ChemPubSoc Europe
DOI: 10.1002/chem.201403736
CHEMISTRY
A European Journal
Full Paper

Photochromic Compounds

Nonsymmetrical 3,4-Dithienylmaleimides by Cross-Coupling Reactions with Indium Organometallics: Synthesis and Photochemical Studies

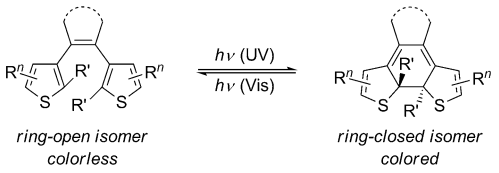
Ángeles Mosquera,[a] M. Isabel Férnandez,[b] Moisés Canle Lopez,[b] José Pérez Sestelo,*[a] and Luis A. Sarandeses*[a]

Dedicated to the memory of Jean-Louis Luche

Abstract: The synthesis and photochemical study of novel nonsymmetrical 1,2-dithienylethenes (DTEs) with a maleimide bridge have been carried out. The synthetic approach to the DTEs was based on successive selective palladium-catalyzed cross-coupling reactions of 5-susbtituted-2-methyl-3-thiophenyl indium reagents with 3,4-dichloromaleimides. The required organoindium reagents were prepared from 2-methyl-3,5-dibromothiophene by a selective (C-5) coupling reaction with triorganoindium compounds (R_3In) and subsequent metal–halogen exchange. The coupling reactions usually gave good yields and have a high atom economy with substoichiometric amounts of R_3In. The results of photochemical studies show that these novel dithienylmaleimides undergo a photocyclization reaction upon irradiation in the UV region and a photocycloreversion after excitation in the visible region, thus they can be used as photochemical switches. ON–OFF operations can be repeated in successive cycles without appreciable loss of effectiveness in the process.

Introduction

Organic photochromic compounds have received increased interest due to their potential applications in optoelectronic molecular devices, such as molecular switches, logic gates, and information storage devices.[1] Among the different families of photochromic materials, 1,2-diarylethenes, in particular 1,2-dithienylethenes (DTEs), which contain a cyclic ethylene bridge bound to two functionalized 2-substituted-3-thiophenyl moieties, are one of the most interesting due to their thermal stability and fatigue resistance.[2] The molecular switching of DTEs is based on an efficient and reversible ON–OFF control photocyclization reaction between colorless ring-opened and colored ring-closed isomers by selective irradiation (Scheme 1).



Scheme 1. Photochromism of DTEs.

Both isomeric forms of the DTEs show marked differences, not only in their absorption spectra, but also in other physical properties, such as the fluorescence intensity,[3] redox potentials,[4] refractive indices,[5] dielectric constants, and geometric structure.[6] The photochemical behavior of these systems has been exploited in numerous fields, for example, the development of optical memory, optoelectronic devices, and organic semiconductors,[7] the control of biological activity in living organisms,[8] the direct conversion of light into mechanical work,[9] or as molecular regulators in DNA interactions.[10] All of these appealing applications have stimulated the development of new synthetic approaches to prepare novel DTEs with selective functions.

Chemical modifications of DTEs have focused on new ethylene bridges and functionalized thiophene units.[11] As a result, there are a large number of DTEs furnished with a perfluoroethylene bridge,[12] although DTEs with cyclopentene,[13] maleimide,[14] maleic anhydride,[15] azulene,[16] and benzothiadiazole[17] bridges have been designed.[18] The ethylene unit is

---

[a] Dr. Á. Mosquera, Prof. Dr. J. Pérez Sestelo, Prof. Dr. L. A. Sarandeses
Departamento de Química Fundamental and
Centro de Investigaciones Científicas Avanzadas (CICA)
Universidade da Coruña, 15071A Coruña (Spain)
Fax: (+34) 981167065
E-mail: luis.sarandeses@udc.es
sestelo@udc.es

[b] Dr. M. I. Férnandez, Prof. Dr. M. Canle Lopez
Departamento de Química Física e Enxeñería Química I
and Centro de Investigaciones Científicas Avanzadas (CICA)
Universidade da Coruña, 15071A Coruña (Spain)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201403736. This includes all experimental details, compound characterization, copies of spectra of new compounds, and photochemical studies.

usually functionalized with two identical thiophene units, thus symmetrical compounds are afforded by double anionic substitution of fluoro substituents of the perfluoroethylene bridge, double cross-coupling reaction, or construction of the cyclic bridge in the final steps. On the other hand, nonsymmetrical DTEs are also compounds of interest; their synthesis by coupling reactions are less common due to low selectivity and are generally prepared by cyclization sequences or selective functionalization of simple dithienylcyclopentenyl precursors.[12b,19]

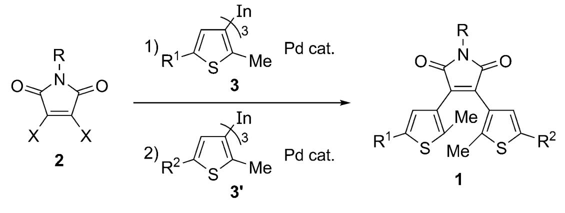
In recent years, our group and others have shown that indium organometallic reagents are useful for metal-catalyzed cross-coupling reactions.[20,21] The main features of these reagents are their high efficiency, versatility, and selectivity. Indeed, triorganoindium reagents (R_3In) have been successfully applied in selective coupling reactions with 3,4-dihalomaleimides, 2,5-dibromothiophene, and dihalopyrimidines.[22] Herein, we report the synthesis and photochemical studies of novel nonsymmetrical DTEs with a maleimide bridge. The compounds were prepared by selective, sequential, iterative cross-coupling reactions with R_3In.

The 3,4-disubstituted maleimide ring is an important moiety in photochromic compounds[23] and light-emitting diodes[24] with promising applications in material science. However, the use of this unit as an ethylene bridge in DTEs has been less-widely studied. Furthermore, the synthesis of nonsymmetrical DTEs will enhance the chemical diversity of these compounds and provide access to further selective functionalization and specific reactivity. Finally, these new compounds should lead to a new class of DTEs with novel photochemical behavior.

Results and Discussion

Synthesis

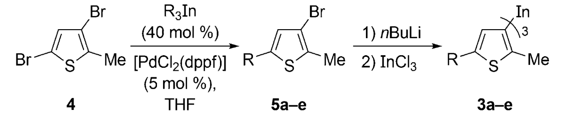
Given the high selectivity exhibited by triorganoindium reagents in coupling reactions to electrophiles with various reactive positions,[22] it was envisaged that nonsymmetrical DTEs with a maleimide bridge (**1**; Scheme 2) could be synthesized by sequential cross-coupling reactions of a 3,4-dihalomaleimides (**2**) with substituted 2-methyl-3-thiophenylindium reagents (**3**).



Scheme 2. Synthetic plan for the synthesis of nonsymmetrical dithienylmaleimides **2**.

As nucleophilic partners, to take advantage of the versatility of the methodology, we chose 5-substituted-2-methyl-3-thiophenyl indium reagents furnished with aryl, heteroaryl, and other promising groups for optoelectronic applications.[2] These organoindium reagents could be prepared from 3,5-dibromo-2-methylthiophene (**4**; Table 1) by another selective (C-5) coupling reaction with an indium organometallic reagent. Further metal–halogen exchange should allow the successive use (in an iterative process) of thiophene **4** as an electrophile and a nucleophile.[25] Overall, the synthetic process can be considered in three main steps: 1) preparation of substituted 2-methyl-3-bromothiophenes **5** as precursors to the organoindium reagents, 2) synthesis of monosubstituted 3-halomaleimides **6** by selective cross-coupling between a tri(3-methylthiophen-3-yl)indium **3** and a 3,4-dihalomaleimide **2**, and 3) synthesis of DTEs **7** by a second coupling reaction.

Table 1. Selective palladium-catalyzed cross-coupling reactions of triorganoindium reagents with 3,5-dibromo-2-methylthiophene (**4**).



Entry	R	T [°C]	Product	Yield [%]
1	phenyl	rt	**5 a**	86
2	naphthalen-1-yl	80	**5 b**	77
3	thiophen-2-yl	80	**5 c**	74
4	benzo[*b*]thiophen-2-yl	80	**5 d**	82
5	phenylethynyl	80	**5 e**	91

The synthesis started with the preparation of 5-substituted-3-bromo-2-methylthiophenes **5** by selective coupling of **4**.[26] Initial screening with different palladium complexes showed that the best results were achieved with $[PdCl_2(dppf)]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) as the catalytic system, a palladium complex previously used in our selective coupling with halothiophenes.[22c] Accordingly, the reaction of Ph_3In[27] (40 mol %) with **4** in THF catalyzed by $[PdCl_2(dppf)]$ (5 mol %) gave the monocoupling product **5 a** in 86 % yield after 15 h at room temperature (Table 1, entry 1). Interestingly, the reaction took place selectively at the C-5 position and all three organic groups attached to indium were efficiently transferred to the electrophile.[28] Under these conditions, the reaction of tri(naphthalen-1-yl)indium (40 mol %) with **4** gave the coupling product **5 b** in low yield (<30 %), but at 80 °C the yield increased to 77 % with a reaction time of only 2 h (Table 1, entry 2).

The methodology was extended to other triorganoindium reagents. As mentioned before, DTEs with heteroaryl moieties, such thiophenyl and benzo[*b*]thiophenyl, are promising candidates for optoelectronic applications.[2,7] In this case, the reaction of tri(thiophen-2-yl)indium with **4**, in the presence of $[PdCl_2(dppf)]$ (5 mol %), in THF at 80 °C gave the bisthiophene **5 c** in 74 % yield (Table 1, entry 3). Analogously, the reaction of **4** with tri(benzo[*b*]thiophen-2-yl)indium selectively afforded the monocoupling product **5 d** in 82 % yield (Table 1, entry 4).

The great interest in alkynylated (hetero)arenes in the fields of organic materials, natural products, and pharmaceuticals[29] led us to assay the coupling reaction with a representative conjugated alkyne, namely tri(phenylethynyl)indium (40 mol %). In this case the coupling product **5e** was obtained in excellent yield (91 %, Table 1, entry 5). In general, these reactions showed high selectivity, without detection of the double coupling products, and gave good yields after short reaction times.

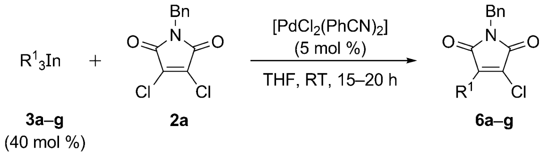
With the 5-substituted-3-bromothiophenes **5a**–**e** in hand, we studied their conversion into the corresponding triorganoindium reagents and the coupling reaction with 3,4-dihalomaleimides **2**. By using our general protocol,[22b] we found that the reaction between the triorganoindium reagent **3a** (120 mol %) and 3,4-dichloromaleimide **2a**, catalyzed by $[PdCl_2(PhCN)_2]$ (5 mol %), selectively gave the monocoupling product **6a** in 70 % yield after 18 h at room temperature (Table 2, entry 1). Interestingly, the reaction with the 3,4-dibromomaleimide analogue gave lower selectivity and yield (51 %).

Under the same experimental conditions, the reaction of 3,4-dichloromaleimide **2a** with the tri(thiophen-3-yl)indium reagents **3b**–**e** bearing aryl, heteroaryl, or alkynyl groups at C-5 (prepared from **5b**–**e**) afforded the monocoupling products **6b**–**e** selectively in good yields (52–76 %, Table 2, entries 2–5). To broaden the chemical diversity of the maleimides, we also performed the selective monocoupling reaction with functionalized indium derivatives, such as the 2-methyl-5-hydroxymethylthiophen-3-yl indium derivative **3f** or tri(2-methylbenzo[*b*]thiophen-3-yl)indium (**3g**). The latent hydroxyl group in **3f** could be used as linker or for subsequent functionalization of the resulting DTE, whereas the benzo[*b*]thiophenyl moiety could be useful to compare thermal stabilities and fatigue resistance. In both cases the coupling product was obtained in good yield (Table 2, entries 6 and 7). Overall, the selectivity of the reactions at room temperature is remarkable given that only 40 mol % of organoindium reagent was used and the double coupling products were not detected.

The last step for the synthesis of nonsymmetrical DTEs was the incorporation of a second thienyl unit into 3-chloro-4-thienylmaleimides **6**. Under previously developed conditions, the reaction of **6a** with **3b** (60 mol %) afforded the coupling product in low yield (< 50 %), probably due to high steric hindrance. Fortunately, after studying different palladium sources ($[Pd(OAc)_2]$, $[Pd_2dba_3]$ (dba = dibenzylideneacetone), $Pd(PtBu_3)_2]$) and ligands (SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl; XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl; and CataCXium A = di(1-adamantyl)-*n*-butylphosphine), we found that $[Pd_2dba_3]$ (2.5 mol %) and SPhos (10 mol %) in THF heated at reflux gave the best results: dithienylmaleimide **7** was obtained in excellent yield (96 %) after 20 h at 80 °C (Table 3, entry 1). Interestingly, ^1H NMR spectroscopic analysis of **7** showed a 32:68 mixture of the open/closed isomers (see Table 5 below) from the photochemical cyclization under ambient light. This observation further emphasizes the behavior of these dithienylmaleimides as photochemical switches.

Under the same reaction conditions, the coupling of the dithienylchloromaleimide **6c** with **3b** afforded DTE **8** in 66 % yield (Table 3, entry 2) and the coupling reactions of chloromaleimide **6g** with various organoindium reagents (**3a**–**3f**) provided the dithienylmaleimides **9**–**13** in good yields (79–96 %, Table 3, entries 3–7). In all cases, except for **8**, the novel DTEs were isolated as a mixture of open and closed isomers in variable ratios (from 89:11 for **10** to 54:46 for **12**; see Table 5 below). The isomers were isolated by HPLC (except for **13**) and crystallization to enable the photochemical and kinetic properties to be studied.

Table 2. Palladium-catalyzed mono-cross-coupling reactions of triorganoindium reagents with **2a**.



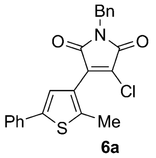
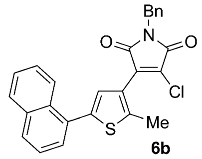
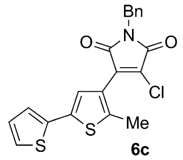
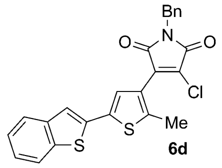
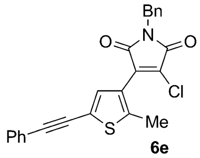
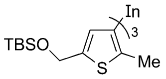
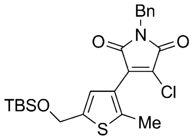
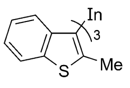
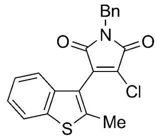
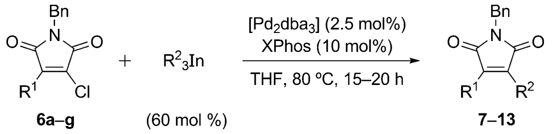
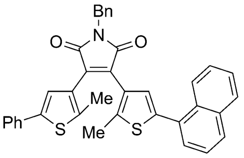
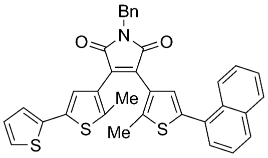
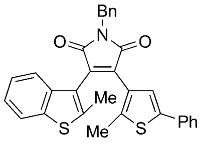
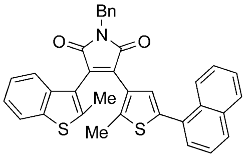
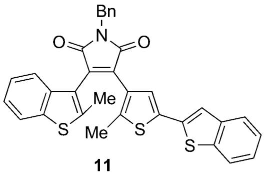
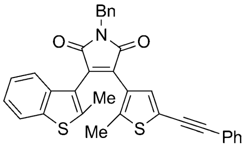
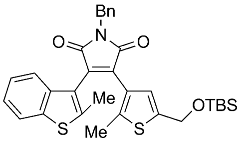
Entry	R^1_3In	Product **6**	Yield [%]
1	**3a**	 **6a**	70
2	**3b**	 **6b**	76
3	**3c**	 **6c**	54
4	**3d**	 **6d**	59
5	**3e**	 **6e**	52
6	 **3f**	 **6f**	62
7	 **3g**	 **6g**	83

Table 3. Palladium-catalyzed cross-coupling reactions of triorganoindium reagents with 3-chloro-4-thienylmaleimides **6**.



Entry	6	R^1_3In	Product	Yield [%]
1	**6a**	**3b**	 **7**	96
2	**6c**	**3b**	 **8**	66
3	**6g**	**3a**	 **9**	92
4	**6g**	**3b**	 **10**	96
5	**6g**	**3d**	 **11**	81
6	**6g**	**3e**	 **12**	90
7	**6g**	**3f**	 **13**	79

Overall, this synthetic sequence enabled us to prepare a series of nonsymmetrical dithienylmaleimides functionalized with valuable groups such as naphthyl, benzo[*b*]thiophenyl, or alkynyl (**10**–**12**) or a group with the possibility of further functionalization, as in **13**. The high selectivity observed for the coupling reactions is remarkable and allows easy access to novel DTEs by using indium organometallic reagents.

Photochemical and kinetic studies

The open isomers resulted in bright-yellow solutions in $CHCl_3$ and their UV spectra showed an intense absorption in the UV range $\lambda = 290–340$ nm, probably due to the presence of aromatic moieties, and a broad absorption band ($\lambda = 400–420$ nm) in the visible range (Table 4). The latter is usually attributed to charge transfer from the electron-rich thiophene to the electron-deficient maleimide ring.[14e,f] The general short range of the absorption band indicates that the substitution at the thiophene has a small effect on the absorption characteristics of the DTEs.

The irradiation of bright-yellow solutions of the compounds in $CHCl_3$ with UV light ($\lambda = 313$ nm) resulted in a rapid color change to dark red (except for **8**, for which photocyclization was not observed), with an increase in the band at $\lambda \approx 410$ nm in the UV spectra and the appearance of a new band in the visible region at $\lambda = 509–574$ nm (extinction coefficient (ε) = $2.2–19.7 \times 10^3\,\text{M}^{-1}\,\text{cm}^{-1}$, Table 4). The λ and ε values are associated with a $\pi \rightarrow \pi^*$ transition allowed both by spin and symmetry, which corresponds to the closed isomers of the irradiated compounds.

Interestingly, the solutions of cyclic isomers became colorless again upon irradiation with visible light ($\lambda > 550$ nm). The photocycloreversion to the opened isomers can be monitored by changes in the UV spectra. The progressive disappearance of the band in the visible range ($\lambda = 509–574$ nm) and decrease in intensity of the band at $\lambda \approx 410$ nm until, finally, the initial spectra are obtained indicates the reversibility of the process. The presence of the same isosbestic points in the spectra confirm the reversibility of the process without secondary reactions. As an example, absorption spectra for the photoconversion of **7** are shown in Figure 1 a.

To test the fatigue resistance and the thermal stability of the materials, the closing–opening cycle (coloration–bleaching) was performed at least twice (Figure 1 b). The sequence was also followed by HPLC (Table 5). Irradiation of pure **7** at $\lambda = 313$ nm showed the photocyclization of the 13:87 ratio of open/closed isomers in the photostationary state (Table 5, entry 1). For **9** and **10**, the photoconversion ratio was reduced to 36:64 and 46:54, respectively, which indicated a lower efficiency for the photocyclization process (Table 5, entries 2 and 3). For **11** and **12** the conversion ratio was close to that observed for **7** (Table 5, entries 4 and 5). Interestingly, the irradiation of these mixtures with visible light ($\lambda > 550$ nm) resulted in the regeneration of the open isomers with higher ratios (open/closed up to 96:4, Table 5). Notably, these values were essentially maintained in a second coloration–bleaching cycle (Table 5).

Dithienylethene **8** is special case. In solution it has a characteristic orange color with a sharp absorption band at $\lambda = 323$ nm and an intense broad band at $\lambda = 480$ nm ($\varepsilon = 15.8 \times 10^3\,\text{M}^{-1}\,\text{cm}^{-1}$; Table 4, entry 2). In this case, photochromism was not detected under irradiation with UV or visible light. Relative to other DTEs prepared, the absorption in the visible range was bathochromically shifted by 65–78 nm and had a higher intensity. This photochemical behavior could be attributed to

Table 4. Absorption characteristics of photochromic dithienylmaleimides **7**–**13**.[a]

Entry	Compound	λ_O [nm] ($\varepsilon=[10^3\ M^{-1}cm^{-1}]$)	λ_C [nm] ($\varepsilon=[10^3\ M^{-1}cm^{-1}]$)	Φ_{O-C}	Φ_{C-O}
1	**7**	293 (29.2), 321 (25.2) 410 (5.0)	322 (31.3), 367 sh[b] (37.5), 387 (43.3), 574 (14.1)	0.39	0.03
2[c]	**8**	323 (27.8), 480 (15.8)	–	–	–
3	**9**	290 (22.7), 415 (5.1)	317 (22.6), 413 (11.0), 542 (7.8)	0.31	0.11
4	**10**	298 sh (14.4), 413 (4.3)	322 (11.5), 335 (11.5), 405 (9.5), 531 (5.8)	0.34	0.26
5	**11**	318 sh (24.9), 339 (28.5), 417 (4.9)	318 sh (24.8), 347 (29.6), 404 (14.6), 555 (12.9)	0.15	0.01
6	**12**	299 sh (24.2), 329 (27.7), 413 (5.0)	318 sh (44.4), 343 (52.1), 416 (23.2), 550 (19.7)	0.27	0.08
7[d]	**13**	247 (18.5), 288 sh (8.3), 401 (4.6)	246 (18.6), 271 sh (12.1), 331 (6.7), 395 (6.9), 509 (2.2)	–	–

[a] λ_O and λ_C are the wavelengths of the absorption band maxima for open (after HPLC separation) and cyclic forms (stationary state after irradiation at $\lambda=313$ nm), respectively. The contribution of the open form to λ_C was not subtracted. Quantum yields for the photocyclization (Φ_{O-C}) and photocycloreversion reactions (Φ_{C-O}) were calculated by the literature method.[31] [b] sh = shoulder. [c] Photoreaction was not detected for compound **8**. [d] The two isomers of **13** were not separated by HPLC. The extinction coefficients were estimated according the extinction coefficient at the isosbestic point at $\lambda=313$ nm.

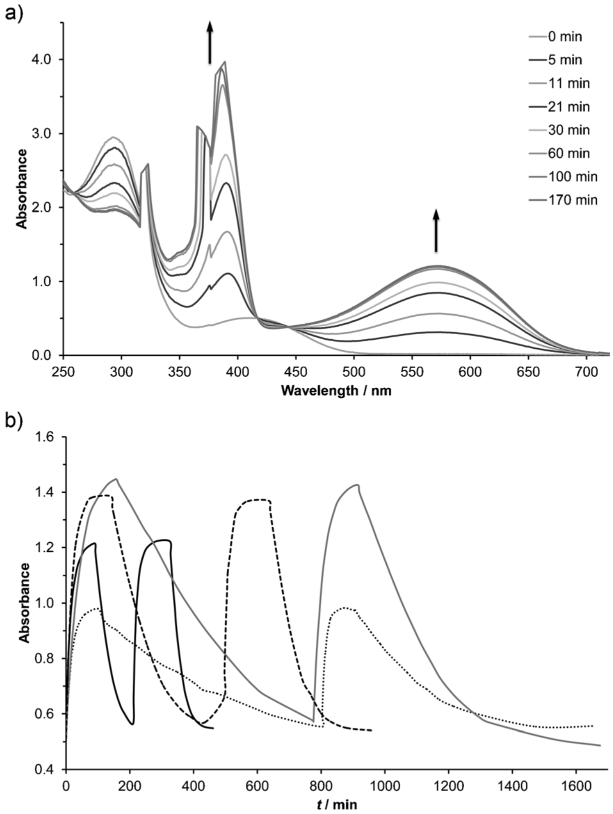


Figure 1. a) Time-resolved spectra for photocyclization of **7** ($\lambda=313$ nm, [**7**] ~ 10^{-4} M, $T=25\,^{\circ}$C) and b) cycling between the open and closed forms of **7** (•••••), **9** (——), **11** (——), and **12** (-----) by repetitive irradiation at $\lambda=313$ nm (ring closure) and $\lambda>550$ nm (ring opening) in $CHCl_3$ at 25 °C (values at $\lambda=410$ nm).

the occurrence of a high charge transfer from the thiophene rings to the electron-deficient maleimide bridge to result in complete inhibition of the photoreaction. The reduction or inhibition of the photoreaction efficiency can be explained by the formation of a twisted intramolecular charge transfer (TICT) excited state, which is characterized by a twist of the single bonds between the thiophenes and the maleimide bridge.[14f,30]

Table 5. Photoconversion ratios of dithienylethenes **7** and **9**–**12** in the photostationary state after two irradiation sequences at $\lambda=313$ nm and $\lambda>550$ nm and with ambient light.[a]

	Cmpd	Ambient light[b]	First irradiation cycle[c]		Second irradiation cycle[c]	
			$\lambda_1=313$ nm	$\lambda_1>550$ nm	$\lambda_2=313$ nm	$\lambda_2>550$ nm
1	**7**	32:68	13:87	94:6	14:86	92:8
2	**9**	58:42	36:64	93:7	33:67	97:3
3	**10**	89:11	46:54	96:4	47:53	97:3
4	**11**	63:37	21:79	79:21	14:86	82:18
5	**12**	54:46	16:84	94:6	16:84	91:9

[a] Photoreaction was not detected for compound **8** and compound **13** was not separated by HPLC. [b] Values correspond to the open/closed ratio of isomers measured by HPLC in the photostationary state after irradiation. [c] λ_1 and λ_2 correspond to the wavelengths of the irradiation light in the first and second cycle, respectively.

Kinetic studies showed that all the photocyclizations follow first-order kinetics (Table 6) and are almost complete after 150–200 min, except for **13**, for which the photostationary state is achieved after 40 min of irradiation. Interestingly, the photocycloreversion requires a longer reaction time (about 400 min) and **13** only required 40 min. This fact can be explained by the conformation of the compound (see below). The reaction rates for these compounds are lower relative to those of other DTEs (i.e., with a perfluorocyclopentene bridge), but similar to those reported previously for other 3,4-dithienylmaleimides. This behavior can be explained by charge transfer between the thiophene and the maleimide bridges, which can affect the efficiency of the photochemical cyclization and diminish the rate and yield of these reactions and, in some cases, can even afford compounds that do not cyclize under irradiation.[14e,f] Finally, the rate constants for the second cycle are slightly faster than the first, probably due to a conformational effect if the required antiparallel conformation was favored after the first photocycloreversion.

To determine the efficiency of the process, the photocyclization and photocycloreversion quantum yields (Φ) were determined by a photokinetic method based on time-resolved absorbance measurements for both the photocoloration and

Table 6. Kinetic rate constants for the photochemical reactions of **7** and **9–13** after two irradiation sequences at $\lambda = 313$ and 550 nm.[a]

		First cycle		Second cycle	
Entry	Compound	k_{313} [s^{-1}]	k_{550} [s^{-1}]	k_{313} [s^{-1}]	k_{550} [s^{-1}]
1	**7**	$(5.8 \pm 0.1) \times 10^{-2}$	$(2.9 \pm 0.1) \times 10^{-3}$	$(8.89 \pm 0.07) \times 10^{-2}$	$(5.0 \pm 0.2) \times 10^{-3}$
2	**9**	$(6.7 \pm 0.2) \times 10^{-2}$	$(2.02 \pm 0.09) \times 10^{-2}$	$(9.6 \pm 0.2) \times 10^{-2}$	$(3.1 \pm 0.1) \times 10^{-2}$
3	**10**	$(5.31 \pm 0.07) \times 10^{-2}$	$(3.2 \pm 0.1) \times 10^{-2}$	$(7.8 \pm 0.1) \times 10^{-2}$	$(7.0 \pm 0.4) \times 10^{-2}$
4	**11**	$(2.40 \pm 0.03) \times 10^{-2}$	$(2.4 \pm 0.1) \times 10^{-3}$	$(3.40 \pm 0.04) \times 10^{-2}$	$(4.3 \pm 0.2) \times 10^{-3}$
5	**12**	$(5.46 \pm 0.06) \times 10^{-2}$	$(8.1 \pm 0.4) \times 10^{-3}$	$(7.65 \pm 0.08) \times 10^{-2}$	$(1.21 \pm 0.05) \times 10^{-2}$
6	**13**	0.106 ± 0.008	0.110 ± 0.002	0.106 ± 0.004	0.10 ± 0.01

[a] k_{313} and k_{550} correspond to the rate constants for photocyclization ($\lambda = 313$ nm) and photocycloreversion ($\lambda = 550$ nm), respectively, in the first and second irradiation cycles.

photobleaching processes (Table 4).[31] The photocyclization (open–closed form) quantum yields fall in the range $\Phi_{O\text{-}C} = 0.15\text{–}0.39$, whereas the photocycloreversion (closed–open form) quantum yields ($\Phi_{C\text{-}O}$) are lower, especially for **7**, **11**, and **12**. These results are consistent with those observed from kinetic data for analogous dithienylethene systems.[1b] Interestingly, X-ray analysis of **10** and **13** showed a parallel conformation for **10**, with the thiophene moieties aligned perpendicularly to the maleimide bridge, and an antiparallel conformation for **13** (Figure 2).[32] It is known that the open-ring isomers of dithienylethenes can exist in two limiting conformations, parallel and antiparallel, and that the conrotatory photocyclization can proceed only from the antiparallel conformer.[33] Even though the two conformations could probably interconvert with each other in solution, the presence of the parallel conformation for **10** could explain the relatively low reactivity towards the photocyclization with respect to **13** in terms of the kinetic rate constants. Nevertheless, because the photochemical and kinetic studies were performed in solution, the differences in reactivity can also be attributed to other factors.

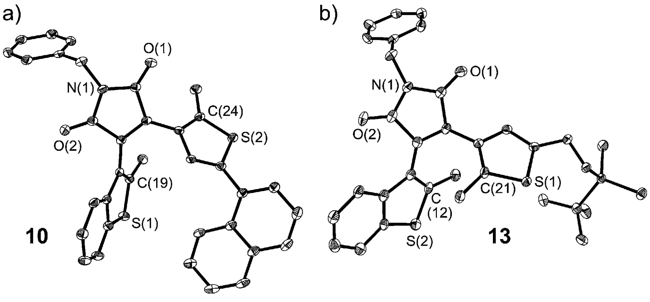


Figure 2. ORTEP drawings (showing 40% probability displacement ellipsoids) of the crystal structures of **10** and **13**.[32] The hydrogen atoms are omitted for clarity.

Conclusion

A series of novel nonsymmetrical DTEs with a maleimide bridge were synthesized by a convergent route based on sequential selective palladium-catalyzed cross-coupling reactions of indium organometallic reagents. This route constitutes a novel entry to the synthesis of nonsymmetrical DTEs, and the high reactivity, selectivity, and atom economy shown by triorganoindium reagents in coupling reactions makes them useful and versatile synthetic tools in this context. In general, photochemical and kinetic studies showed that these compounds undergo a photocyclization reaction upon irradiation with UV light and a photocycloreversion when treated with visible light. This behavior could allow the use of these molecules as photochemical switches. ON–OFF operations can be repeated in successive cycles without an appreciable loss in effectiveness of the process. Further studies on the synthesis and photochemical studies of novel DTEs are currently ongoing in our laboratories.

Acknowledgements

We are grateful to the Spanish Ministerio de Ciencia e Innovación (MICINN) and Ministerio de Economía y Competitividad (MINECO) (grant numbers CTQ2009–07180, CTQ2012–31200, and ACI2010–1093), the Xunta de Galicia (grant number INCITE08PXIB103167PR), and the EDRF funds for financial support. A.M. also thanks the Spanish Ministerio de Educación y Ciencia (MEC) for a predoctoral fellowship (Formación de Personal Investigador). We also acknowledge the assistance of Prof. Alberto Fernández for processing the X-ray data.

Keywords: C–C coupling · indium · palladium catalysis · photochemical reactions · photochromism

[1] a) *Molecular Switches*, 2ednd ed(Eds.: B. L. Feringa, W. R. Browne), Wiley-VCH, Weinheim, **2011**. For reviews, see: b) S. Kobatake, M. Irie, *Annu. Rep. Prog. Chem. Sect. C: Phys. Chem.* **2003**, *99*, 277 – 313; c) H. Tian, Y. Feng, *J. Mater. Chem.* **2008**, *18*, 1617 – 1622; d) V. A. Barachevsky, M. M. Krayushkin, *Russ. Chem. Bull.* **2008**, *57*, 867 – 875; e) J. Cusido, E. Deniz, F. M. Raymo, *Eur. J. Org. Chem.* **2009**, 2031 – 2045; f) C. Brieke, F. Rohrbach, A. Gottschalk, G. Mayer, A. Heckel, *Angew. Chem.* **2012**, *124*, 8572 – 8604; *Angew. Chem. Int. Ed.* **2012**, *51*, 8446 – 8476.

[2] a) L. Ubaghs, D. Sud, N. R. Branda, in *Handbook of Thiophene-based Materials: Applications in Organic Electronics and Photonics* (Eds.; I. F. Perepichka, D. Perepichka) Wiley, Chichester, **2009**, Vol. 2, pp. 783 – 811. For reviews, see: b) M. Irie, *Chem. Rev.* **2000**, *100*, 1685 – 1716; c) H. Tian, S. Yang, *Chem. Soc. Rev.* **2004**, *33*, 85 – 97; d) S. Kobatake, M. Irie, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 195 – 210; e) H. D. Samachetty, N. R. Branda, *Pure Appl. Chem.* **2006**, *78*, 2351 – 2359; f) H. Tian, S. Wang, *Chem. Commun.* **2007**, 781 – 792; g) C. Yun, J. You, J. Kim, J. Huh, E. Kim, *J. Photochem. Photobiol. C* **2009**, *10*, 111 – 129; h) A. Perrier, F. Maurel, D. Jacquemin, *Acc. Chem. Res.* **2012**, *45*, 1173 – 1182; i) H. Logtenberg, W. R. Browne, *Org. Biomol. Chem.* **2013**, *11*, 233 – 243; j) T. Hirose, K. Matsuda, *Org. Biomol. Chem.* **2013**, *11*, 873 – 880.

[3] a) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* **2002**, *420*, 759 – 760; b) F. M. Raymo, M. Tomasulo, *J. Phys. Chem. A* **2005**, *109*, 7343 – 7352.

[4] a) A. Peters, N. R. Branda, *J. Am. Chem. Soc.* **2003**, *125*, 3404 – 3405; b) H. Logtenberg, W. R. Browne, *Org. Biomol. Chem.* **2013**, *11*, 233 – 243.

[5] M.-S. Kim, H. Maruyama, T. Kawai, M. Irie, *Chem. Mater.* **2003**, *15*, 4539 – 4543.

[6] For recent examples, see: a) Y. Li, A. Urbas, Q. Li, *J. Org. Chem.* **2011**, *76*, 7148 – 7156; b) H. Hayasaka, T. Miyashita, M. Nakayama, K. Kuwada, K. Akagi, *J. Am. Chem. Soc.* **2012**, *134*, 3758 – 3765; c) T. Hirose, K. Matsuda, *Org. Biomol. Chem.* **2013**, *11*, 873 – 880.

[7] a) F. M. Raymo, M. Tomasulo, *Chem. Eur. J.* **2006**, *12*, 3186 – 3193; b) E. Orgiu, N. Crivillers, M. Herder, L. Grubert, M. Pätzel, J. Frisch, E. Pavlica, D. T. Duong, G. Bratina, A. Salleo, N. Koch, S. Hecht, P. Samorì, *Nat. Chem.* **2012**, *4*, 675 – 679.

[8] U. Al-Atar, R. Fernandes, B. Johnsen, D. Baillie, N. R. Branda, *J. Am. Chem. Soc.* **2009**, *131*, 15966 – 15967.

[9] M. Morimoto, M. Irie, *J. Am. Chem. Soc.* **2010**, *132*, 14172 – 14178.

[10] a) K. Fujimoto, M. Kajino, I. Sakaguchi, M. Inouye, *Chem. Eur. J.* **2012**, *18*, 9834 – 9840; b) H. Cahová, A. Jäschke, *Angew. Chem.* **2013**, *125*, 3268 – 3272; *Angew. Chem. Int. Ed.* **2013**, *52*, 3186 – 3190.

[11] G. Szalóki, J.-L. Pozzo, *Chem. Eur. J.* **2013**, *19*, 11124 – 11132.

[12] a) S. Hiroto, K. Suzuki, H. Kamiya, H. Shinokubo, *Chem. Commun.* **2011**, *47*, 7149 – 7151; b) H. Kamiya, S. Yanagisawa, S. Hiroto, K. Itami, H. Shinokubo, *Org. Lett.* **2011**, *13*, 6394 – 6397.

[13] a) J. J. D. de Jong, L. N. Lucas, R. Hania, A. Pugzlys, R. M. Kellogg, B. L. Feringa, K. Duppen, J. H. V. Esch, *Eur. J. Org. Chem.* **2003**, 1887 – 1893; b) P. R. Hania, A. Pugzlys, L. N. Lucas, J. J. D. de Jong, B. L. Feringa, J. H. van Esch, H. T. Jonkman, K. Duppen, *J. Phys. Chem. A* **2005**, *109*, 9437 – 9442; c) V. A. Migulin, M. M. Krayushkin, V. A. Barachevsky, O. I. Kobeleva, T. M. Valova, K. A. Lyssenko, *J. Org. Chem.* **2012**, *77*, 332 – 340.

[14] a) T. Yamaguchi, K. Uchida, M. Irie, *J. Am. Chem. Soc.* **1997**, *119*, 6066 – 6071; b) M. M. Krayushkin, V. Z. Shirinyan, L. I. Belen'kii, A. A. Shimkin, A. Y. Martynkin, B. M. Uzhinov, *Russ. J. Org. Chem.* **2002**, *38*, 1335 – 1338; c) S. V. Shorunov, M. M. Krayushkin, F. M. Stoyanovich, M. Irie, *Russ. J. Org. Chem.* **2006**, *42*, 1490 – 1497; d) A. El Yahyaoui, G. Félix, A. Heynderickx, C. Moustrou, A. Samat, *Tetrahedron* **2007**, *63*, 9482 – 9487; e) M. Ohsumi, M. Hazama, T. Fukaminato, M. Irie, *Chem. Commun.* **2008**, 3281 – 3283; f) M. Herder, M. Utecht, N. Manicke, L. Grubert, M. Pätzel, P. Saalfrank, S. Hecht, *Chem. Sci.* **2013**, *4*, 1028 – 1040.

[15] a) M. Irie, M. Mohri, *J. Org. Chem.* **1988**, *53*, 803 – 808; b) M. M. Krayushkin, V. N. Yarovenko, S. L. Semenov, V. Z. Shirinyan, A. Y. Martynkin, B. M. Uzhinov, *Russ. J. Org. Chem.* **2002**, *38*, 1331 – 1334; c) S. V. Shorunov, F. M. Stoyanovich, M. M. Krayushkin, *Russ. Chem. Bull.* **2004**, *53*, 2338 – 2339.

[16] J.-I. Kitai, T. Kobayashi, W. Uchida, M. Hatakeyama, S. Yokojima, S. Nakamura, K. Uchida, *J. Org. Chem.* **2012**, *77*, 3270 – 3276.

[17] W. Zhu, X. Meng, Y. Yang, Q. Zhang, Y. Xie, H. Tian, *Chem. Eur. J.* **2010**, *16*, 899 – 906.

[18] a) H.-H. Liu, Y. Chen, *J. Phys. Chem. A* **2009**, *113*, 5550 – 5553; b) G. Duan, W.-T. Wong, V. W.-W. Yam, *New J. Chem.* **2011**, *35*, 2267 – 2278; c) B. M. Neilson, V. M. Lynch, C. W. Bielawski, *Angew. Chem.* **2011**, *123*, 10506 – 10510; *Angew. Chem. Int. Ed.* **2011**, *50*, 10322 – 10326; d) W. Zhu, Y. Yang, R. Métivier, Q. Zhang, R. Guillot, Y. Xie, H. Tian, K. Nakatani, *Angew. Chem.* **2011**, *123*, 11178 – 11182; *Angew. Chem. Int. Ed.* **2011**, *50*, 10986 – 10990; e) B. M. Neilson, C. W. Bielawski, *J. Am. Chem. Soc.* **2012**, *134*, 12693 – 12699; f) S. Chen, L.-J. Chen, H.-B. Yang, H. Tian, W. Zhu, *J. Am. Chem. Soc.* **2012**, *134*, 13596 – 13599; g) Y. Wu, Y. Xie, Q. Zhang, H. Tian, W. Zhu, A. D. Q. Li, *Angew. Chem. Int. Ed.* **2014**, *53*, 2090 – 2094.

[19] a) V. A. Migulin, M. M. Krayushkin, V. A. Barachevsky, O. I. Kobeleva, T. M. Valova, K. A. Lyssenko, *J. Org. Chem.* **2012**, *77*, 332 – 340; b) G. Liu, S. Pu, R. Wang, *Org. Lett.* **2013**, *15*, 980 – 983; c) V. Z. Shirinian, A. G. Lvov, M. M. Krayushkin, E. D. Lubuzh, B. V. Nabatov, *J. Org. Chem.* **2014**, *79*, 3440 – 3451.

[20] Z.-L. Shen, S.-Y. Wang, Y.-K. Chok, Y.-H. Xu, T.-P. Loh, *Chem. Rev.* **2013**, *113*, 271 – 401.

[21] a) I. Pérez, J. Pérez Sestelo, L. A. Sarandeses, *Org. Lett.* **1999**, *1*, 1267 – 1269; b) I. Pérez, J. Pérez Sestelo, L. A. Sarandeses, *J. Am. Chem. Soc.* **2001**, *123*, 4155 – 4160; c) M. A. Pena, I. Pérez, J. Pérez Sestelo, L. A. Sarandeses, *Chem. Commun.* **2002**, 2246 – 2247; d) M. A. Pena, J. Pérez Sestelo, L. A. Sarandeses, *Synthesis* **2003**, 780 – 784; e) D. Rodríguez, J. Pérez Sestelo, L. A. Sarandeses, *J. Org. Chem.* **2003**, *68*, 2518 – 2520; f) D. Rodríguez, J. Pérez Sestelo, L. A. Sarandeses, *J. Org. Chem.* **2004**, *69*, 8136 – 8139; g) R. Riveiros, D. Rodríguez, J. Pérez Sestelo, L. A. Sarandeses, *Org. Lett.* **2006**, *8*, 1403 – 1406; h) M. A. Pena, J. Pérez Sestelo, L. A. Sarandeses, *J. Org. Chem.* **2007**, *72*, 1271 – 1275; i) J. Caeiro, J. Pérez Sestelo, L. A. Sarandeses, *Chem. Eur. J.* **2008**, *14*, 741 – 746; j) R. Riveiros, L. Saya, J. Pérez Sestelo, L. A. Sarandeses, *Eur. J. Org. Chem.* **2008**, 1959 – 1966; k) Á. Mosquera, M. A. Pena, J. Pérez Sestelo, L. A. Sarandeses, *Eur. J. Org. Chem.* **2013**, 2555 – 2562.

[22] a) Á. Mosquera, R. Riveiros, J. Pérez Sestelo, L. A. Sarandeses, *Org. Lett.* **2008**, *10*, 3745 – 3748; b) L. Bouissane, J. Pérez Sestelo, L. A. Sarandeses, *Org. Lett.* **2009**, *11*, 1285 – 1288; c) M. M. Martínez, M. Peña-López, J. Pérez Sestelo, L. A. Sarandeses, *Org. Biomol. Chem.* **2012**, *10*, 3892 – 3898; d) M. M. Martínez, C. Pérez-Caaveiro, M. Peña-López, L. A. Sarandeses, J. Pérez Sestelo, *Org. Biomol. Chem.* **2012**, *10*, 9045 – 9051.

[23] C. Elsner, T. Cordes, P. Dietrich, M. Zastrow, T. T. Herzog, K. Rück-Braun, W. Zinth, *J. Phys. Chem. A* **2009**, *113*, 1033 – 1039.

[24] a) C.-W. Chiu, T. J. Chow, C.-H. Chuen, H.-M. Lin, Y.-T. Tao, *Chem. Mater.* **2003**, *15*, 4527 – 4532; b) B. K. Kaletaş, C. Mandl, G. van der Zwan, M. Fanti, F. Zerbetto, L. De Cola, B. König, R. M. Williams, *J. Phys. Chem. A* **2005**, *109*, 6440 – 6449.

[25] C. Wang, F. Glorius, *Angew. Chem.* **2009**, *121*, 5342 – 5346; *Angew. Chem. Int. Ed.* **2009**, *48*, 5240 – 5244.

[26] S. Schröter, C. Stock, T. Bach, *Tetrahedron* **2005**, *61*, 2245 – 2267.

[27] Triorganoindium reagents were prepared in situ from the corresponding organolithium reagent (100 mol %) and $InCl_3$ (35 mol %) in solution in THF, and were used without isolation. Direct synthesis from indium metal and the corresponding bromides can be also performed, see: a) Y.-H. Chen, P. Knochel, *Angew. Chem.* **2008**, *120*, 7760 – 7763; *Angew. Chem. Int. Ed.* **2008**, *47*, 7648 – 7651; b) V. Papoian, T. Minehan, *J. Org. Chem.* **2008**, *73*, 7376 – 7379; c) Z.-L. Shen, K. K. K. Goh, Y.-S. Yang, Y.-C. Lai, C. H. A. Wong, H.-L. Cheong, T.-P. Loh, *Angew. Chem.* **2011**, *123*, 531 – 534; *Angew. Chem. Int. Ed.* **2011**, *50*, 511 – 514; d) L. Adak, N. Yoshikai, *J. Org. Chem.* **2011**, *76*, 7563 – 7568; e) S. Bernhardt, Z.-L. Shen, P. Knochel, *Chem. Eur. J.* **2013**, *19*, 828 – 833.

[28] Other Pd^0 or Pd^{II} catalytic systems ($[Pd(PPh_3)_4]$, $[Pd_2dba_3]\cdot$DavePhos, $[PdCl_2(PhCN)_2]$, $[PdCl_2(DPEphos)]$ (DavePhos = 2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl; DPEphos = bis[(2-diphenylphosphino)phenyl] ether) afforded lower yields of the monocoupling product **5 a** under the same reaction conditions (40–63 %).

[29] *Acetylene Chemistry: Chemistry, Biology and Material Science* (Eds.: F. Diederich, P. J. Stang, R. R. Tykwinski), Wiley-VCH, Weinheim, **2005**.

[30] a) M. Irie, K. Sayo, *J. Phys. Chem.* **1992**, *96*, 7671 – 7674; b) Z. R. Grabowski, K. Rotkiewicz, W. Rettig, *Chem. Rev.* **2003**, *103*, 3899 – 4032.

[31] a) G. Ottavi, F. Ortica, G. Favaro, *Int. J. Chem. Kinet.* **1999**, *31*, 303 – 313; b) F. Ortica, P. Smimmo, C. Zuccaccia, U. Mazzucato, G. Favaro, N. Impagnatiello, A. Heynderickx, C. Moustrou, *J. Photochem. Photobiol. A* **2007**, *188*, 90 – 97.

[32] CCDC-1005631 (**10**), and 1005632 (**13**) 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.

[33] S. Kobatake, M. Irie, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 195 – 210.

Received: May 29, 2014

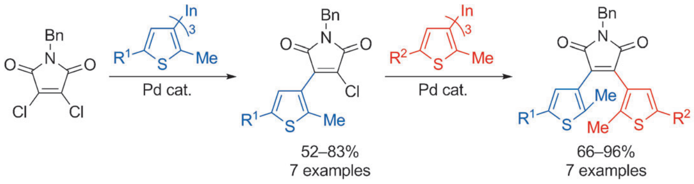
FULL PAPER

Photochromic Compounds

*Á. Mosquera, M. I. Férnandez,
M. Canle Lopez, J. Pérez Sestelo,*
L. A. Sarandeses**

■■ – ■■

Nonsymmetrical 3,4-Dithienylmaleimides by Cross-Coupling Reactions with Indium Organometallics: Synthesis and Photochemical Studies



Photochromic compounds: Triorganoindium reagents are useful reagents for the synthesis of nonsymmetrical 3,4-dithienylmaleimides by palladium-catalyzed cross-coupling reactions (see scheme). Photochemical studies show that these novel compounds undergo photocyclization–photocycloreversion upon irradiation, which allows their use as photochemical switches.