ORGANIC
LETTERS

2007
Vol. 9, No. 11
2139−2142

Efficient Synthesis and Properties of Isomeric Photochromic Diarylethenes Having a Pyrrole Unit

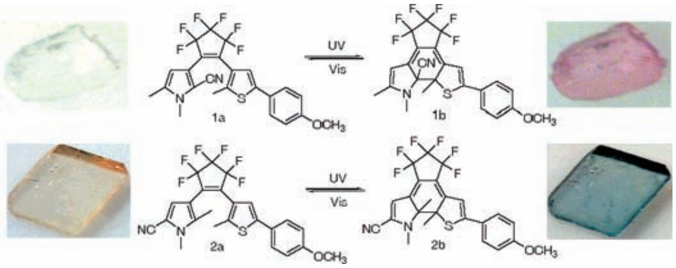
Shouzhi Pu,* Gang Liu, Liang Shen, and Jingkun Xu

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science & Technology Normal University, Nanchang 330013, People's Republic of China

pushouzhi@tsinghua.org.cn

Received March 14, 2007

ABSTRACT



Two new isomeric photochromic diarylethenes with a pyrrole unit have been developed. Their properties, including photochromic behavior, crystal structures, and fluorescent properties, have been investigated. The two isomeric compounds show distinctly different photochromism, both in solution and in the single-crystalline phase: one turns red upon photocyclization whereas the other turns blue, which may be attributed to the different substituent effects.

Photochromic diarylethene derivatives have attracted much attention as highly promising candidates for optoelectronic devices such as optical memories and photoswitches, mainly due to the excellent thermal stability of the respective isomers, notable fatigue resistance, and high reactivity in the solid state.[1] Recently, the design and synthesis of novel diarylethene systems with different aryl moieties has become an active area of research. Among the diarylethenes hitherto reported, most of the heteroaryl moieties have been thiophene or benzothiophene rings,[2] with just a few reports concerning other heteroaryl moieties, such as furan,[3] thiazole,[4] indole,[5] benzofuran,[6] indene,[7] pyrazole,[8] etc. The majority of the research work reported to date has been devoted to the development of these molecules and investigative studies of their fundamental properties, and the results obtained have contributed to a broad understanding of the photochromism of diarylethenes.[9] At the same time, the results have also demonstrated that the photochromic performance of each type of diarylethene is strongly dependent on the nature of the aryl groups. For instance, diarylethenes with thiophene or benzothiophene moieties exhibit excellent thermal stability and outstanding fatigue resistance,[1] whereas diarylethenes

---

(1) (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (b) Tian, H.; Yang, S. J. *Chem. Soc. Rev.* **2004**, *33*, 85. (c) Kawata, S.; Kawata, Y. *Chem. Rev.* **2000**, *100*, 1777. (d) Matsuda, K.; Irie, M. *J. Photochem. Photobiol. C* **2004**, *5*, 169. (e) Raymo, F. M.; Tomasulo, M. *Chem. Soc. Rev.* **2005**, *34*, 327. (f) Morimoto, M.; Irie, M. *Chem. Commun.* **2005**, 3895.

(2) (a) Higashiguchi, K.; Matsuda, K.; Tanifuji, N.; Irie, M. *J. Am. Chem. Soc.* **2005**, *127*, 8922. (b) Frigoli, M.; Welch, C.; Mehl, G. H. *J. Am. Chem. Soc.* **2004**, *126*, 15382. (c) Moriyama, Y.; Matsuda, K.; Tanifuji, N.; Irie, S.; Irie, M. *Org. Lett.* **2005**, *7*, 3315. (d) Tanifuji, N.; Matsuda, K.; Irie, M. *Org. Lett.* **2005**, *7*, 3777. (e) Zhou, Z. G.; Xiao, S. Z.; Xu, J.; Liu, Z. Q.; Shi, M.; Li, F. Y.; Yi, T.; Huang, C. H. *Org. Lett.* **2006**, *8*, 3911. (f) Jeong, Y. C.; Yang, S. I.; Kim, E.; Ahn, K. H. *Tetrahedron* **2006**, *62*, 5855. (g) Kim, E.; Kim, M.; Kim, K. *Tetrahedron* **2006**, *62*, 6814.

(3) Deng, X. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 7703.

(4) (a) Uchida, K.; Ishikawa, T.; Takeshita, M.; Irie, M. *Tetrahedron* **1998**, *54*, 6627. (b) Takami, S.; Irie, M. *Tetrahedron* **2004**, *60*, 6155.

(5) (a) Yagi, K.; Irie, M. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1625. (b) Yagi, K.; Soong, C. F.; Irie, M. *J. Org. Chem.* **2001**, *66*, 5419.

(6) Yamaguchi, T.; Irie, M. *J. Org. Chem.* **2005**, *70*, 10323.

(7) Yamaguchi, T.; Irie, M. *Tetrahedron Lett.* **2006**, *47*, 1267.

(8) (a) Pu, S. Z.; Yang, T. S.; Xu, J. K.; Chen, B. *Tetrahedron Lett.* **2006**, *47*, 6473. (b) Yang, T. S.; Pu, S. Z.; Chen, B.; Xu, J. K. *Can. J. Chem.* **2007**, *85*, 12.

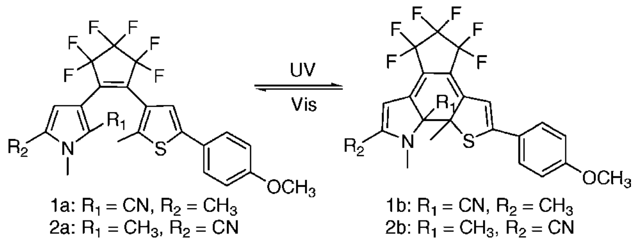
(9) Lee, J. K.-W.; Ko, C.-C.; Wong, K. M.-C.; Zhu, N. Y.; Yam, V. W.-W. *Organometallics* **2007**, *26*, 12.

10.1021/ol070622q CCC: $37.00

with a pyrazole unit have a relatively high cycloreversion quantum yield.[8] Pyrrole is an attractive aryl unit because of its biological characteristics, and its structure is similar to those of thiophene and furan. As far as we are aware, there has been only one example of a photochromic pyrrole derivative, as reported by Uchida et al.[10] They synthesized a symmetrical diarylethene bearing two pyrrole rings, but indicated that it was thermally unstable and reverted to the open-ring form even at room temperature in the dark. To the best of our knowledge, photochromic hybrid diarylethene derivatives bearing both pyrrole and thiophene moieties have not hitherto been reported.

Generally, all diarylethene compounds reported to date have seemingly been synthesized separately, i.e., only one target product was obtained following a series of synthetic operations. The cognate synthesis of two or more isomeric diarylethenes by a parallel series of synthetic operations has never been reported. In this Letter, we describe the parallel preparation of two new hybrid isomeric diarylethenes bearing a pyrrole unit, namely 1-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-3-pyrryl)hexafluorocyclopentene (**1a**) and 1-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl)hexafluorocyclopentene (**2a**) (Scheme 1). Interestingly, these two isomeric diarylethenes **1** and **2** show distinctly different photochromic properties both in solution and in the single-crystalline phase.

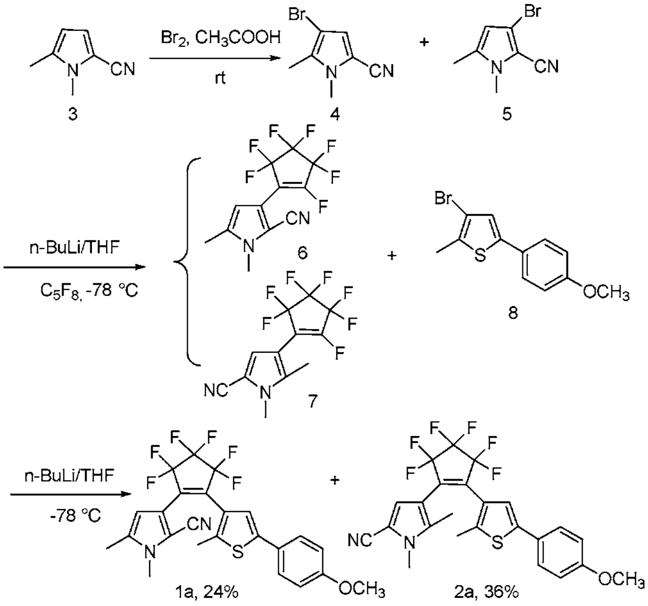
Scheme 1. Mechanistic Rationale of the Photochromic Property of **1** and **2**



The synthetic route to the photochromic diarylethenes **1a** and **2a** is illustrated in Scheme 2. First, compounds **4** and **5** were obtained in a combined yield of 78% by brominating compound **1** in acetic acid at room temperature. Lithiation of the mixture of **4** and **5** followed by the addition of excess octafluorocyclopentene simultaneously generated compounds **6** and **7**, which could be further treated with the anion generated from 3-bromo-2-methyl-5-(4-methoxyphenyl)thiophene (**8**)[11] to yield isomeric diarylethenes **1a** and **2a**. Their structures were confirmed by NMR, MS, and elemental analysis, IR spectroscopy, and X-ray single-crystal diffraction analysis (Supporting Information).

The changes in the absorption spectra of diarylethenes **1** and **2** induced by photoirradiation at room temperature in hexane are shown in Figure 1. Upon irradiation with 297 nm light, the colorless solution of **1a** turned red due to the appearance of a new visible absorption band centered at 537 nm attributable to the closed-ring isomer **1b**. The red solution reverted to colorless upon irradiation with visible light ($\lambda > 450$ nm), indicating that **1b** returned to the initial state **1a**, and a clear isosbestic point was observed at 314 nm. Similarly, upon irradiation with 297 nm light, the colorless solution of **2a** turned blue and an absorption maximum developed at 592 nm as the closed-ring isomer **2b** was generated. The blue color disappeared upon irradiation with visible light ($\lambda > 450$ nm), and an isosbestic point was observed at 317 nm. The cyclization and cycloreversion quantum yields of **1** were determined to be 0.53 and 0.44, respectively. The corresponding cyclization and cycloreversion quantum yields of **2** were measured as 0.55 and 0.10, respectively. It is notable that the cycloreversion quantum

Scheme 2. Synthetic Route to **1** and **2**



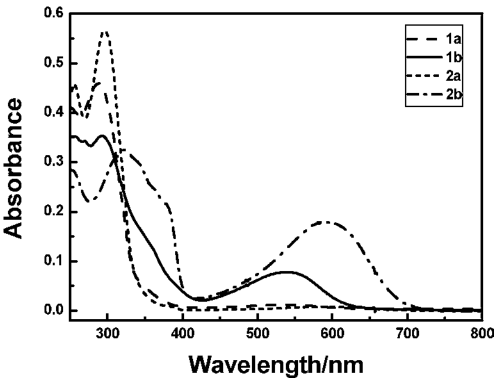


Figure 1. Changes in the absorption spectra of diarylethenes **1** and **2** in hexane solution at room temperature (2.0×10^{-5} M).

---

(10) Uchida, K.; Matsuoka, T.; Sayo, K.; Iwamoto, M.; Hayashi, S.; Irie, M. *Chem. Lett.* **1999**, 835.

(11) (a) Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305. (b) Sun, F.; Zhang, F. S.; Guo, H. B.; Zhou, X. H.; Wang, R. J.; Zhao, F. Q. *Tetrahedron* **2003**, *59*, 7615.

yield of **2** is lower than that of **1**. These facts indicate that, in solution, the two isomeric compounds show remarkable differences in their photochromic behavior. The photochromic properties of diarylethenes **1** and **2** are summarized in Table 1. From these data, it can easily be seen that the photochromic features (including the absorption maxima, molar absorption coefficients, and quantum yields) of diarylethenes **1** and **2** are distinctly different.

Table 1. Photochromic Parameters of Compounds **1** and **2** in Hexane at 2.0 × 10^{-5} M

compd	λ_{max}/nm[a] (ϵ/mol^{-1} cm^{-1})	λ_{max}/nm[b] (ϵ/L mol^{-1} cm^{-1})	ϕ[c]	
			ϕ_{a-b}	ϕ_{b-a}
1	288 (2.3 × 10^4)	537 (3.9 × 10^3)	0.53	0.55
2	296 (2.8 × 10^4)	592 (9.0 × 10^3)	0.44	0.10

[a] Absorption maxima of open-ring forms. [b] Absorption maxima of closed-ring forms. [c] Quantum yields of cyclization (ϕ_{a-b}) and cycloreversion (ϕ_{b-a}), respectively.

To further understand the differences between isomers **1** and **2**, we compared the photophysical properties of the closed-ring isomer **1b** with those of **2b**. Compared to those of **1b**, the absorption maximum of **2b** is red-shifted by 55 nm and the molar absorption coefficient of **2b** is threefold larger. The results indicate that the positions of the methyl (CH_3) and cyano (CN) substituents have a significant effect on the photochromic properties of the two isomeric diarylethene compounds. Although substituent effects on the photochromic behavior of diarylethene derivatives have been reported previously,[1a,8,10,12] no such substituent effect has hitherto been reported for isomers of diarylethene derivatives.

Figure 2 indicates the extent of the conjugation in the closed-ring isomers **1b** and **2b**. In the case of **1b**, the cyano group was involved in the cyclization reaction, and the weakly electron-donating methyl group participates in the conjugation system. In the case of **2b**, the methyl group was involved in the cyclization reaction, and the strongly electron-withdrawing cyano group is conjugated with the methoxy group (OCH_3) through the ethylene moiety. As a result, **2b** becomes a push−pull conjugated system (D−π−A), with the strongly electron-withdrawing cyano group and the electron-donating methoxy group as the acceptor and donor, respectively. Therefore, **2b** exhibits a more marked intramolecular charge transition (ICT) than **1b**, which is consistent with the red-shifted absorption maximum and the strong molar absorption coefficient of **2b** in comparison with those of **1b**.

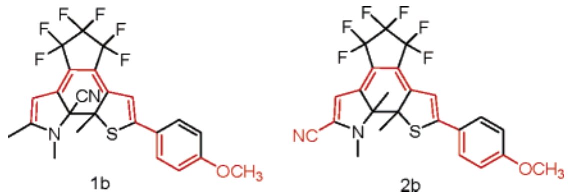


Figure 2. Sketches of the extent of conjugation in the closed-ring systems **1b** and **2b**.

The thermal stabilities of the open-ring and closed-ring isomers of **1** and **2** were examined by storing solutions in hexane at room temperature in the dark and then exposing them to air for more than 2 months. In all cases, no changes in their UV/vis spectra were observed and, indeed, no decomposition was detected when these compounds were exposed to air for more than a year. The fatigue resistances of **1** and **2** were examined in air at room temperature. Solutions of **1** and **2** in hexane were alternately irradiated with light of wavelength 297 nm for 200 s and with visible light (λ > 450 nm) for 60 s. The fatigue-resistant characteristics of **1** and **2** in solution (see the Supporting Information) indicated that 90% of each of **1b** and **2b** was destroyed after 12 repeat cycles. This may be ascribed to degradation resulting from the formation of an epoxide.[13] However, the fatigue resistances of **1** and **2** in the solid state are very strong. After 500 repeat cycles, the two isomeric compounds still showed good photochromism with only ∼20% degradation of each of **1b** and **2b**, both in PMMA film and in the single-crystalline phase (see the Supporting Information). This remarkable improvement may result from effectively suppressing the oxygen diffusion.[1a]

Single crystals of **1a** and **2a** were obtained by recrystallization from chloroform. Their ORTEP drawings are shown in Figure 3, which indicate that both of them are packed in *anti*-parallel conformations[14] in the crystalline phase. The distances between the two reactive carbons of **1a** (C5···C9)

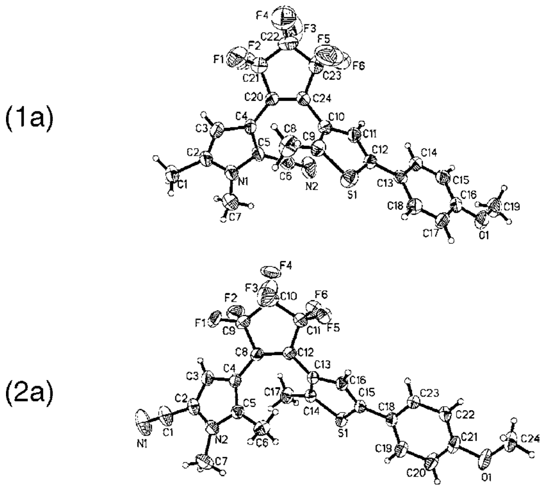


Figure 3. ORTEP drawings of **1a** and **2a** (ellipsoids are drawn at the 35% level).[16]

---

(12) (a) Morimitsu, K.; Shibata, K.; Irie, M. *J. Org. Chem.* **2002**, *67*, 4574. (b) Uchida, K.; Matsuoka, T.; Kobatake, S.; Yamaguchi, T.; Irie, M. *Tetrahedron* **2001**, *57*, 4559. (c) Takami, S.; Irie, M. *Tetrahedron* **2004**, *60*, 6155. (d) Pu, S. Z.; Yang, T. S.; Xu, J. K.; Shen, L.; Li. G. Z.; Xiao, Q.; Chen, B. *Tetrahedron* **2005**, *61*, 6623.

and **2a** (C5···C14) are 3.69 and 3.54 Å, respectively. Generally, such a molecule can undergo photocyclization if it is fixed in an *anti*-parallel mode and the distance between the reacting carbon atoms of the aryl rings is less than 4.2 Å.[1f,15] Therefore, **1a** and **2a** exhibit photochromism in the crystalline phase. This was verified by the fact that photoirradiation of single crystals of **1a** and **2a** resulted in observable color changes (Figure 4). Upon irradiation with 297 nm light, colorless crystals of **1a** and **2a** became red and blue, respectively. The colored crystals returned to colorless upon irradiation with visible light of the appropriate wavelength. The photographs in Figure 4 clearly demonstrate that the photochromic processes of diarylethenes **1** and **2** occur in the crystalline phase.

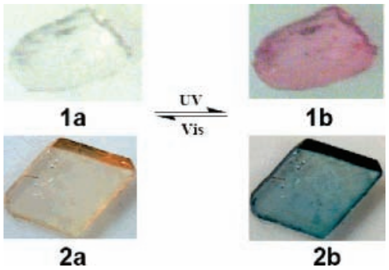


Figure 4. Photographs demonstrating the photochromic processes of diarylethenes **1** and **2** in the crystalline phase.

Furthermore, the fluorescence spectra of **1a** and **2a** in hexane at room temperature are illustrated in Figure 5. Both compounds show good fluorescence at their respective excitation wavelengths. The fluorescent emissions of **1a** and **2a** were observed at 423 and 421 nm upon excitation at 335 and 320 nm, respectively. The fluorescence quantum yields of **1a** and **2a** were determined as 0.019 and 0.016, respectively, using anthracene (0.27 in acetonitrile) as a reference. Thus, it is clear that the position of the substituent on the pyrryl group has a significant effect on the emission intensity, but does not noticeably affect the position of the emission peak. In addition, **1** and **2** exhibited changes in their fluorescences during the process of photoisomerization, as has been observed for most of the reported diarylethenes.[17] The emission intensities of **1a** and **2a** were decreased by photocyclization upon irradiation with 297 nm light. The emission intensities of **1** and **2** in a photostationary state were quenched to ca. 65% and 48%, respectively. The comparatively low cyclization conversions and the existence of parallel conformations of **1a** and **2a** may be the main cause for the moderate change in fluorescence induced by photoirradiation. Compound **2** shows a more marked change in fluorescence upon photocyclization than compound **1** because of its higher absorption efficiency.

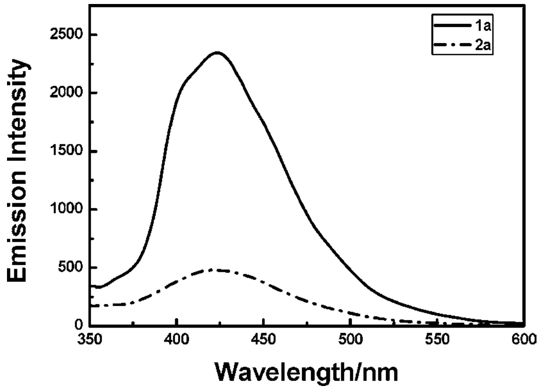


Figure 5. Fluorescence spectra of **1a** and **2a** in hexane (1.0×10^{-4} M) at room temperature, excited at 335 and 320 nm, respectively.

In summary, two new isomeric diarylethenes with a pyrrole unit have been synthesized concomitantly by a parallel series of reaction steps and their properties have been investigated. This new photochromic system showed good thermal stability and strong fatigue resistance in the solid state. Importantly, the two isomeric compounds showed remarkable differences in their photochromic and fluorescent properties, both in solution and in the single-crystalline phase. The results of this study may be useful for the design and synthesis of efficient photoactive diarylethene derivatives with tunable properties.

Acknowledgment. The authors thank the NSFC of China (20564001, 50503009, and 50663001) and the NSFJC (050017) for financial support.

Supporting Information Available: Synthetic and experimental details and a CIF file for **1a** and **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL070622Q

---

(13) Higashiguchi, K.; Matsuda, K.; Yamada, T.; Kawai, T.; Irie, M. *Chem. Lett.* **2000**, 1358.

(14) (a) Irie, M.; Miyatake, O.; Uchida, K. *J. Am. Chem. Soc.* **1992**, *114*, 8715. (b) Kobatake, S.; Irie, M. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 195. (c) Pu, S. Z.; Zhang, F. S.; Sun, F.; Wang, R. J.; Zhou, X. H.; Chan, S.-K. *Tetrahedron Lett.* **2003**, *44*, 1011.

(15) (a) Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. *Chem. Commun.* **2002**, 2804. (b) Morimoto, M.; Irie, M. *Chem. Eur. J.* **2006**, *12*, 4275. (c) Shibata, K.; Muto, K.; Kobatake, S.; Irie, M. *J. Phys. Chem. A* **2002**, *106*, 209. (d) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433.

(16) Crystal data for **1a:** $C_{24}H_{18.67}F_6N_2O_{1.33}S$: $M = 502.47$, monoclinic ($P21/c$), $a = 14.856(18)$ Å, $b = 22.866(3)$ Å, $c = 21.756(3)$ Å, $\alpha = 90°$, $\beta = 102.71(2)°$, $\gamma = 90°$, $V = 7209.7(15)$ Å^3, $Z = 12$, $\mu = 0.202$ mm^{-1}, R1 [$I > 2\sigma(I)$] = 0.0844, wR2 [$I > 2\sigma(I)$] = 0.2141, R1 (all data) = 0.2253, wR2 (all data) = 0.3204, GOF = 0.999. The CCDC number of **1a** is 639785. Crystal data for **2a:** $C_{24}H_{18}F_6N_2OS$: $M = 496.46$, monoclinic ($P21/c$), $a = 23.120(3)$ Å, $b = 8.947(11)$ Å, $c = 11.442(13)$ Å, $\alpha = 90°$, $\beta = 101.84(10)°$, $\gamma = 90°$, $V = 2316.6(5)$ Å^3, $Z = 4$, $\mu = 0.207$ mm^{-1}, R1 [$I > 2\sigma(I)$] = 0.0537, wR2 [$I > 2\sigma(I)$] = 0.1364, R1 (all data) = 0.0715, wR2 (all data) = 0.1524, GOF = 1.038. The CCDC number of **2a** is 639786.

(17) (a) Frigoli, M.; Mehl, G. H. *Chem. Eur. J.* **2004**, *10*, 5243. (b) Pu, S. Z.; Yang, T. S.; Li, G. Z.; Xu, J. K.; Chen, B. *Tetrahedron Lett.* **2006**, *47*, 3167. (c) Xiao, S. Z.; Yi, T.; Zhou, Y. F.; Zhao, Q.; Li, F. Y.; Huang, C. H. *Tetrahedron* **2006**, *62*, 10072.