Angewandte
Zuschriften

Molecular Switches Hot Paper

Deutsche Ausgabe: DOI: 10.1002/ange.201410945
Internationale Ausgabe: DOI: 10.1002/anie.201410945

Visible-Light-Triggered Molecular Photoswitch Based on Reversible *E*/*Z* Isomerization of a 1,2-Dicyanoethene Derivative**

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Abstract: *A designed bis(dithienyl) dicyanoethene-based, strictly E/Z photoswitch (4TCE) operates through state-selective (E and Z isomer) photoactivation with visible light. The E and Z isomers of 4TCE exhibit remarkably different spectroscopic characteristics, including a large separation (70 nm) in their absorption maxima (λ_{max}) and a 2.5-fold increase in molar extinction coefficient from cis to trans. The energetically stable trans form can be completely converted to the cis form within minutes when exposed to white light, whereas the reverse isomerization occurs readily upon irradiation by blue light ($\lambda < 480$ nm) or completely by thermal conversion at elevated temperatures. These features together with excellent thermal stability and photostability of both isomers make this new E/Z photoswitch a promising building block for photoswitchable materials that operate without the need for UV light.*

Photochromic molecules have attracted substantial research interest because of their promising applications to biomolecules, energy management, information storage, and nanotechnology.[1] Molecule-based photochromism can be realized either by reversible *E*/*Z* photoisomerization or photocyclization reactions (Figure 1).[2] Only one of these mechanisms should be operative for a photoswitch so as to avoid having more than the two essential switching states ("on" and "off") in a given application.

Photoswitching through *E*/*Z* photoisomerization is exemplified by azobenzene and its derivatives[3] (Figure 1, Pathway 1). Azo compounds undergo large-scale structural changes from their more stable *trans* form to their *cis* form upon irradiation with UV light; this process can be reversed thermally or through irradiation with blue light. These compounds have been widely used as photoswitches for organic electronics,[4] energy conversion,[5] and photocontrol of biological systems,[6] yet their applications are limited somewhat by two intrinsic drawbacks: 1) possible UV-induced photodamage of other moieties attached to the azo group,[7] and 2) overlap between n–π* bands of the two isomers leading to low conversion yield ($\Phi_{Z\rightarrow E} = 53\,\%$ and $\Phi_{E\rightarrow Z} = 24\,\%$).[8] Introducing electron-donating groups at the *ortho* or *para* positions of the phenyl rings can effectively red-shift the spectrum, while adjusting energy levels of n orbitals by attaching proper groups at the *ortho* positions can increase splitting of n–π* bands of both isomers.[2,7,9] However, these modifications usually require a complicated synthesis and in some cases cause a distortion of the coplanar *trans* form, which decreases desirable π conjugation and solid-state packing.[2] These drawbacks could be avoided with "non-azo" *E*/*Z* photoswitches, yet surprisingly little effort has been devoted to developing such visible-light-triggered, highly photoconvertible switches that are readily synthesized using simple reactions.

In principle, diarylethenes hold promise as alternative, "non-azo" *E*/*Z* photoswitches.[10] The first reported diarylethene that showed reversible photochromism was *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (CMTE, Figure 1).[11] It has been used to construct photoswitchable materials in various matrices.[12] However, photoexcitation of CMTE induces both *E*/*Z* isomerization and photocyclization (Figure 1, Pathway 2),[13] thus producing three coexisting species rather than two. A remedy for reducing this photochemical complexity is to shut off *E*/*Z* isomerization by incorporating the double bond into a five-membered ring, thus permitting only interconversion through cyclization. This design strategy led to the development[14] of (perfluoro)cyclopentene dithienylethenes (Figure 1), which inspired extensive follow-up research on their photoswitching characteristics.[15] However, no means of suppressing photocyclization while employing *E*/*Z* isomerization for photochromism has ever been proposed, despite the fact that chemical modification of the dicyanoethene unit holds great promise for tailoring the spectroscopic characteristics of photoswitchable materials for visible-light utilization. Overcrowded alkenes make up another significant class of diarylethene compounds and have been extensively studied as molecular motors.[16] These alkenes exhibit large separations in λ_{max} between the *E* and *Z* isomers, so that efficient photoisomerization could be one of the driving forces to realize unidirectional rotation around the C=C bond. Nevertheless, their absorption bands are still located in the UV region such that light with relatively high energy is required to trigger photoisomerization.

Our design strategy for a robust "non-azo" *E*/*Z* photoswitch that operates through excitation by visible light is to remove the methyl groups from CMTE and link 1,2-dicya-

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[**] We are grateful to NIOSH grant 5R21OH010190-02 and the donors of the ACS Petroleum Research Fund (A.E.B. and J.Z.) for support. Resources of the NERSC, supported by the U.S. Department of Energy (Contract No. DE-AC02-05CH11231), were used for calculations.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201410945.

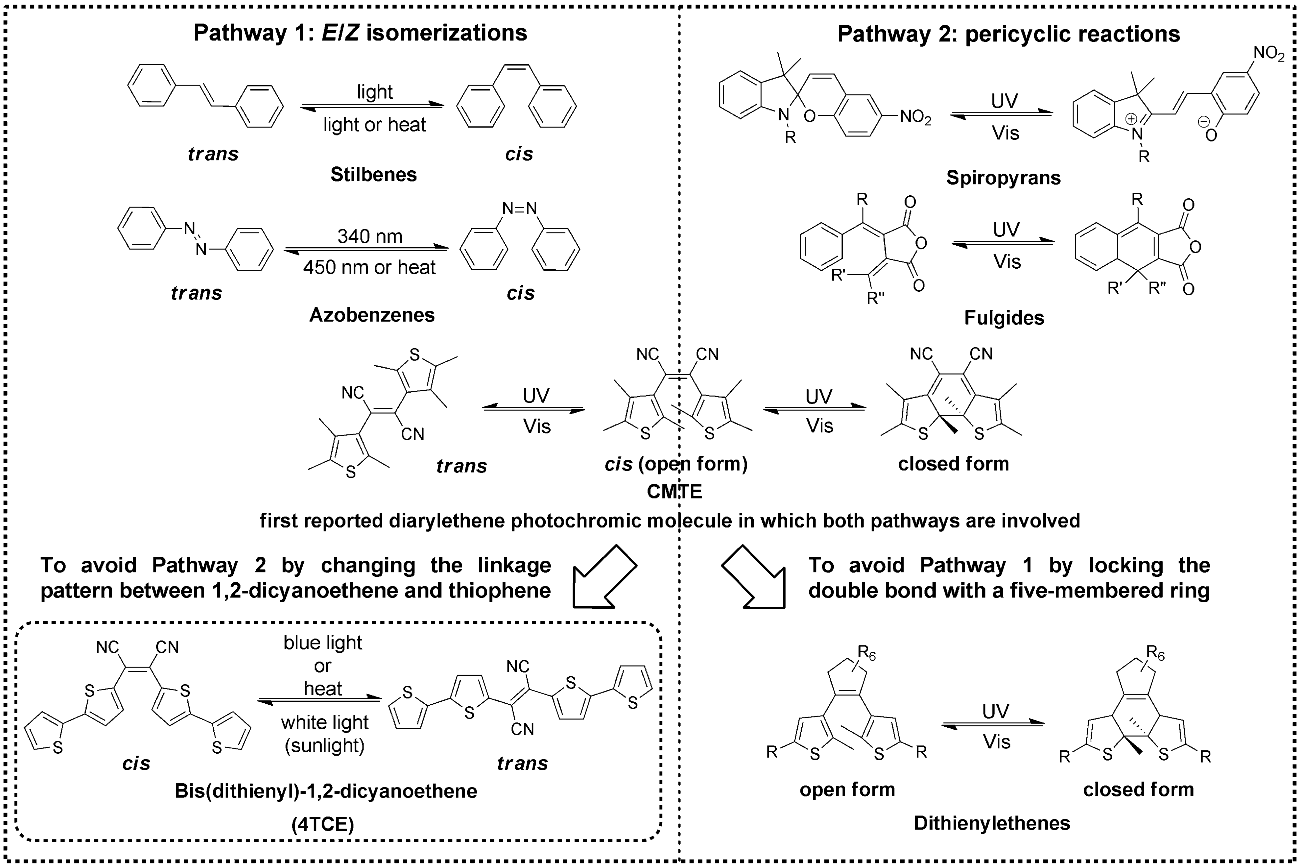

Figure 1. Two pathways to realize photochromism and representative photochromic systems. The design principle leading to the 4TCE photoswitch is presented. Structures of *cis* and *trans* isomers of 4TCE and conditions that trigger its *E*/*Z* isomerization are shown in the dashed box.

noethene directly to the α position of thiophene. This design disables the photocyclization pathway because of the lower reactivity of the proton in the β position of thiophene and increased strain for ring formation. Previous studies on CMTE focused on its electronic and optical properties rather than the extension or modification of the core unit, mainly because the occupation of the α positions in thiophene prohibited further functionalization. Importantly, the availability of a second α thiophene position in our design lends itself to conjugation extension, greater differentiation between *E* and *Z* structures, and greater distinction of absorption behaviors of the isomers (e.g. larger separation of λ_{max} and differences in molar extinction coefficient (ε)). Furthermore, cyano groups are retained, the strong electron affinity of which should lower LUMO levels and decrease excitation energies and thus induce red-shifted absorption spectra (analogous to cyclopentene dithienylethenes), which are highly desirable in photoswitchable molecules.

Herein, we report a bis(dithienyl)-substituted 1,2-dicyanoethene (4TCE, Figure 1) as a novel photoswitch that operates only through *E*/*Z* isomerization. Two isomers of this new photoswitch were successfully separated and their molecular structures were unambiguously characterized by single-crystal X-ray crystallography. Moreover, photochromic studies demonstrate that this molecule presents interesting characteristics that can address issues of azo and CMTE-based photoswitches as discussed above, including that 1) the *Z* and *E* isomers of 4TCE show λ_{max} at 450 and 520 nm in solution, thus providing a larger λ_{max} separation (70 nm) between two isomers compared to those of unmodified azo compounds; 2) the *E* isomer shows a prominently higher ε at λ_{max} than the *Z* isomer, allowing more efficient conversion of the former to the latter; 3) the *E* isomer is stable in the dark and can be easily converted to the *Z* isomer when exposed to white light (or sunlight, 100 % conversion) within minutes, while the reverse process can be triggered with blue light (< 480 nm, ≈ 60 % conversion) or by heating (> 80 °C, 100 % conversion), thus both photoisomerizations can occur without UV light; 4) no noticeable photodegradation is detected during multiple switching cycles, thus indicating high photostability. More importantly, this new photoswitchable system can be readily extended by cross-coupling dibromo 1,2-dithienyl-1,2-dicyanoethene (**1**, Scheme S1, Supporting Information) with various units bearing functional groups, thus allowing the design of a diverse array of photoswitchable materials for specific applications.

The 4TCE was easily prepared by Stille coupling between 2-(tributylstannyl)thiophene and compound **1**, which was synthesized following an oxidative coupling procedure for the bis(4-bromophenyl)fumaronitrile, as shown in Scheme S1 (see the Supporting Information). The two isomers of 4TCE can be separated easily by column chromatography because of a large difference in their molecular dipole moments (9.30 and 0.23 Debye for Z and E, respectively, estimated by calculations). The molecular structures of the two isomers were confirmed by NMR spectroscopy (Figure S1) and single-crystal X-ray crystallography. As shown in Figure 2, the *cis* isomer adopts a bent conformation with a dihedral angle between the cyano group and the bisthienyl substituent of about 55.3° at one side and 20.1° at another side, while the *trans* isomer possesses a nearly planar geometry with one outer thiophene ring slightly warped. Because of the significantly twisted conformation of the *cis* isomer, its π–π stacking is not efficient. Tilted stacking arrangements in dimers are observed for *trans* 4TCE with an interplanar distance of about 3.56 Å because of excellent coplanarity. In addition, the end-to-end distances of the two isomers are approximately 9.25 and 16.20 Å, meaning a difference of around 7 Å, two times larger than that of azobenzene (≈3.5 Å).[6a] It can thus be expected that the E/Z isomerization of 4TCE can cause a more significant morphological change than azo compounds.

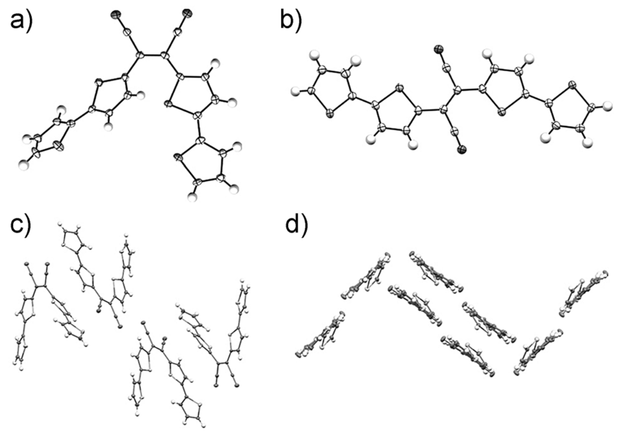

Figure 2. Displacement ellipsoid plots of the two isomers of 4TCE.[20] a) *cis* isomer, b) *trans* isomer, c) crystal packing of the *cis* isomer and d) crystal packing of the *trans* isomer. Thermal ellipsoids at 50% probability.

UV-Vis absorption spectra of pure *cis* and *trans* isomers of 4TCE in solution were recorded before investigating their photoswitching behaviors. In toluene, both isomers display two absorption bands with λ_{max} around 520 nm (with a shoulder at 490 nm) for *trans* and 450 nm (with a shoulder at 420 nm) for *cis* (Figure 3 a). Higher-energy transitions also appear at 320 and 305 nm for the *cis* and *trans* forms, respectively. It is worth noting that the λ_{max} separation between the two isomers is as large as 70 nm, quite larger than that of azobenzene isomers (both of which have n–π* bands near 440 nm).[6a] This observation can be explained by differences in conjugation. In the *cis* isomer, the distorted conformation reduces π-electron delocalization, while the almost planar *trans* isomer promotes excellent π conjugation and results in a lower excitation energy (red-shifted absorption band). The ε of the *trans* isomer in the visible region is strikingly larger than that of the *cis* isomer (2.5 times at λ_{max}). By contrast, in the UV and blue regions (below the isosbestic point) the absorbance of the *trans* isomer is weaker relative to that of the *cis* isomer. These results imply that $E \rightarrow Z$ isomerization may be driven selectively when a sample is excited by visible light, whereas blue light could be used to preferentially trigger the reverse isomerization. The 4TCE isomers exhibit similar spectroscopic characteristics in other solvents (Figure S2).

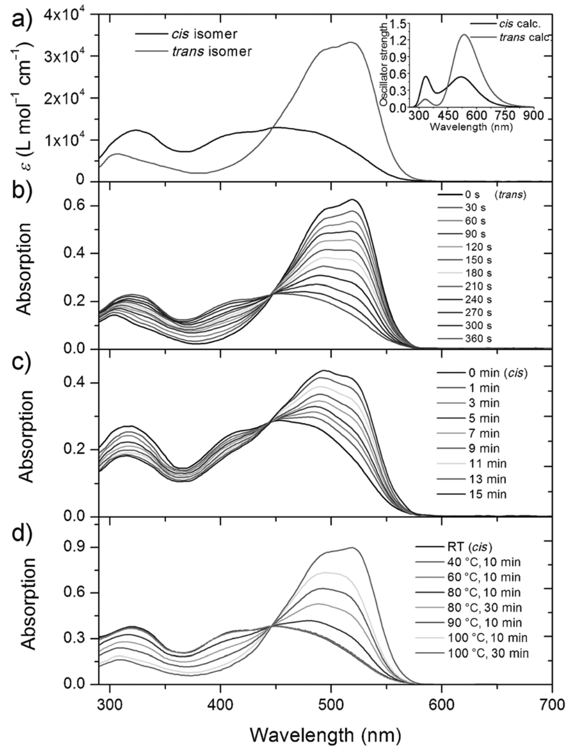

Figure 3. a) UV-Vis absorption spectra of pure *cis* and *trans* isomers of 4TCE in toluene (10^{-5} M, the same below) at room temperature. Inset: calculated UV-Vis spectra. b) $E \rightarrow Z$ photoisomerization of 4TCE, irradiated by white light. c) $Z \rightarrow E$ photoisomerization of the 4TCE, irradiated by blue light at 420 nm. d) Thermal $Z \rightarrow E$ isomerization of 4TCE.

The photoswitching properties of 4TCE were studied in toluene solution using the UV-Vis absorption spectroscopy. The *trans* conformation is stable in the dark. However, it will rapidly isomerize to the *cis* form upon exposure to room light, as can be observed even by the naked eye. The changes in the UV-Vis spectra during $E \rightarrow Z$ photoisomerization are shown in Figure 3 b. Judging by the difference in ε for the two pure isomers, $E \rightarrow Z$ isomerization is complete within several minutes. $Z \rightarrow E$ isomerization was investigated by irradiating the sample of the *cis* isomer with light of various wavelengths and was found to occur at $\lambda < 440$ nm (Figure 3 c). The rate of $Z \rightarrow E$ isomerization is lower than that of the $E \rightarrow Z$ isomerization and the conversion efficiency reaches around 60% at the photostationary state (PSS). In contrast, complete $Z \rightarrow E$ isomerization can be realized by heating the sample. As shown in Figure 3 d, the *cis* isomer starts converting to the *trans* isomer at 80 °C. Increasing the temperature increases the rate of thermal isomerization. The conversion is complete within 30 min when the *cis* isomer is heated to 100 °C. The conditions for thermal isomerization reflect excellent thermal stability of the *cis* isomer. No change in its ε or the shape of the spectra is observed after storage at room temperature for 2 weeks (in the dark). Throughout these isomerization processes, only two species (Z and E isomers) were observed, as indicated by a single isosbestic point at 446 nm.

Studies on the photochromic behavior in other solvents were also carried out. In polar solvents such as acetonitrile and methanol, $Z \rightarrow E$ isomerization can take place with lower-energy light at 480 nm, while the reverse process still occurs under white light but at a lower rate (Table S1). It is believed that the solvent-polarity effect plays a significant role in the isomerization rate as a result of a large difference in the dipole moments of the isomers.[17]

For a sustainable application, a photoswitch should possess an excellent photostability for consistent response over multiple switching cycles. To investigate this feature, the UV-Vis absorption of 4TCE in solution was monitored during the alternate irradiation with blue (420 nm) and white light. No significant photodegradation could be detected during 20 irradiation cycles (Figure S4), thus demonstrating the excellent reversibility and photostability of this new photoswitch.

Quantum chemical calculations (ground-state DFT and excited-state TDDFT) on both isomers were performed at the B3LYP/6-31G* level using the Gaussian 09 package[18] in order to better understand their electronic structures and spectroscopy. The optimized ground-state geometries of both isomers (Figure S5) are quite similar to those obtained by the X-ray diffraction. UV-Vis spectra predicted from TDDFT calculations coincide well with experimental results in terms of spectral shape and relative absorption intensity (Figure 3 a inset). For the *cis* isomer, there are three significant electronic transitions, nominally, HOMO→LUMO (S_1), HOMO-1→LUMO (S_2), and HOMO→LUMO + 1 (S_4) transitions (Table S2). Therefore, the broad absorption bands from 380 to 550 nm can be assigned to the S_1 and S_2 transitions, whereas the band around 320 nm is associated with the S_4 transition. Similar oscillator strengths of S_1 and S_4 transitions lead to nearly the same absorption intensity of both bands. Photoexcitation in one or both of these transitions triggers the conversion from *cis* to *trans*.

Figure 4 illustrates these energy levels and corresponding frontier orbitals. For the HOMO-1 and HOMO orbitals, the electron distribution is largely located at the bisthienyl moiety, whereas the LUMO exhibits substantial electron density located near the cyano groups. This reflects an electronic push–pull effect between the electron-donating thiophene units and electron-withdrawing cyano groups. By contrast, only one primary transition (HOMO→LUMO (S_1)) occurs in the UV-Vis spectrum of the *trans* isomer and is associated with the predominant absorption band at 520 nm. Other transitions with very small oscillator strengths contribute to the weak band around 305 nm. The frontier orbitals share qualitatively similar characteristics to those of the *cis* isomer. Qualitative differences in the shapes of these orbitals can be attributed to different molecular symmetry, where the *trans* form imposed by C_{2h} symmetry is more constrained than the *cis* form with C_s (nominal C_{2v}) symmetry. The more constrained symmetry of the *trans* isomer also gives rise to a greater relative oscillator strength for the S_0-to-S_1 transition (2.5 times larger than that of the *cis* isomer, in agreement with experimental results). Overall, our calculations support the feasibility of initiating isomer-selective photoisomerization in 4TCE by excitation through different electronic transitions.

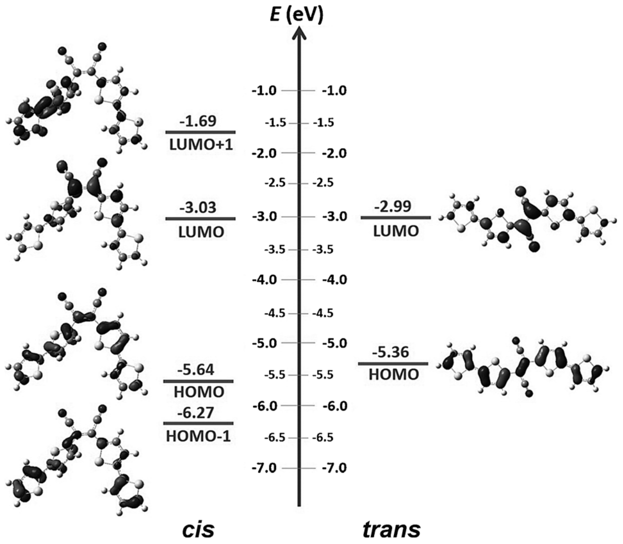

Figure 4. Energy levels and corresponding frontier molecular orbitals of both isomers calculated at B3LYP/6-31G* level.

In addition, DFT calculations show that the optimized ground-state energy of the *trans* isomer is about 4 kcal mol^{-1} lower than that of the *cis* isomer, which is in agreement with the observation of the relative stability of the *trans* isomer in the dark. However, the *cis* isomer is more stable under room light, as discussed above. According to the theoretical analysis and experimental results, we can attribute this observation to the fact that the *trans* isomer has a larger oscillator strength relative to the *cis* isomer in the visible region, particularly in the green region of the solar irradiation spectrum, which makes it easily excited by white light leading to isomerization by way of a non-adiabatic transition in the excited state. It can thus be predicted that green light will more effectively trigger $E \rightarrow Z$ isomerization. To verify this hypothesis, a sample of the *trans* isomer was irradiated with green light (515 nm) and a complete conversion from *trans* to *cis* occurred in only 30 s. On the contrary, the *cis* isomer does not have significantly higher absorptivity compared to the *trans* isomer in the UV and blue regions, which leads to incomplete $Z \rightarrow E$ isomerization.

In summary, we have presented the promising photoswitch molecule 4TCE, based only on reversible E/Z isomerization. Its two isomers exhibit significantly different molecular geometries leading to highly contrasting coplanarities, effective conjugations, molecular dipole moments, end-to-end distances, and symmetries. Spectral studies on pure isomers showed a large separation between their $\lambda_{\max}$ and a variation in their relative absorption strengths. As a result, 4TCE can be efficiently switched between its *cis* and *trans* forms by irradiating with blue and white light, such that it is a useful photoswitch with manageable photoisomerization, high conversion efficiency, and no requirement of a UV light trigger. Theoretical calculations strongly support the experimental observations. Conceivably, using the established synthetic protocol, additional 1,2-dicyanoethene-based compounds can be prepared and easily modified with functional groups for further red-shifting the absorption and splitting the bands of the two isomers in order to improve the $Z \rightarrow E$ photoconversion efficiency. This class of photochromic materials may open up a new channel for photoswitches to communicate with organic electronics and biomolecules, as well as provide a potential opportunity to make use of solar energy, as one of the isomerization processes can be effectively triggered by sunlight. The subunit also represents a rare opportunity to combine photoisomerization with electron-transport capability, as the diphenyl dicyano analogue has been incorporated into n-channel semiconductors.[19]

Keywords: 1,2-dicyanoethene · diarylethenes · molecular switches · photochromism · photoisomerization

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 4782–4786
Angew. Chem. **2015**, *127*, 4864–4868

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[20] CCDC 1033561 (*cis* isomer) and CCDC 1033562 (*trans* isomer) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: November 11, 2014
Revised: January 2, 2015