physical Properties of Maleic, Fumaric and Malic Acids. *J. Am. Chem. Soc.* **1923**, *45*, 1003−1008.

(12) Kinsella, J. E.; Bruckner, G.; Mai, J.; Shimp, J. Metabolism of trans fatty acids with emphasis on the effects of trans,trans-octadecadienoate on lipid composition, essential fatty acid, and prostaglandins: an overview. *Am. J. Clin. Nutr.* **1981**, *34*, 2307−2318.

(13) Qin, L.; Liu, X.; Yu, Y. Soft Actuators of Liquid Crystal Polymers Fueled by Light from Ultraviolet to Near Infrared. *Adv. Opt. Mater.* **2021**, *9*, 2001743.

(14) Hu, Y.; Li, Z.; Lan, T.; Chen, W. Photoactuators for Direct Optical-to-Mechanical Energy Conversion: From Nanocomponent Assembly to Macroscopic Deformation. *Adv. Mater.* **2016**, *28*, 10548−10556.

(15) Wang, Y.; Li, Q. Light-Driven Chiral Molecular Switches or Motors in Liquid Crystals. *Adv. Mater.* **2012**, *24*, 1926−1945.

(16) Mahimwalla, Z.; Yager, K. G.; Mamiya, J.-i.; Shishido, A.; Priimagi, A.; Barrett, C. J. Azobenzene photomechanics: prospects and potential applications. *Polym. Bull.* **2012**, *69*, 967−1006.

(17) Hubbard, R.; Wald, G. Cis-trans Isomers of Vitamin A and Retinene in the Rhodopsin System. *J. Gen. Physiol.* **1952**, *36*, 269−315.

(18) Sullivan, B. P.; Meyer, T. J. Comparisons of the physical and chemical properties of isomeric pairs. 2. Photochemical, thermal and electrochemical cis-trans isomerizations of $M(Ph_2PCH_2PPh_2)_2Cl_2$ (M = RuII, OsII). *Inorg. Chem.* **1982**, *21*, 1037−1040.

(19) Liu, H.; Dai, Y.; Gao, Y.; Gao, H.; Yao, L.; Zhang, S.; Xie, Z.; Wang, K.; Zou, B.; Yang, B.; Ma, Y. Monodisperse π−π Stacking Anthracene Dimer under Pressure: Unique Fluorescence Behaviors and Experimental Determination of Interplanar Distance at Excimer Equilibrium Geometry. *Adv. Opt. Mater.* **2018**, *6*, No. 1800085.

(20) Takizawa, K.; Wakita, J.; Sekiguchi, K.; Ando, S. Variations in Aggregation Structures and Fluorescence Properties of a Semialiphatic Fluorinated Polyimide Induced by Very High Pressure. *Macromolecules* **2012**, *45*, 4764−4771.

(21) Tang, W. S.; Strobel, T. A. Pressure-Induced Solid-State Polymerization of Optically-Tunable Diphenyl-Substituted Diacetylene. *ACS Appl. Polym. Mater.* **2019**, *1*, 3286−3294.

(22) Dong, Y.; Xu, B.; Zhang, J.; Tan, X.; Wang, L.; Chen, J.; Lv, H.; Wen, S.; Li, B.; Ye, L.; Zou, B.; Tian, W. Piezochromic Luminescence Based on the Molecular Aggregation of 9,10-Bis((E)-2-(pyrid-2-yl)vinyl)anthracene. *Angew. Chem. Int. Ed.* **2012**, *51*, 10782−10785.

(23) Wang, L.; Wang, K.; Zou, B.; Ye, K.; Zhang, H.; Wang, Y. Luminescent Chromism of Boron Diketonate Crystals: Distinct Responses to Different Stresses. *Adv. Mater.* **2015**, *27*, 2918−2922.

(24) Wang, Q.; Li, S.; He, L.; Qian, Y.; Li, X.; Sun, W.; Liu, M.; Li, J.; Li, Y.; Yang, G. Pressure-Induced Emission Enhancement of a Series of Dicyanovinyl-Substituted Aromatics: Pressure Tuning of the Molecular Population with Different Conformations. *ChemPhysChem* **2008**, *9*, 1146−1152.

(25) Liu, H.; Gu, Y.; Dai, Y.; Wang, K.; Zhang, S.; Chen, G.; Zou, B.; Yang, B. Pressure-Induced Blue-Shifted and Enhanced Emission: A Cooperative Effect between Aggregation-Induced Emission and Energy-Transfer Suppression. *J. Am. Chem. Soc.* **2020**, *142*, 1153−1158.

(26) Gu, Y.; Wang, K.; Dai, Y.; Xiao, G.; Ma, Y.; Qiao, Y.; Zou, B. Pressure-Induced Emission Enhancement of Carbazole: The Restriction of Intramolecular Vibration. *J. Phys. Chem. Lett.* **2017**, *8*, 4191−4196.

(27) Wang, L.; Ye, K.-Q.; Zhang, H.-Y. Organic materials with hydrostatic pressure induced mechanochromic properties. *Chin. Chem. Lett.* **2016**, *27*, 1367−1375.

(28) Mao, H. K.; Xu, J.; Bell, P. M. Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions. *J. Geophys. Res. Solid Earth* **1986**, *91*, 4673−4676.

(29) Prescher, C.; Prakapenka, V. B. DIOPTAS: a program for reduction of two-dimensional X-ray diffraction data and data exploration. *High Pressure Res.* **2015**, *35*, 223−230.

(30) Gu, Y.; Shao, G.; Tian, Z.; Li, H.; Wang, K.; Zou, B. Two different emission enhancement of trans-stilbene crystal under high pressure: Different evolution of structure. *Chin. Phys. B* **2021**, *31*, 017901.

(31) Kubelka, P.; Munk, F. An article on optics of paint layers. *Z. Tech. Phys* **1931**, *12*, 593−609.

(32) Companion, A. L. Theory and Applications of Diffuse Reflectance Spectroscopy. In *Developments in Applied Spectroscopy* Davis, E. N., Ed.; Springer US: Boston, MA, 1965; pp 221−234.

(33) Makuła, P.; Pacia, M.; Macyk, W. How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV−Vis Spectra. *J. Phys. Chem. Lett.* **2018**, *9*, 6814−6817.

(34) Harada, J.; Ogawa, K. Invisible but Common Motion in Organic Crystals: A Pedal Motion in Stilbenes and Azobenzenes. *J. Am. Chem. Soc.* **2001**, *123*, 10884−10888.

(35) Neckers, D. C.; Volman, D. H.; von Bünau, G. *Adv. Photochem.* **1994**, *19*, 5−7.

(36) Taylor, T. W. J.; Murray, A. R. 395. Isomeric change in certain stilbenes. *J. Chem. Soc.* **1938**, 2078−2086.

(37) Kistiakowsky, G. B.; Smith, W. R. Kinetics of Thermal Cis-Trans Isomerization. III. *J. Am. Chem. Soc.* **1934**, *56*, 638−642.

(38) Bortolus, P.; Cauzzo, G. Thermal isomerization of stilbene and styrylpyridines in the liquid state. *Trans. Faraday Soc.* **1970**, *66*, 1161−1164.

(39) Santoro, A. V.; Barrett, E. J.; Hoyer, H. W. Kinetics of cis-trans isomerization by differential thermal analysis. *J. Am. Chem. Soc.* **1967**, *89*, 4545−4546.

(40) Minezawa, N.; Gordon, M. S. Photoisomerization of Stilbene: A Spin-Flip Density Functional Theory Approach. *J. Phys. Chem. A* **2011**, *115*, 7901−7911.

(41) Han, W.-G.; Lovell, T.; Liu, T.; Noodleman, L. Density Functional Studies of the Ground- and Excited-State Potential-Energy Curves of Stilbene cis−trans Isomerization. *ChemPhysChem* **2002**, *3*, 167−178.

(42) Kawaguchi, Y. The new photoisomerization mechanism of stilbene. *J. Chem. Phys.* **1994**, *100*, 8856−8868.

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