

Substituent effect of diarylethenes on IR spectra for application of non-destructive readout of photochromic recording

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ABSTRACT: Photochromic diarylethene derivatives, 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1**), 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**2**), and 1,2-bis(2-methoxy-5-phenyl-3-thienyl)perfluorocyclopentene (**3**) were prepared to study substituent effects on IR spectra. The origin of the change of IR spectra due to the substituents may be categorized into (1) change in structure, (2) change in charge distribution, and (3) new normal modes due to the newly introduced substituent, which was examined by *ab initio* quantum chemical calculations. Comparisons between the experimental and computational IR spectra clarified the difference of the substituent effects between open- and closed-ring isomers. Such understanding should be useful for designing diarylethene derivatives in use for non-destructive readout by IR light. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: IR spectrum; photochromism; substituent; *ab initio*; quantum chemical calculation

INTRODUCTION

Photochromism is defined as the reversible photocoloration of a single chemical species between two states having different absorption spectra, brought about by the action of an electromagnetic radiation in at least one of the back-and-forth directions. Photochromic molecules attract much attention from both fundamental as well as practical points of view due to their potential for applications to optical devices such as optical memories and switches.¹ Among photochromic compounds, diarylethenes are regarded as the best candidate due to the

thermal stability of both isomers and their fatigue resistant properties.² For practical applications to optical memory, non-destructive readout capability is indispensable. When the recorded information is readout by the light which electronically excites the photochromic compounds, information is lost during the reading process. Several reports have attempted to avoid it. One approach uses readout light, which cannot cause any photoreaction.^{3–9} We reported IR readout of photochromic recording as non-destructive readout.¹⁰ For IR readout, since the absorption coefficients of IR bands are absolutely smaller than bands in the UV–Vis regions, high conversion to the closed-ring isomer at the photostationally state and the complete separation of the IR bands of open- and closed-ring isomers is indispensable. We have already shown the IR readout of the multi-frequency readout of photochromic recording using three different photochromic compounds and IR readout in the near-field.^{11,12} Since we observed the importance of the general aspects of the IR spectral features of diarylethene derivatives during this study, we studied

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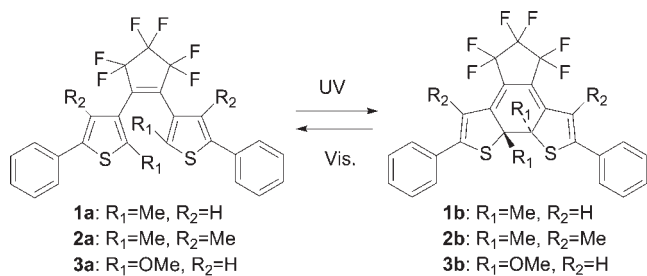
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the substituents effect of open- and closed-ring isomers of diarylethenes on IR spectra.

RESULTS AND DISCUSSION

Synthesis and UV-Vis spectral changes of diarylethene derivatives

Diarylethenes **1**, **2**, and **3** (Scheme 1) were prepared according to the literature.^{12–16} Diarylethene **2** has a methyl group at the 4-position, while **1** has no methyl groups at that position. Diarylethene **3** has methoxy groups at the 2-position of each thiophene ring instead of the methyl group of **1**. Absorption maximum wavelengths and molar absorption coefficients are summarized in Table 1. Upon irradiation with UV light, these derivatives show blue coloration that disappeared under visible light irradiation. They have large quantum yields of cyclization (coloration) reaction and small quantum yields of cycloreversion, which is convenient to achieve high conversion to the closed-ring isomer at the photostationally state. Although the quantum yield (0.001) of cycloreversion reaction is small, some diarylethenes are reported to be suitable for photo-memory and recording even in a single molecular level.^{17,18}



Scheme 1. Diarylethene derivatives

Computational analysis of IR spectra

The IR spectra of the open- (a) and closed-ring (b) isomers of diarylethenes **1**, **2**, and **3** measured in carbon tetrachloride solutions are shown in Figures 1–3. Spectra calculated by the Hartree–Fock (HF) method and the density functional theory (DFT) with the B3LYP exchange-correlation functional^{19–21} in Gaussian 03²² are also shown for **1**, **2**, and **3**. The 6-31G(d) basis set is employed for both HF and DFT. The frequencies

obtained by the HF/6-31G(d) and B3LYP/6-31G(d) calculations are scaled by a factor of 0.8953 and 0.9614,²³ respectively. In the following, we show the results with C₂ symmetry.

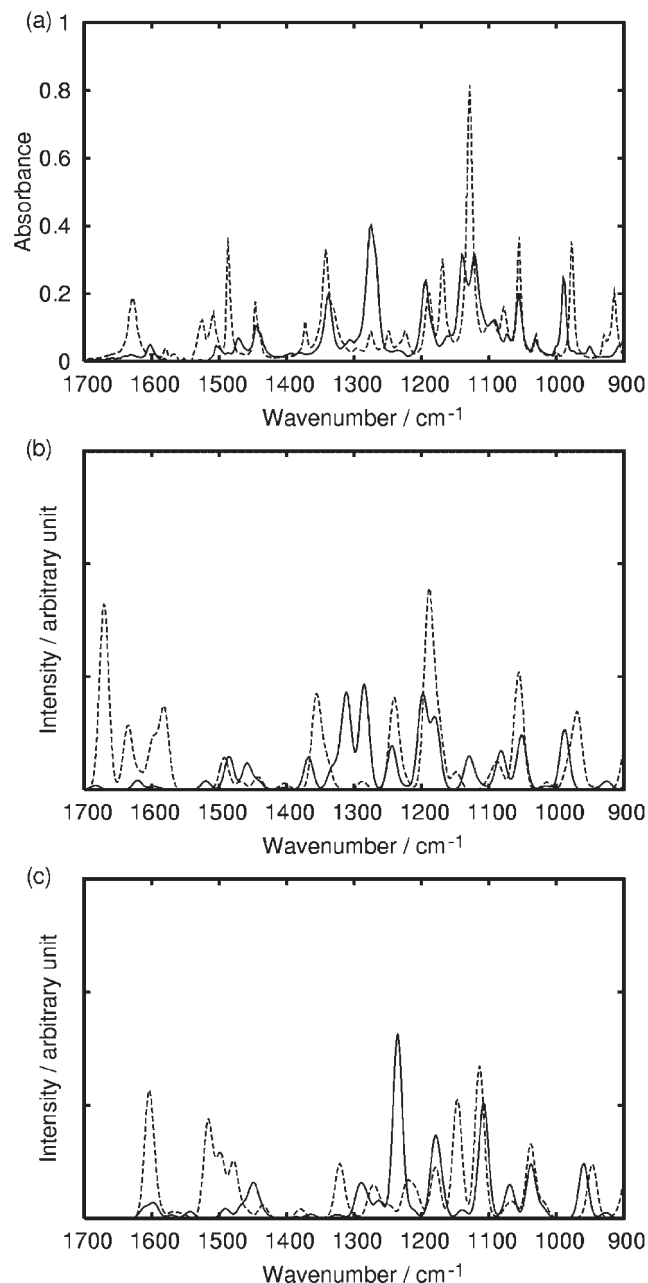


Figure 1. Observed infrared spectra: (a) of open-ring isomer **1a** (solid line) and closed-ring isomer **1b** (broken line) in CCl₄ solution (1.14×10^{-2} M), and calculated spectra by HF/6-31G(d); (b) by B3LYP/6-31G(d); (c) of open-ring isomer **1a** (solid line) and closed-ring isomer **1b** (broken line)

Table 1. Spectral properties and quantum yields of diarylethene derivatives

	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	ϕ_{ab}		$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	ϕ_{ba}
1a	280 (3.56)	0.59	1b	575 (1.56)	0.013
2a	262 (2.8)	0.46	2b	562 (1.1)	0.015
3a	267 (2.4), 309 (3.3)	0.44	3b	625 (1.5)	$<1.7 \times 10^{-5}$

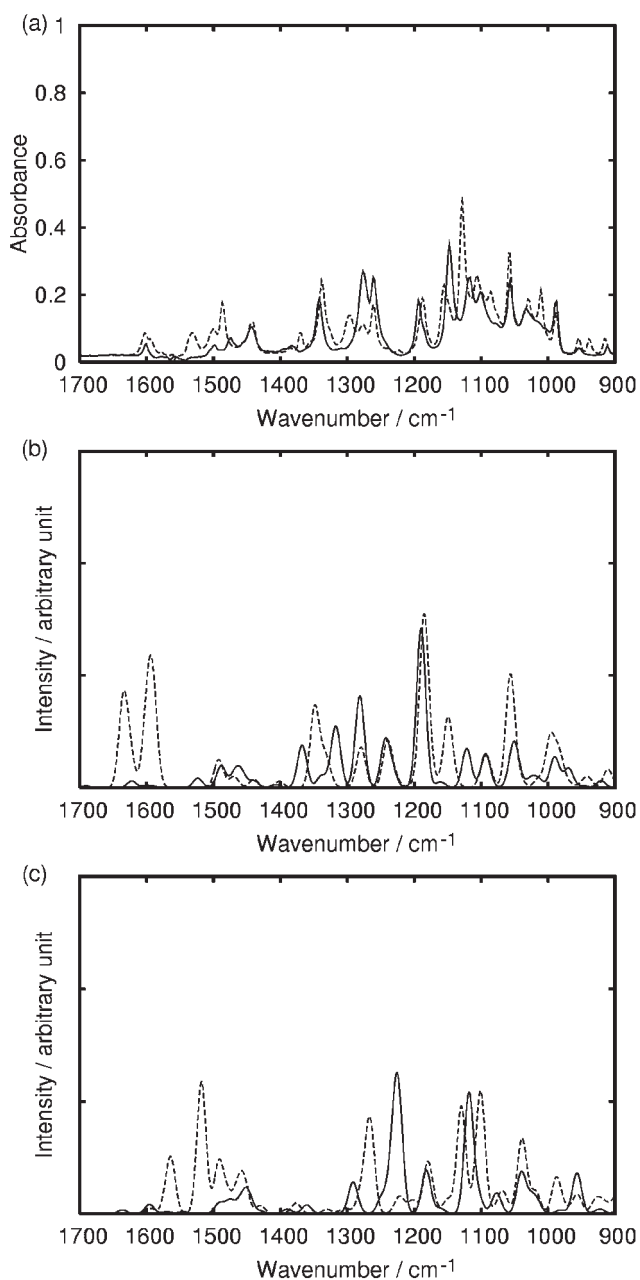


Figure 2. Observed infrared spectra: (a) of open-ring isomer **2a** (solid line) and closed-ring isomer **2b** (broken line) in CCl_4 solution (1.18×10^{-2} M), and calculated spectra by HF/6-31G(d); (b) B3LYP/6-31G(d); (c) of open-ring isomer **2a** (solid line) and closed-ring isomer **2b** (broken line)

By comparing experimental and computational IR spectra, we found that spectra less than 1350 cm^{-1} are better reproduced by HF/6-31G(d), but IR spectra calculated by B3LYP/6-31G(d) better agree with the experimental results greater than 1350 cm^{-1} . Spectra deviation calculated by HF/6-31G(d) from the experimental one is especially large for closed-ring isomers due to the extended double bonds, which require correlation for the proper evaluation of IR spectra.⁸ To obtain accurate IR spectra over the spectral region shown in Figures 1–3, we need to further consider anharmonicity,

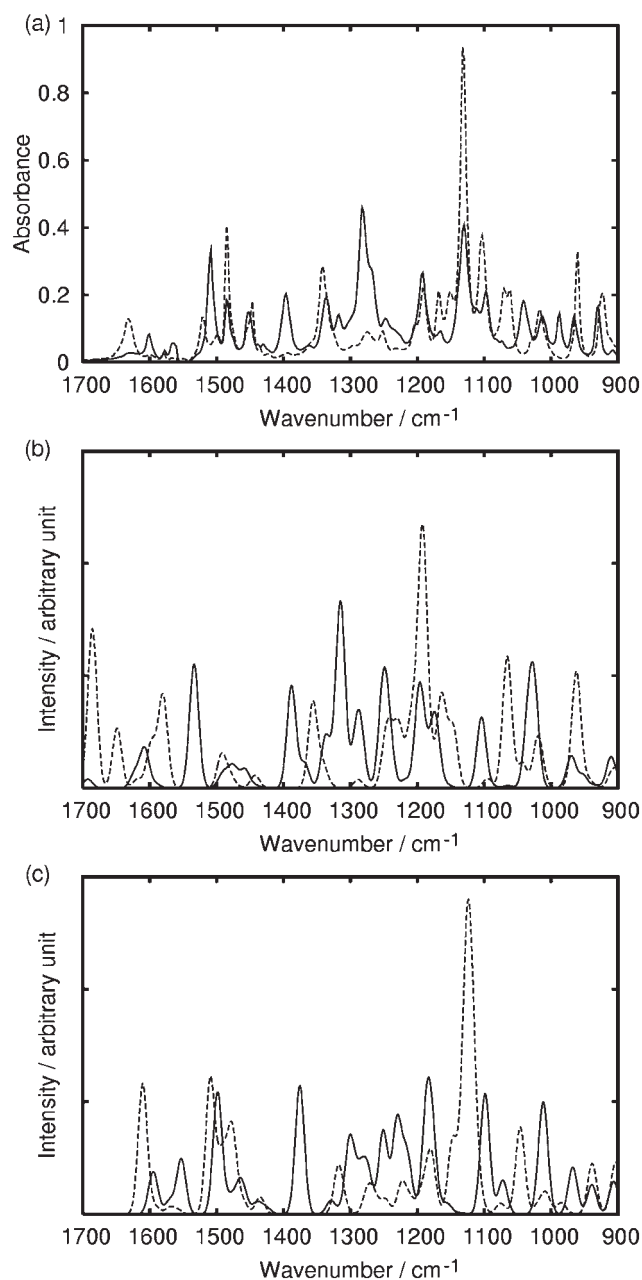


Figure 3. Observed infrared spectra: (a) of open-ring isomer **3a** (solid line) and closed-ring isomer **3b** (broken line) in CCl_4 solution (5.64×10^{-4} M), and calculated spectra by HF/6-31G(d); (b) B3LYP/6-31G(d); (c) of open-ring isomer **3a** (solid line) and closed-ring isomer **3b** (broken line)

which is computationally too much demanding for molecules of such size. Thus, in practice, we use HF/6-31G(d) for less than 1350 cm^{-1} and B3LYP for greater than 1350 cm^{-1} .

Among experimental IR spectra for the open-ring isomers, the spectrum of **3a** is clearly different from others. In contrast, the spectra of the closed-ring isomer are similar, but the spectrum of **2b** is relatively different from others.

In the following, we examine the origin of these differences in IR spectra by comparing the structures as well as the charge distributions.

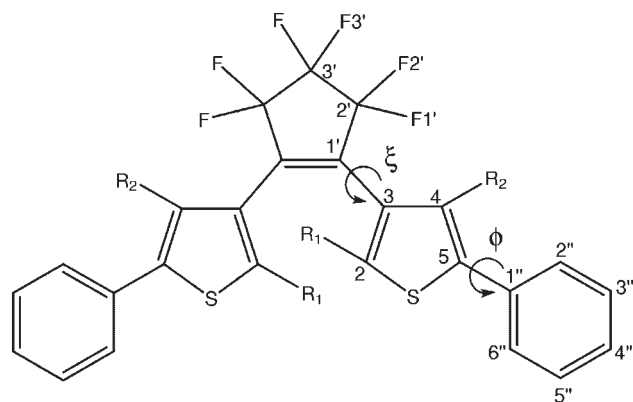


Figure 4. Numbering of atoms and dihedral angles ξ ($C2'-C1'-C3-C4$) and ϕ ($C4-C5-C1''-C2''$)

Substituent effect on structure

The conformational structures of diarylethenes shown in Scheme 1 are mainly characterized by dihedral angles ξ ($C2'-C1'-C3-C4$) and ϕ ($C4-C5-C1''-C2''$), as shown in Figure 4.

The dihedral angles of open-ring isomer **1a** are $\xi = -56.5^\circ$ and $\phi = -38.0^\circ$ and $\xi = -44.2^\circ$ and $\phi = -25.5^\circ$ for the HF and B3LYP, respectively. The dihedral angles of **3a** are similar to those of **1a**, as shown in Table 2. In contrast, the methyl group at the 4-position of thiophene works as a steric hindrance and changes ξ and ϕ dramatically.

Dihedral angle ξ for the closed-ring isomer is not flexible and thus is less affected by the substituent difference, whereas dihedral angle ϕ is affected. Therefore, ϕ of **2b** is distinctively different from others (Table 2).

Substituent effect on charge distribution

Charge distribution is one factor to determine IR intensity, that is, a normal mode with large vibrational amplitude of an atom that carries large effective charge and will have large IR intensity as long as the excitation is symmetry allowed. Here, we analyze charge distribution by the generalized atomic polar tensors (GAPT) atomic

charge.²⁴ The GAPT atomic charge Q^A of atom A is defined by

$$Q^A = \frac{1}{3} \left(\frac{\partial \mu_x}{\partial x_A} + \frac{\partial \mu_y}{\partial y_A} + \frac{\partial \mu_z}{\partial z_A} \right) \quad (1)$$

where (μ_x, μ_y, μ_z) is a dipole moment of a system and (x_A, y_A, z_A) is the position of atom A . Since GAPT atomic charge Q^A is given by the change of the dipole moment due to the change of the position of atom A , it is a convenient measure to discuss IR intensity. In the following, we discuss the GAPT atomic charge calculated by B3LYP/6-31G(d).

The GAPT atomic charges of **1a** and **1b** are shown in Figures 5a and 6a, respectively. Both open- and closed-ring isomers have large charge on the fluorine atoms ($F1'$, $F2'$, and $F3'$) and fluorinated carbon atoms ($C2'$ and $C3'$). In addition, relatively large GAPT atomic charges are found along the delocalized π -orbitals for closed-ring isomer **1b** ($C1'$, $C3$, $C4$, and $C5$). In contrast, open-ring isomer **1a** lacks such a large GAPT atomic charge except for the fluorinated five-membered ring. This is the main reason that absorption by **1b** is relatively stronger than **1a** in most parts of the $900-1700 \text{ cm}^{-1}$ spectral region.

For Figure 5b and c, the deviation of the charge distribution from **1a** due to the substituent effect is shown. Similarly, for Figure 6b and c, the deviation of the charge distribution from **1b** due to the effect is shown as well. We only show deviation larger than 0.02 to clarify the substituent effect.

The substituent effect on charge distribution is localized near the substituent. The effect is large at the carbon atom bearing the substituent ($C2$ for R_1 and $C4$ for R_2). The exception is **2a** where the largest change of atomic charge is found at $C2'$, which might reflect the change of the dihedral angle ξ (Table 2). A change in ξ may affect the charge distribution at $F1'$ and $F2'$ and thus may change the atomic charge of $C2'$.

The change in the charge distribution of **3a** is much larger than **3b**. This results in a significant increase of the absolute value of the atomic charges of $C2$, $C3$, $C4$, $C1''$, and $C1'$ compared to **1a**. Consequently, the IR intensity of the open-ring isomer is much larger than **1a**.

The methoxy group carries a large atomic charge (O -0.861 and C 0.505 for **3a**, and O -0.617 and C 0.427 for **3b**) compared to the methyl group (C 0.055 for **1a**, C

Table 2. Dihedral angles ξ and ϕ defined in Figure 4

	ξ		ϕ			ξ		ϕ	
	HF	B3LYP	HF	B3LYP		HF	B3LYP	HF	B3LYP
1a	-56.5°	-44.2°	-38.0°	-25.5°	1b	-3.3	-3.7	-34.7	-19.3
2a	-100.4°	-103.3°	-56.8°	-44.8°	2b	-6.9	-8.3	-64.1	-50.2
3a	-52.6°	-32.6°	-36.0°	-24.2°	3b	-5.1	-6.2	-33.7	-17.7

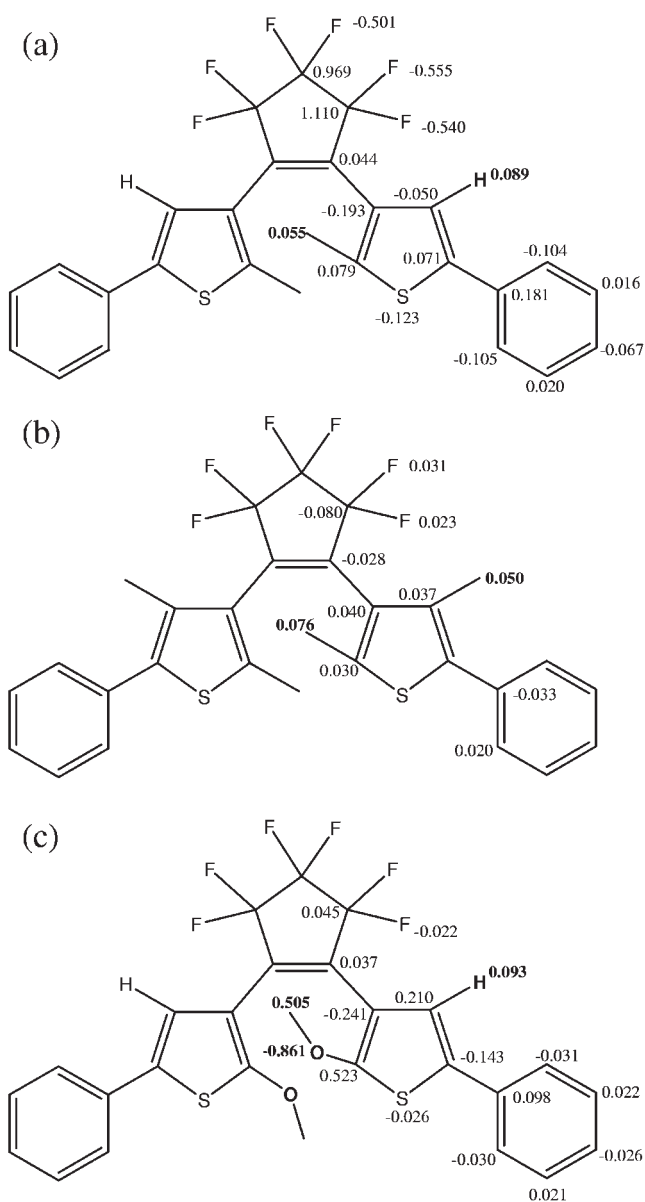


Figure 5. GAPT atomic charge of open-ring isomer **1a** (a) at heavy atoms. Deviation of charge distribution from **1a** due to substituent effect in **2a** (b) and **3a** (c). In (b) and (c), only the value, which is larger than 0.02, is shown

0.033 for **1b**, C 0.076 for R₁ of **2a**, C 0.050 for R₂ of **2a**, C 0.027 for R₁ of **2b**, and C 0.038 for R₂ of **2b**). Thus, substituent as itself contributes to the IR spectra. The atomic charges of hydrogen atoms at R₂ of **1a** and **3a** are large (0.089 and 0.093, respectively) compared to other atomic charges of hydrogen atoms.

Peak splitting around 1120 cm⁻¹ for open-ring isomer

The strong IR band observed at 1128 cm⁻¹ for **1b** splits into two peaks (1120 and 1140 cm⁻¹) for **1a**. However, finding similar features is difficult around 1120 cm⁻¹ for **2**

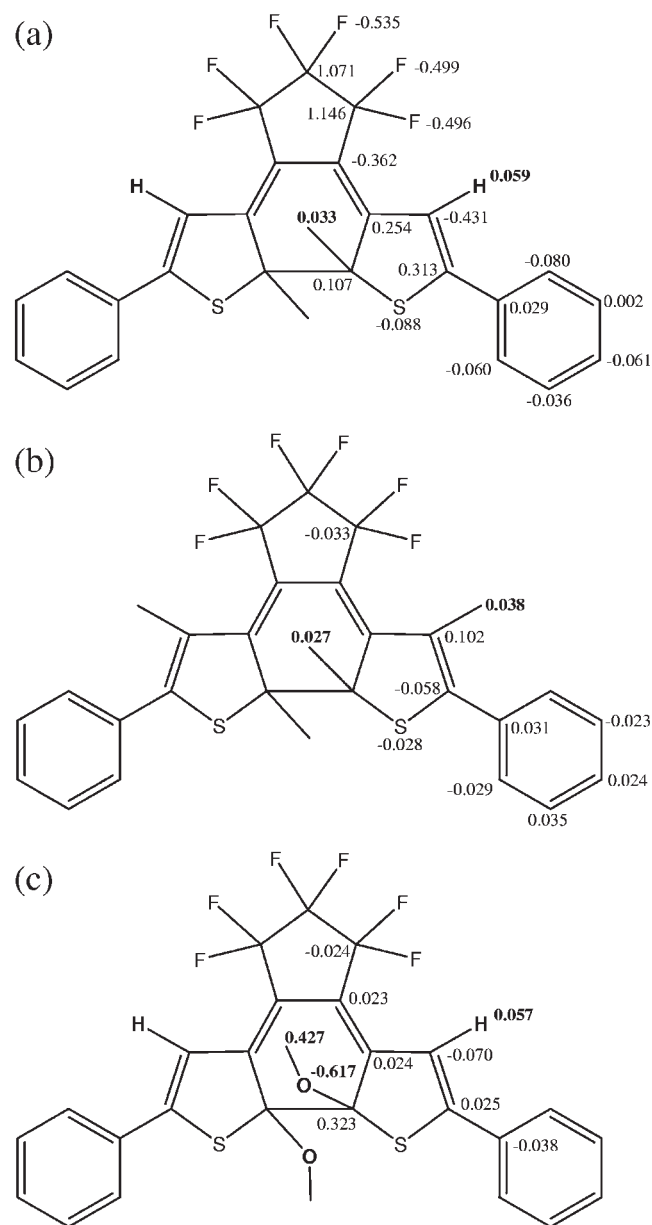


Figure 6. GAPT atomic charge of closed-ring isomer **1b** (a) at heavy atoms. Deviation of charge distribution from **1b** due to substituent effect in **2b** (b) and **3b** (c). In (b) and (c), only the value larger than 0.02 is shown

and **3**. The difference is due to the substituent effect, which will be explained in the following.

The peak at 1128 cm⁻¹ for **1b** is mainly due to the out-of-plane vibration of two carbon atoms in the fluorinated five-membered ring. This vibrational mode can be seen much easier from a top view (Figure 7a). The large IR intensity reflects the large vibrational amplitude of the fluorinated five-membered ring, which has large atomic charges (Figures 5 and 6). On the other hand, the two vibrational modes at 1120 and 1140 cm⁻¹ for **1a** are mainly due to the superposition of the vibrational mode of **1b** at 1128 cm⁻¹ and the CH bending mode of thiophene but in opposite phases (Figure 7b and c).

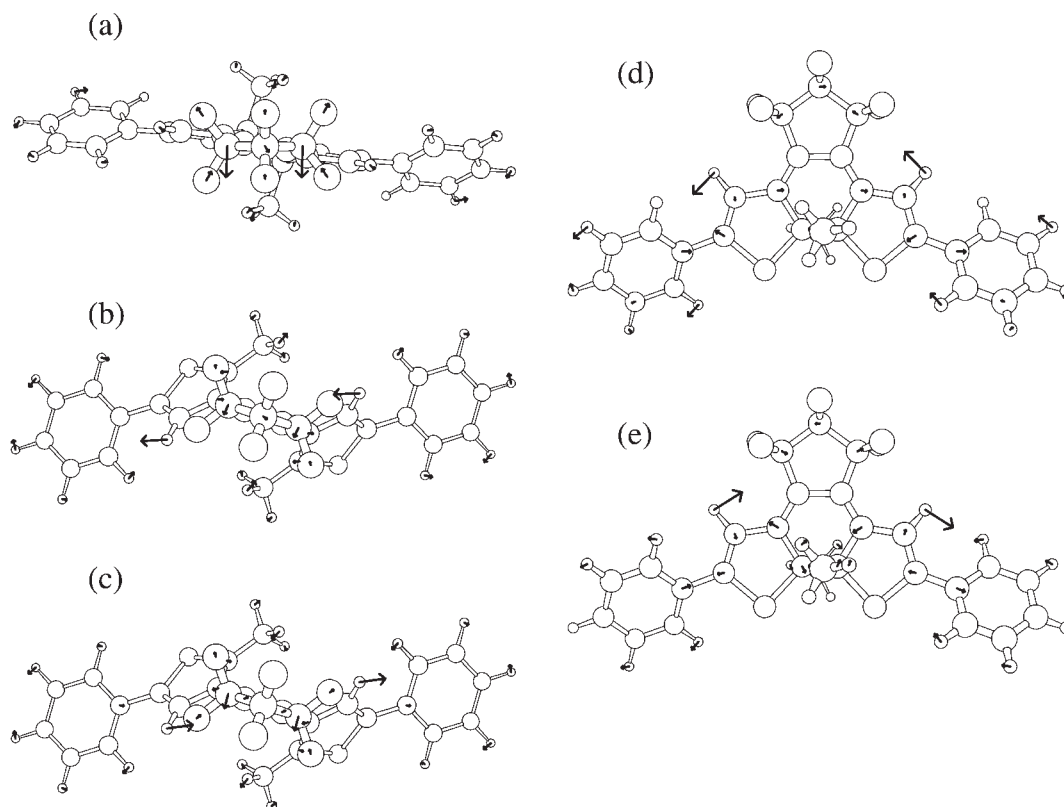


Figure 7. Calculated vibrational modes of **1**: (a) 1189 cm^{-1} mode for **1b**; (b) 1179 cm^{-1} mode for **1a** (c) 1199 cm^{-1} mode for **1a**; (d) 1220 cm^{-1} mode for **1b**; (e) 1227 cm^{-1} mode for **1b**

The CH bending vibrational modes for **1b** are blue-shifted compared to **1a**. Calculated frequencies with the CH bending mode for **1b** are at 1220 and 1227 cm^{-1} (Figure 7d and e, respectively), which are $30\text{--}40\text{ cm}^{-1}$ blue-shifted compared to the calculated vibrational mode of 1189 cm^{-1} , which corresponds to the observed vibrational mode at a frequency of 1128 cm^{-1} . Since the computational IR intensity of these modes is small (3 and 24 km/mol , respectively), it does not show up in the IR spectrum.

The blue shift is mainly due to steric hindrance between the hydrogen atom of the thiophene and the *ortho* hydrogen atom of the phenyl group. The distances between the two H atoms are 2.56 and 2.44 \AA for **1a** and **1b**, respectively. The smaller distance between the two H atoms for **1b** reflects the delocalized π -conjugation for the closed-ring isomer; the dihedral angle between the thiophene and phenyl groups is smaller for the closed-ring isomer than the open-ring isomer (Table 2). The importance of the dihedral angle has been discussed by Bianco *et al.*^{7b}

In contrast, **2** has a methyl group instead of H at the 4-position of the thiophene ring. Thus, there is no vibrational mode in **2**, which corresponds to the CH bending mode of thiophene in **1**. Consequently, there is no splitting around 1120 cm^{-1} .

Molecule **3** has an identical situation for 4-position of the thiophene ring. However, we do not find splitting in the spectrum. This might be due to the difference between the atomic charges of **1a** and **3a** at C4 (Figure 5). The difference may cause the change of frequency of the CH bending mode of thiophene.

Peak around 1280 cm^{-1}

The IR spectra of the open-ring isomers also have similar band around 1280 cm^{-1} . From the experimental IR spectra, it is evident that the band consists of vibrational modes assigned to the calculated modes of 1283 , 1287 , and 1309 cm^{-1} for **1a** (Figure 8a–c, respectively). These three modes are attributed to the stretching mode of C—C in the fluorinated five-membered ring, the CH bending mode of thiophene, and the CH bending mode of the phenyl group but with different combinations, as depicted in Figure 8. Similar vibrational modes are found for **3a**, but due to the existence of the methyl groups, the CH bending mode of thiophene is missing for **2a**. The closed-ring isomer also has similar vibrational modes, which however do not have large IR intensity due to the different charge distribution. Therefore, significant contrast between open- and closed-ring isomers is found

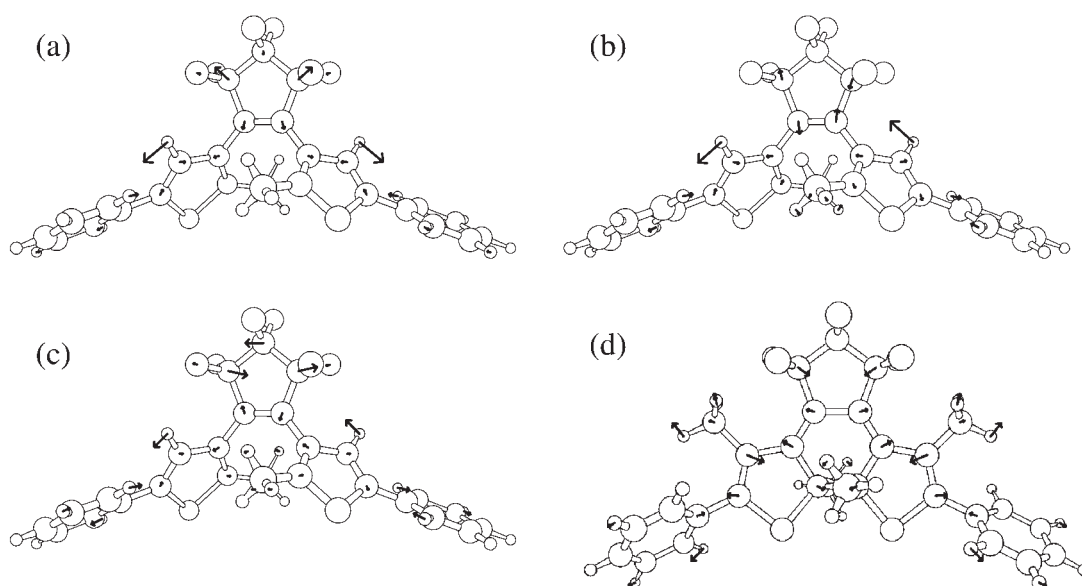


Figure 8. Calculated vibrational modes around 1280 cm^{-1} : (a) 1283 cm^{-1} mode for **1a**; (b) 1287 cm^{-1} mode for **1a**; (c) 1309 cm^{-1} mode for **1a**; (d) 1279 cm^{-1} mode for **2b**

around this band for **1** and **3**. The IR spectrum of closed-ring isomer **2b** shows a weak band due to a different mode (Figure 8d). This vibrational mode has a component of methyl groups and thus is different from the vibrational mode of other closed-ring isomers **1b** and **3b**.

Peak around 1340 cm^{-1}

Experimentally, the peak around 1340 cm^{-1} is always found for Figures 1–3. The vibrational mode is only slightly affected by the substituent effect as well as by the open- and closed-ring isomers. The corresponding vibrational modes of **2a** and **2b** are shown in Figure 9. (The vibrational modes of **1a**, **1b**, **3a**, and **3b** are similar.) The IR band is assigned as the stretching mode of the C—C bonds of the fluorinated five-membered ring (C2' and C3'). The atomic charges of C2' and C3' are large and the changes of the atomic charges due to the substituent effect

and isomerization are relatively small (Figures 5 and 6). The change of the structure in **2a** and **2b** is also unlikely to affect the frequency of this vibrational mode. Therefore, the peak is always found around 1340 cm^{-1} .

Peak around 1400 cm^{-1}

Experimentally, no peak was found around 1400 cm^{-1} except **3a**. This mode is assigned to the calculated mode of 1376 cm^{-1} with the C—C stretching mode of C1'—C3 and C3—C4, the C—O stretching mode of C2—O, and the CH bending mode of the methoxy group (Figure 10a). Since the methoxy group plays an important role in vibration, this mode is not found for **1** and **2**. Since the mode involves the vibration of C2, and since cyclization intrinsically changes the vibration around C2, there is no similar vibrational mode in **3b**, either. Large IR intensity is due to the vibrations of C2 and C3, which have large atomic charges (Figure 5).

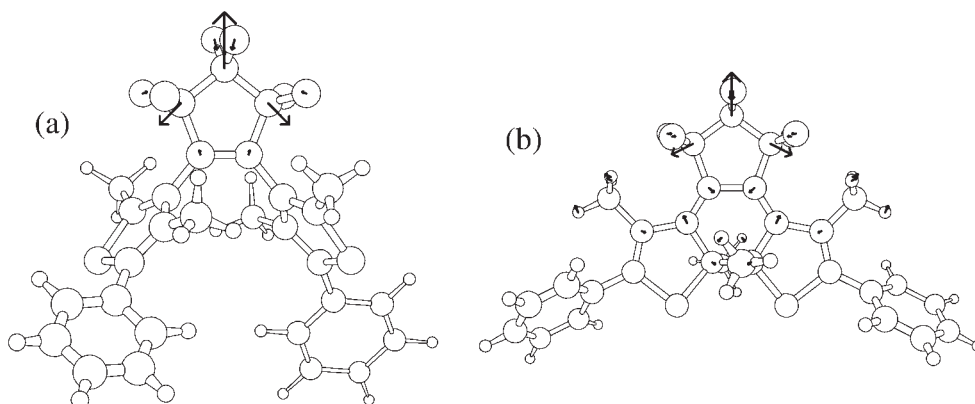


Figure 9. Calculated vibrational modes of **2**: (a) 1367 cm^{-1} mode for **2a**; (b) 1349 cm^{-1} mode for **2b**

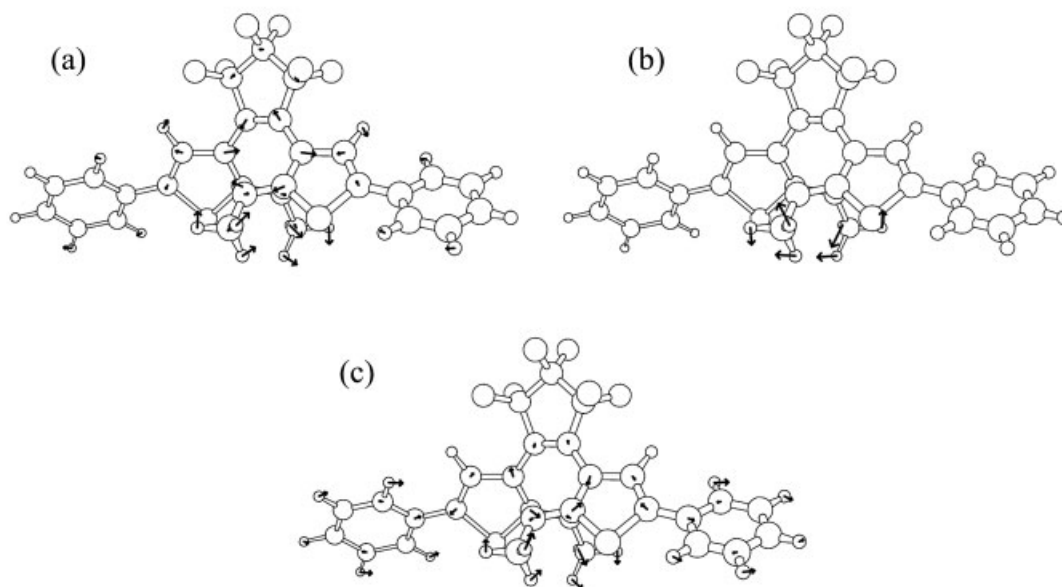


Figure 10. Calculated vibrational modes of **3a**: (a) 1376 cm^{-1} ; (b) 1466 cm^{-1} ; (c) 1499 cm^{-1}

Peaks around 1500 cm^{-1} for open-ring isomer **3a**

Open-ring isomer **3a** shows two major peaks around 1500 cm^{-1} unlike other open-ring isomers **1a** and **2a**. The lower frequency mode is assigned to the calculated mode of 1466 cm^{-1} (Figure 10b), which is the CH bending mode of the methoxy group. Therefore, the peak is only found in **3a**. Higher frequency mode is assigned to the calculated mode of 1499 cm^{-1} (Figure 10c). This mode consists of the stretching mode of the C=C bond of thiophene, the stretching mode of the C2—O bond, and the CH bending mode of the methoxy and phenyl groups. In this case, the peak is only found in **3a** and has large IR intensity just like the 1400 cm^{-1} mode.

CONCLUSION

We examined the substituent effect on the IR spectra of diarylethene. The substituent effect is categorized into three types: (i) it changes the stable conformational structure of the molecule, which mainly results in the change of vibrational modes; (ii) it changes the charge distribution, which mainly results in the change of IR intensity; (iii) it creates new vibrational modes. We investigated overall spectral differences as well as specific modes around 1120 , 1280 , 1340 , 1400 , and 1500 cm^{-1} , and substituents effects are clearly assigned to these three categories. With the compounds investigated here, peaks

are found at similar positions such as 1280 cm^{-1} . The vibrational modes of these peaks are hardly affected by the substituents. GAPT atomic charge analysis is effective for understanding IR intensity. By careful examination of structure and charge distribution, we are able to design diarylethene derivative with modes like 1400 cm^{-1} in **3a** with larger IR intensity.

EXPERIMENTAL

General methods

Absorption spectra were measured using a Hitachi U-3410 spectrophotometer. UV light was irradiated using a TOPCON PU-2 black light. Visible light irradiation was carried out by using an Ushio 500 W high-pressure Mercury lamp with a Toshiba Y-50 cut-off filter. IR spectra were measured using a Horiba FT-710 FTIR interferometer. To obtain the IR spectra of the closed-ring isomers, the closed-ring isomers were isolated on a preparative TLC (Merck 1.11798.0001) by using hexane as an eluent.

Computational details: Molecular structures were optimized and vibrational analysis performed by the HF method with 6-31G(d) basis set in Gaussian 03, Revision C.02.²² In addition, the same procedures were performed by DFT with the B3LYP exchange-correlation functional.^{19–21} Calculated frequencies were scaled by 0.8953^{23} and 0.9614^{23} for HF and B3LYP, respectively.

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