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BRIEF COMMUNICATION

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Energy profile of formal 1,2-dyotropic rearrangement of diarylethenes

Eric Koffi Kouame*,, Andrey G. Lvov*,****

**Irkutsk National Research Technical University,*
Irkutsk, Russian Federation
***A. E. Favorsky Irkutsk Institute of Chemistry SB RAS, Irkutsk, Russian Federation*
Corresponding author: Eric Koffi Kouame, erickofikouame@gmail.com

Abstract. *Diarylethenes with thiophene substituents belong to photoswitchable compounds (photoswitches or photochromes). Upon UV irradiation, their colorless open-ring isomers (**DAE-o**) convert to the colored closed-ring isomers (**DAE-c**), while the back reaction is induced only by visible light irradiation. A multiple photoswitching of diarylethenes usually results in irreversible photorearrangement of **DAE-c** to the so-called annulated isomers **DAE-a**, that are stable thermally and photochemically. In the present communication, structures of a series of diarylethenes as well as their isomers were optimized on the B3LYP/6-31G(d) level of theory. It was disclosed for the first time, that **DAE-a** destabilized relatively **DAE-c** by 1.71–14.00 kcal/mol. These results are important for design of photocontrollable molecules and materials, operated in the one-way (permanent manner).*

Keywords: *Photochromism, diarylethene, dyotropic rearrangement, annulated isomer, DFT calculations*

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КРАТКИЕ СООБЩЕНИЯ

УДК 544.52

Энергетический профиль формальной 1,2-диотропной перегруппировки диарилэтенов

Кофи Эрик Куаме*,, Андрей Геннадьевич Львов*,****

**Иркутский национальный исследовательский технический университет,*
г. Иркутск, Российская Федерация
***Иркутский институт химии им. А. Е. Фаворского СО РАН, г. Иркутск, Российская Федерация*
Автор, ответственный за переписку: Кофи Эрик Куаме, erickofikouame@gmail.com

Аннотация. *Диарилэтены с тиофеновыми заместителями относятся к фотопереключаемым соединениям (фотопереключателям или фотохромам). При облучении УФ-светом их исходная форма (**ДАЭ-о**) превращается в фотоиндуцированный изомер (**ДАЭ-с**), при этом обратная реакция индуцируется облучением видимым светом. Множественное фотопереключение обычно приводит к необратимой фотоперегруппировке **ДАЭ-с** в аннелированные изомеры **ДАЭ-а**, которые устойчивы фотохимически и термически. В данной работе нами были оптимизированы структуры ряда диарилэтенов, а также их изомеров на уровне теории B3LYP/6-31G(d). Впервые обнаружено, что **ДАЭ-а** дестабилизированы относительно **ДАЭ-с** на 1,71–14,00 ккал/моль. Эти результаты важны для разработки молекул и материалов, которые способны необратимо менять свои свойства под действием света.*

Ключевые слова: *фотохромизм, диарилэтен, диотропная перегруппировка, аннелированный изомер, DFT-расчеты*

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INTRODUCTION

Photochromism is a phenomenon of a reversible change of the structure of a compound under the action of light [1]. In organic chemistry, a vast number of various classes of photochromic compounds was developed during last decades. Photochromic diarylethenes, comprising two (hetero)aromatic moieties attached to the central double bond, were introduced by M. Irie in 1988 [2]. When irradiated with ultraviolet light (UV), the open form of diarylethenes **DAE-o** isomerizes into the colored closed-ring isomer **DAE-c** (Fig. 1); the reverse reaction proceeds under the action of visible light (VIS). Several thousand coloring / bleaching cycles could be carried out for the certain diarylethenes [3]. The closed-ring isomer **DAE-c** is thermally stable and usually converts to **DAE-o** photochemically. These features make diarylethenes promising components of new generation of advanced materials and technologies, including molecular electronics, stimuli-responsive catalytic systems, and probes for bioconjugation and fluorescence microscopy [4].

The main side reaction of the photochromic process is a formal 1,2-dyotropic rearrangement of **DAE-c** into the “annulated” isomer **DAE-a** [5]. The latter is formed during prolonged UV irradiation, while the quantum yield of the process strongly depends on the DAE structure [6, 7]. A possible mechanism of the rearrangement consists in the initial elongation of one C-S bond leading *via* a biradical intermediate to a bicyclohexene (BCH) structure, which undergoes a thermal isomerization to the annulated isomer (Fig. 2) [8]. The conversion of the central cyclohexadiene core to a methylcyclopentene diradical (MCPD) structure and its isomerization to the BCH intermediate also has been considered. Alternatively, a concerted reaction pathway *via* the exchange of the positions of a carbon and sulfur atom along the central C-C bond would directly lead to the annulated isomer.

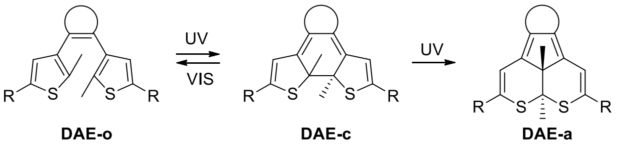

Fig. 1. Photoswitching of diarylethenes

Рис. 1. Фотопереключение диарилэтенов

Dyotropic rearrangement of phenanthroline-based diarylethene ligand was proposed for irreversible change of transition metal properties within complex, in particular, in the case of paramagnetic iron (II) complex [9]. Dynamic three-component system, based on the interconversion between **DAE-o**, **DAE-c** and **DAE-a** was proposed to control of 2D multicomponent molecular ordering on surfaces [10, 11]. The irreversible photorearrangement can be using for development of read-only-memory devices [12]. The asymmetric annulated isomer was presented as an efficient probe for disclosing structures effects on CD (circular dichroism) spectra [13].

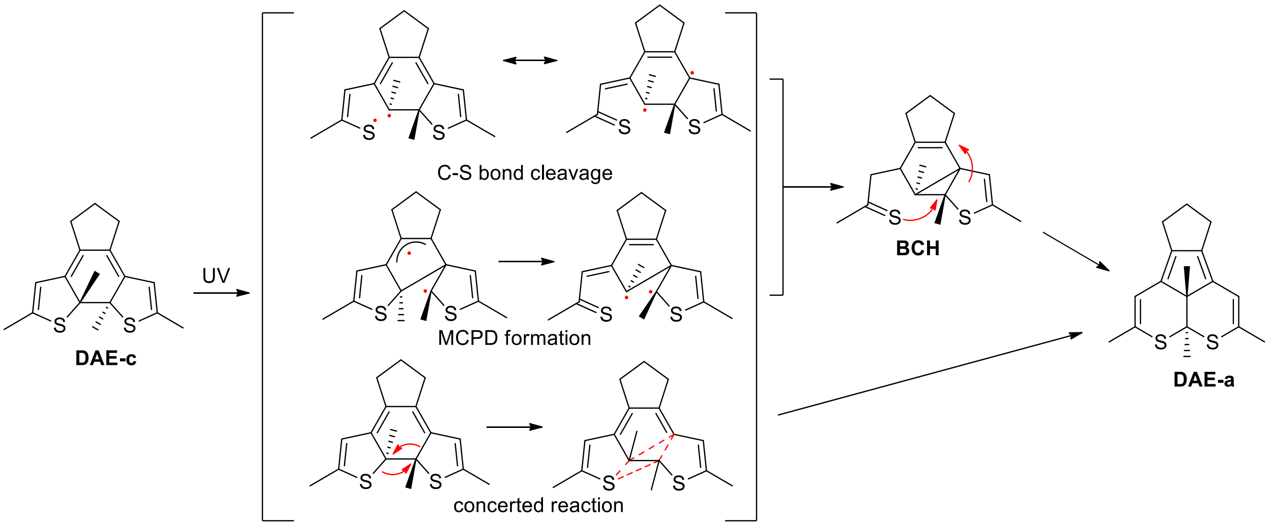

Fig. 2. Proposed mechanism of **DAE-a** formation

Рис. 2. Предложенный механизм образования **DAE-a**

For practical applications, it is important to know the relative stability of open-ring, closed-ring and annulated isomers of diarylethenes. The photogenerated isomers **DAE-c** usually are slightly destabilized regarding the open-ring isomer **DAE-o** [14], but the high thermal barrier of the thermal cycloreversion prevents the dark back reaction. At the same time, little is known on the relative stability of the annulated isomer regarding the closed-ring isomer. In this work, we have calculated a relative stability of isomers for **1o** as well as previously reported diarylethenes, **2o** [2], **3o** [15], **4o** [16], **5o** [17], **6o** [18], **7o** [19], **8o** [5], **9o** [5] by using the B3LYP/6-31G(d) method (Fig. 3). This approach provides quick access to optimized structures of photochromic diarylethenes [20, 21].

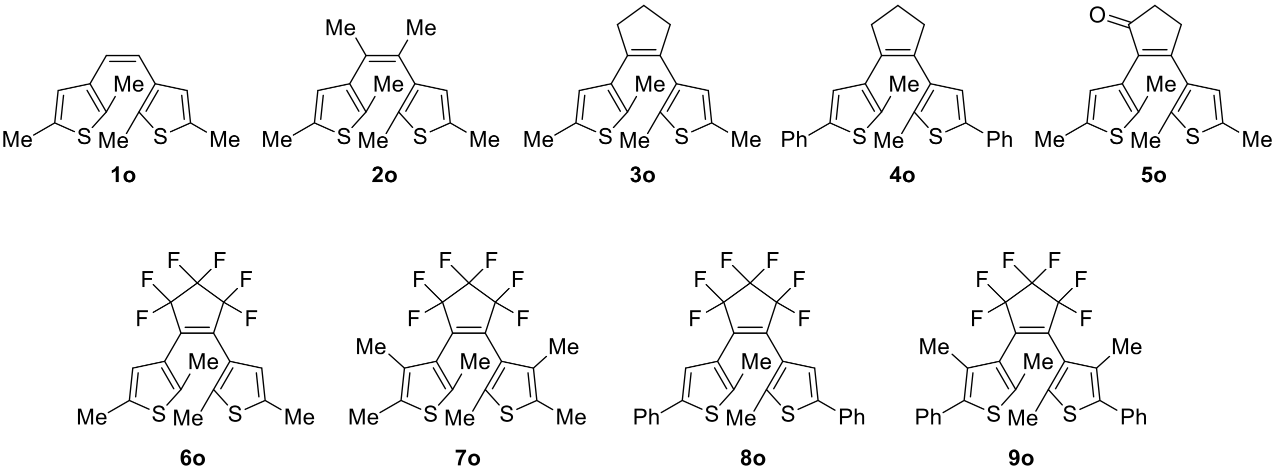

Fig. 3. Relative isomer stability for **1o**, as well as diarylethenes, **2o, 3o, 4o, 5o, 6o, 7o, 8o, 9o** by the B3LYP/6 method -31G(d)

Рис. 3. Относительная стабильность изомеров **1o**, а также диарилэтенов **2o, 3o, 4o, 5o, 6o, 7o, 8o, 9o** по методу B3LYP/6 -31G(d)

RESULTS AND DISCUSSION

Density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d) level of theory [22, 23] using the Gaussian 09 program package[1]. Minimum structures were obtained from ground state optimizations. Calculations of vibrational frequencies were performed to prove that each optimized structure corresponds to a true minimum on the potential energy surface. All energies were calculated without zero-point correction.

Fig. 4 presents optimized geometries of diarylethene **1o** and its isomers. The open-ring isomer comprises a flexible structure featured by free rotation of thiophene rings around C-C bond [24]. It leads to the existence of parallel and antiparallell conformers [25], which usually are in the equilibrium. Only antiparallel conformers are photoactive according to Woodward−Hoffmann rule [26]. According to performed calculations, antiparallel confomers are more stable for diarylethenes **1o**-**9o**.

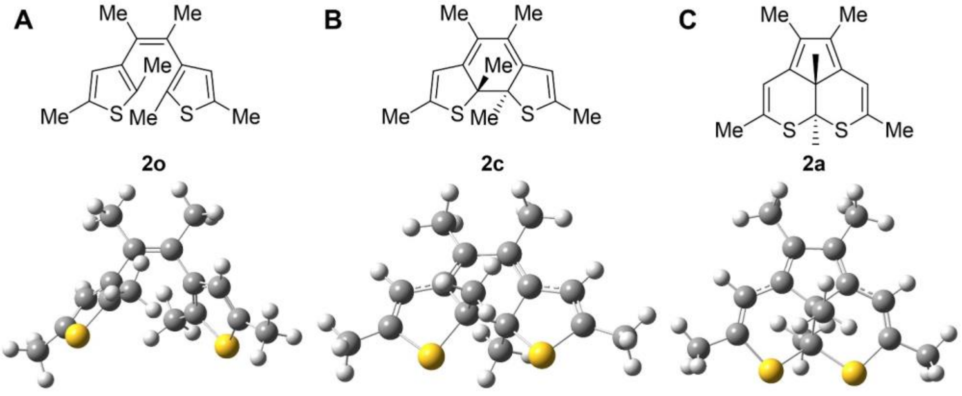

Fig. 4. Optimized structures for DAE **2o** and its photoisomers

Рис. 4. Оптимизированные структуры диарилэтена **2o** и его фотоизомеров

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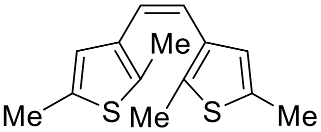
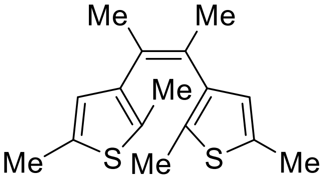
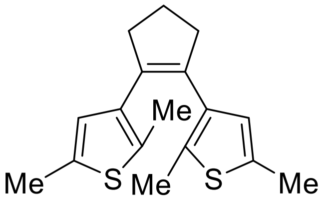
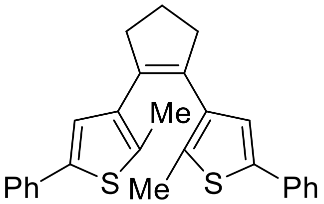
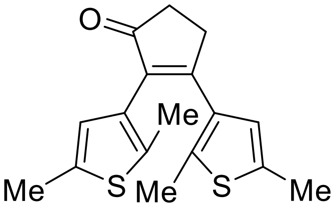
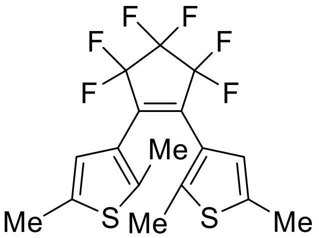
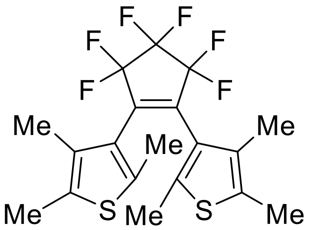
[1] Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., et al. Gaussian 09W, Revision 7.0. Wallingford CT: Gaussian Inc., 2009.

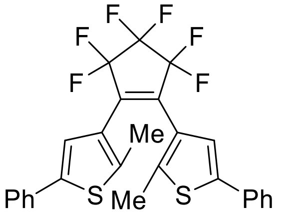
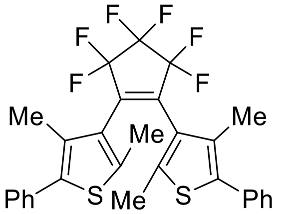
The relative energies for diarylethenes **1**–**9** are presented at the Table. According to this data, closed-ring isomers are destabilized in comparison with open-ring isomers by 6.28–12.46 kcal/mol. The energy of the annulated isomers is higher than that of E(**DAE-c**) by 1.71–14.00 kcal/mol. The lowest (in absolute values) differences were found for diarylethene **2o**. Thus, the relative stability can be ranged as follows: E(**DAE-a**) > > E(**DAE-c**) > E(**DAE-o**).

Calculated energy differences between diarylethene isomers

Расчетная разница энергий между изомерами диарилэтена

№	**Structure**	**ΔEoc, kcal/mol**	**ΔEao, kcal/mol**	**ΔEca, kcal/mol**
		E(DAE-c)-E(DAE-o)	**E(DAE-a)-E(DAE-o)**	**E(DAE-a)-E(DAE-c)**
1o		8.46	14.86	6.40
2o		6.28	7.99	1.71
3o		9.92	18.51	8.59
4o		10.81	20.15	9.34
5o		10.95	22.53	11.58
6o		11.80	23.57	11.77
7o		11.20	23.72	12.52

End of table

8o		12.46	25.55	13.09
9o		12.04	26.04	14.00

CONCLUSIONS

In conclusion, the performed calculations disclosed the relative destabilization of annulated isomers in comparison with closed-ring isomers. These results should be taken into account during future applications of **DAE-a** as a new class of photostable dyes.

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INFORMATION ABOUT THE AUTHORS

Eric Koffi Kouame,
Postgraduate Student,
Irkutsk National Research Technical University,
83, Lermontov St., Irkutsk, 664074,
Russian Federation;
A. E. Favorsky Irkutsk Institute
of Chemistry SB RAS,
1, Favorsky St., Irkutsk, 664033,
Russian Federation,
erickofikouame@gmail.com
https://orcid.org/0000-0002-6351-3335

Andrey G. Lvov,
Cand. Sci. (Chemistry), Leading Researcher,
Irkutsk National Research Technical University,
83, Lermontov St., Irkutsk, 664074,
Russian Federation;
Head of Laboratory,
A. E. Favorsky Irkutsk Institute
of Chemistry SB RAS,
1, Favorsky St., Irkutsk, 664033,
Russian Federation,

СВЕДЕНИЯ ОБ АВТОРАХ

К. Э. Куаме,
аспирант,
Иркутский национальный исследовательский
технический университет,
664074, г. Иркутск, ул. Лермонтова, 83,
Российская Федерация;
Иркутский институт химии им. А. Е. Фаворского
СО РАН,
664033, г. Иркутск, ул. Фаворского, 1,
Российская Федерация,
erickofikouame@gmail.com
https://orcid.org/0000-0002-6351-3335

А. Г. Львов,
к.х.н., ведущий научный сотрудник,
Иркутский национальный исследовательский
технический университет,
664074, г. Иркутск, ул. Лермонтова, 83,
Российская Федерация;
заведующий лабораторией,
Иркутский институт химии им. А. Е. Фаворского
СО РАН,
664033, г. Иркутск, ул. Фаворского, 1,

lvov-andre@yandex.ru
https://orcid.org/0000-0003-2951-2651

Contribution of the authors

The authors contributed equally to this article.

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Российская Федерация,
lvov-andre@yandex.ru
https://orcid.org/0000-0003-2951-2651

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