The structure and characteristics of photochromic dithienylethenes

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ABSTRACT. The data on X-ray diffraction analysis for dihetarylethenes with perfluorocyclopentene (F), maleic anhydride (M) and cyclobutenedione (S) bridges between thienyl fragments were summarized and their photochromic properties were discussed. It was established that benzoxazole and benzothiazole substituents in position 5 of thiophene rings are coplanar to the plane of thiophene cycles. Thienyl fragments in A form of all dithienylethenes are considerably turned relative to the plane of bridging cycle. It means that there is no conjugation between π-electrons of aromatic heterocycles and double bond of the bridge.

Flattening of molecule framework and the envelope conformation of thienyl cycles because of aromaticity loss are characteristic features of the form B structure with F-bridge. In all cases (excluding the compounds with alkylthio substituents in position 2 of thiophene cycle) the photochromic transition A → B is observed independently of different nature and structure of functional groups.

1. INTRODUCTION

In recent years the photochromic materials have been considered as promising systems for information storage [1, 2]. Such compounds should fit a variety of requirements. Two of them are fundamental and responsible for principal possibility of photochromes as elements of optical memory. First of them—fatigue resistance—is typical of many materials. Fatigue resistance as applied to photochromes is determined as the quantity of cycles of A and B interconversion at the irradiation corresponding to the decomposition of 20% of the sample [2]. The second fundamental characteristics, determining the applicability and being specific of photochromes, is thermal irreversibility of photoconversion. Most of photochromes transfer from one form to the other one losing the recorded information. It was an insuperable obstacle in their application as memory elements for optoelectronic devices.

A fundamental change has come at the end of eighties of 20th century when M. Irie has suggested 1,2-dihetarylethenes [3, 4] (Scheme 1) as thermally irreversible photochromes. Thiophene, furan and pyrrole structures and their benzocondensed analogs have been taken as heterocyclic substituents. Perfluorocyclopentene, phthalic anhydride and phthalimide were used in early publications as ethene bridges. In recent publications cyclopentene, imidazole, oxazole, cyclobutenedione etc. were suggested [5–9]. In most cases alkyl groups were used as substituents R2 and R3.

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Irie has shown that photochromic dihetarylethenes possess not only the thermal irreversibility but a high fatigue resistance comprising in some cases thousands cycles. These unique characteristics arise a considerable interest to dihetarylethenes. Up to now about ten reviews were published [3, 10–16]. The last of them was published in last year [2]. Basically, they dealt with the methods of preparation, physicochemical and optical properties of these compounds. The structure of dihetarylethenes is discussed in these reviews rather stingly. But it is obvious that photochromic properties of these compounds are determined by the nature of functional groups, by their position in hetaryl fragments, and by the specificity of steric structure of molecules both in open (A) and in cyclic (B) forms. X-ray diffraction analysis provides such information for single crystals. It is significant that some dihetarylethenes exhibit photochromic activity even in crystals [17, 18].

The objective of the present paper—to summarize the literature data on the crystal and molecular structures of dihetarylethenes having perfluorocyclopentene, maleic anhydride and cyclobutenedione as ethenic bridges between thienyl fragments.

2. PERFLUOROCYCLOPENTENE DERIVATIVES

2.1. Open forms of dithienylethenes. Dihetarylethenes with various substituents in positions 2 and 5 of thiophene rings are the best studied. The numbering of atoms in heterocycle is shown at the Scheme 2; perfluorocyclopentene is denoted as F; thiophene cycles—as T1 and T2; benzoxazole—as B. Let us consider first the structure of compounds with alkyl groups in positions 2 and 2' of thiophene cycles. The structure of 1,2-bis(2,5-dimethyl-...
3-thienyl)hexafluorocyclopentene (1) is rather simple (Scheme 2). Crystal and molecular structure is studied by X-ray diffraction analysis both in A and in B forms [18, 19]. The peculiarity of this compound is the ability of single crystal for repeated (>10⁴ times) photochromic transition A ←→ B without the destruction of crystal structure: colourless crystals of 1A after the irradiation by UV-light λ = 366 nm are transformed into 1B form of red colour. The latter is stable in dark up to 10⁰C and is transformed back into form 1A by the action of the visible light. Spatial superposition of crystal structures 1A and 1B has shown that dihedral angles \( T_1/F, T_2/F, T_3/T_2 \) considerably decrease. In 1A they are equal to 46°, 78°; 46°, 77°; 62°, 25°, respectively and in 1B—12°, 14°; 11°, 62°; 177°, 170°. It means that thienyl fragments turn around ~ 35° relatively to plane cycle F without the destruction of the crystal. The mechanism of such transition is not explained yet, but it seems that it is associated with the specific packing of molecules in the crystal. Nevertheless this property is very important since it provides the use of single crystals for optical memory and for erasing of the recording.

The replacement of alkyl groups in positions 5 and 5' for sulfonyl ones deteriorates the photochemical characteristics. Contrary to compound 1 sulfonyl derivative 2 is photochromic only in solutions: at the irradiation by UV-light (\( \lambda = 313 \) nm) a colourless ethanolic solution of 2A changes to dark violet solution, containing form 2B.

However, according to data of paper [21] the full photoreversibility of cyclization reaction is not observed: at the irradiation coloured ethanolic solution of 2B by the light \( \lambda = 546 \) nm isosbestic points in the absorbance spectra are absent. It testifies that some other transformations take place together with photochromic process for compound 2.

The full photoreversibility of isomers at the irradiation of ethanolic solution of 3A by the light \( \lambda = 313 \) nm and form 3B—by the light \( \lambda = 578 \) nm is common for 1,2-bis[5-(benzoxazol-2-yl)-2-methylthien-3-yl]perfluorocyclopentene (3) [22] (Scheme 4). The structure of 3A [20] made up of two crystallographically independent molecules slightly differing only by deflection angles of benzoxazole fragments (B) relative to thiophene cycles and by torsion angles in cycle F. Contrary to structures of 1A and 2A cycle F in this compound has a form of envelope with a vertex, lying opposite to double bond. Other peculiarity of compound 3 is the formation of plane spatially elongated conjugated system thiophene-benzoxazole. The deflection angle of benzoxazole fragments relative to cycles...
T does not exceed 2–3°. Greater dihedral angle in one of conformers of molecule 3A (17°) is caused by the field of the crystal lattice and does not influence the conjugation character. The conjugation in plane system is also confirmed by the appreciable shortening of C – C bonds between thiophene and benzoxazole cycles down to 1.442Å in comparison with the standard value of this bond (1.48Å). Thus, two planar conjugated systems thiophene-benzoxazole are turned relative to each other through 55–60° in molecule 3A. The conjugation between these systems is absent. Each of them is rotated relative to F-cycle through ~53.6°. The intramolecular distance C(2) · · · C′(2) equal to 3.59Å as well as in 1A and 2A corresponds to normal van der Waals contact.

It was suggested that the introduction of “fluorophor” benzoxazole groups in positions 5 and 5’ of thienyl cycles would result in the fluorescence in compound 3. However, the fluorescence was detected neither in open nor in cyclic forms of the photochrome [22].

There is a little information on the structure and properties of photochromes with substituents in positions 2 and 4 of thienyl rings. According to the spectral investigations [17] 1,2-bis(2,4-dimethyl-3-thienyl)hexafluorocyclopentene (4) has a capability for phototransformation A ←→ B in single crystal more than 100 times without the destruction of crystal structure (Scheme 5).

Both isomers (A-colourless, B-red colour) are thermally stable up to 100° C. X-ray diffraction analysis has been carried out for isomer 4A. However, in paper [17] only the packing of molecules in crystal is shown and it was mentioned that the plane of cycle F is perpendicular to the plane ac of unit cell.

We have synthesized and studied 1,2-bis (4-methoxy-carbonyl-2-ethen-5-ethylthiothien-3-yl)hexafluorocyclopentene (5) in which all hydrogen atoms of heterocycles are substituted (Scheme 6) [23]. As it was shown by X-ray diffraction analysis the conformation of molecule 5A has some peculiarities in comparison with previously considered structures.

Firstly, the cycle F is considerably compressed as compared with the structure 3B: the deviation of envelope vertex from the cycle plane is equal only to 0.12Å. Dihedral angles T^1/F, T^2/F, T^3/T^2 are close to
It is considerably greater than similar angles in compounds with two functional groups (1–3)A. Secondly, thienyl fragments are unfolded in opposite directions relative to cycle F (Scheme 5). As a result, the distance between the atoms C(2) · · · C’(2) (4.45Å) is much greater than the normal van der Waals contact and therefore is geometrically unfavorable for cyclization reaction. In fact, the compound 5 in crystal state does not change the colour at the irradiation by UV-light.

In ethanolic solution this compound behaves as typical photochrome: there is full photoreversibility of the reaction and side processes are absent. For practical use of such photochromes, that is, before the preparation of the films, it is necessary to irradiate them previously and prepare the films or mixture in the absence of visible light.

Many data indicate that high fatigue resistance is common to photochromic dihetarylethenes with condensed substituents such as benzothiophenes, indoles, thienothiophenes etc. [2, 24]. The interest in the synthesis and structure investigation of such compounds arises. The fatigue resistance of imidazole derivative of 1,2-bis(2-methylbenzo[b]thiophen-3-yl)hexafluorocyclopentene (6) (Scheme 8) is equal to $1.3 \cdot 10^4$ [25]. Both isomers are thermally stable up to 1000°.

Besides it compound 6 has a photocontrolled intramolecular magnetic interaction. The structure of open form 6A was determined by X-ray diffraction analysis, however, X-ray diffraction data are not given, except mentioning that dihedral angles between benzothiophene rings and cycle F are equal to 86.1° and π-conjugation between benzothiophene cycles is absent.

All compounds considered above are alkylsubstituted in position 2 of thienyl cycle. The replacement of alkyl substituents by alkylthio groups changes completely physicochemical and spectral characteristics. In particular, 1,2-bis(2-ethylthio-3-thienyl)-hexafluorocyclopentene (Scheme 9) has not photochromic properties [26].

X-ray diffraction analysis data of isomer 7A indicate that the conformation of the molecule does not differ considerably from the structures 1A–6A: cycle F-plane, thioalkyl groups are situated on different sides of this plane, dihedral angles T1/F, T2/F (55.9; 59.6°) are close to similar angles in the molecules (1–3)A. Only dihedral angle T1/T2 is considerably greater: by 16° as compared with 1A, 3A and by 23° as compared with 2A. It results in the increasing of C(2) · · · C’(2) distance up to 3.97Å.

Dihetarylethene 7 is not photochromic in solutions also, as well as 5-formyl and 5-carboxyderivatives of 7. The oxidation of SET-groups into sulfonic ones in compound 7 is also not accompanied by the appearance of photochromic properties. The compound 8 in which one of alkylthiogroup is replaced by ethyl group (Scheme 10) is not photochrome.

It should be mentioned that the side processes pre-
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Scheme 8.

Scheme 9.

Scheme 10.

dominate at the irradiation of compound 2. Such difference in photochemical properties of the compounds with sulphur-containing substituents 2, 7, 8 and products (1,3–6) cannot be explained only by the difference of van der Waals radii of atoms C and S (1.71 and 1.84Å). The cause is, possibly, the dipole-dipole repulsion of unshared electron pairs of S atoms of thienyl cycles and alkylthio groups. Theoretically, the repulsion is smallest if the planes of thienyl group and valent bonds of S atom of alkylthio group are orthogonal. In real molecules this angle is slightly different from orthogonal: for example, in 2-alkylthio-3-thiophenecarbaldoximes it varies in the range 102–118° [27]. In molecule 7 this angle is equal to 114° that is, definite spatially-controlled mutual orientation of alkylthio groups and thienyl fragments is observed independently of compound nature. It causes the limitation of free rotation of alkylthio group relative to the cycle T. It seems that it prevents the reorganisation of the bonds in sextet at the formation of form B in the case of alkylthio groups, while such limitation does not exist for alkyl group.

It should be concluded that a considerable turn of cyclopentene and thienyl fragments (46–86°), indicating the absence of conjugation between π-electrons of aromatic heterocycles and double bond of fluorinated ring is characteristic of all studied dithienylperfluorocyclopentenes in open form A.

2.2. Cyclized forms of photochromes. Spatial structure of form B of photochromes is little studied: it is associated with the difficulties of the production of single crystals suitable for X-ray diffraction a separation. We have synthesized the cyclized form of photochromic 1,2-bis[2-methyl-5-(2-benzothiazolyl)-6-trifluoromethylthieno[3,2-b]thienyl-2]hexafluorocyclopentene (9B) (Scheme 11) and studied it by X-ray diffraction method [28]. The structure of this molecule is characterized by the following features.

The cycle F looks like an envelope with vertex which is deflected from the base by 0.58Å. The cycles T1, T2 in thieno[3,2:b]thienylfragments have also the envelope conformations, that is, the aromaticity in thienyl cycles bonded with ring F is broken. Other seven atoms of thieno[3,2:b]thienyl form plane systems in each half
of the molecule (D¹, D²). These systems and fragments F and B make up the flattened skeleton of the molecule (except fluorine atoms), since dihedral angles D/F, D²/F, D¹/D², B¹/T¹ are small (0.32; 2.97; 3.27 and 1.39°, respectively). The angle B²/T² is slightly greater (11.45°) and it is evidently caused by the action of the crystal lattice field. The alternation of C – C bond lengths of different multiplicity factor in flattened fragment of the molecule indicate the formation of new conjugated system of polyene type. The six-membered cycle formed as a result of the cyclization acquires the conformation of “twisted sofa” with methyl substituents in positions 2, 2' trans-oriented relative to the plane of the molecule.

The molecule 1B (Scheme 12) [18] has a similar structure: the cycles F, T¹, T¹ have the envelope conformation, the six-membered cycle—the conformation of “twisted sofa”. The values of dihedral angles T¹/F (−12.14), T²/F (11.62) and T¹/T² (177.17°) indicate the flattened structure of molecule (except F and H atoms of methyl groups).

New system of conjugated bonds can be separated out in plane fragment of molecule as well as in 9B.

The structure of bis(4-chlorobenzoate)-1,2-bis(5-hydroxymethyl)-2-methyl[3-thienyl]hexafluorocyclopentene (10B) (Scheme 13) was also studied by X-ray diffraction method [29].

It was mentioned that the unit cell of crystal contains 4 independent molecules which differ in torsion angles in F-cycles (by 5–6°) and by torsion angles –C – CH₂ – O – C – p– chlorobenzoate groups. All five-membered cycles have envelope conformations. Other structural data are not given.

Thus, the forms B of photochromes with perfluorocyclopentene bridge are characterized by the following analysis and enantiomers features: a) the skeleton of the molecule is practically planar; b) all five-membered cy-
angles and dihedral angle $T_1$ exceed 1. The forms $A$ of photochromes mentioned above do not exist. Indirectly these conclusions are in accordance with the results of quantum-chemical calculations for three pairs of molecules: $2(A,B)$, $3(A,B)$ and $6(A,B)$. It was found that the greatest reduction of energy gap between frontier orbitals takes place in molecule 3 both in open and cyclized forms [33]. The greatest bathochromic shift of absorption spectrum maximum is observed for this compound. It indicates the forma-

\[ \text{Scheme 14.} \]

cles have envelope conformation; c) thieryl cycles lose the aromaticity; d) new system of conjugated bonds is formed.

3. THE DERIVATIVES OF CYCLOBUTENEDIONE AND MALEIC ANHYDRIDE

The photochromic diheteroylethenes based on the maleic anhydride are widely studied as perfluorocyclopentene derivatives. They also possess the thermal irreversibility and high fatigue resistance. The investigations were inhibited by the labour-consume of their preparation, however, recently the suitable method of their synthesis by the oxidation of cyclobutenedione derivatives was suggested [30]. In the literature there are contradictory data on the photochromic properties of the latter [31]. It stimulated us to synthesize and to study the structure of 1,2-di(2,5-dimethyl-3-thienyl)cyclobutenedione (11) (Scheme 14) [30]. The attempts of obtaining the cyclic form by the irradiation with UV-light were not successful neither in crystal nor in solutions.

X-ray diffraction analysis of open form 11A has shown some peculiarities of the molecular structure. First, the methyl substituents in positions 2 of thieryl fragments have trans/cis orientation relative to double bond of cyclobutene ring $S$. In the case of trans-orientation the cycle $T^1$ is turned relative to plane $S$ by the angle (22.00°) less than cycle $T^2$ (36.78°). Both angles and dihedral angle $T^1/T^2$ (47.89°) are the least among similar angles, found in structures (1–7)A. Secondly, the $C = C$ bond length in cyclobutenedione is elongated up to 1.387A0 and corresponds to one and half bond order. On the contrary, $C – C$ bonds between cyclobutene and thiophene rings (1.444A0) are slightly shortened as compared with ordinary one. It should be pointed out that the bond lengths in $F$ cycles for all open forms $A$ of photochromes mentioned above do not exceed 1.333A0. These facts and rather small turn of fragments $B$ and $T^1$ testifies the partial conjugation of double bond of cyclobutenedione fragment with thiophene cycle. It increases the aromatization energy of the system and gives the conformational stability of form 11A in solutions.

It seems that an ability of double bond of cyclobutenedione to $\pi$-electron interaction with thiophenyl ring is its specific property. In literature there are some examples supporting this fact. For example, in 1-cyclohexenyl-1-cyclobutenedione [32] the double bond in cyclobutenedione fragment is elongated up to 1.395A0 and ordinary bond between cycles is shortened down to 1.433A0. Thus, the nature of double bond in cyclic bridge can play an important role in selection of photochromic materials: the photochromes with cyclic bridges not having $\pi$-electron interaction with hetaryl groups are preferential.

3,4-bis(2,5-dimethyl-thienyl) 2,5-furan dione (12) (Scheme 15) prepared by the oxidation of compound 11, is a photochrome [30]; in solutions it is converted into form $B$ at the irradiation by UV-light $\lambda = 313$ nm, but at the irradiation by light $\lambda = 458$ nm form $B$ is converted into form $A$.

The molecule of this isomer has C2 symmetry: the molecular axis passes through O atom and the middle of double bond of furan-2,5-dione. In crystal the molecular axis coincides with crystallographic axis of second order. Both methyl substituents in positions 2 and 2’ of thieryl fragments have cis-orientation relative to the double bond of maleic anhydride (cycle M). Dihedral angles $T/M$ and $T^1/T^2$ (47.00°) are practically the same as in the structure 1A. The distance $C(1) \cdots C'(1)$ corresponds to normal van der Waals contact. The similarity of crystal structure of 12A and 1A allows to suppose the possibility of photochromic transition in the compound 12 in crystals.

4. CONCLUSION

Among photochromes with $F$ and $M$ bridges considered above only compound 7 with ethylthio group in position 2 of thiophene ring forms stable form $A$ insensitive to UV-irradiation. In all other cases the photochromic transition $A \rightarrow B$ is observed in spite of different chemical nature and structure of functional groups. The character of this transition is considerably affected not so much by the nature of functional group in positions 4, 5 of thieryl cycle as by the spatial structure of aryl fragment: the compounds with planar spatially extended structure of aryl fragment have the best photochromic characteristics. It seems that such structure is most suitable for synchronous turn of these fragments relative to cycle $F$ at conrotator mechanism of cyclization reaction.

Indirectly these conclusions are in accordance with the results of quantum-chemical calculations for three pairs of molecules: $2(A,B)$, $3(A,B)$ and $6(A,B)$. It was found that the greatest reduction of energy gap between frontier orbitals takes place in molecule 3 both in open and cyclized forms [33]. The greatest bathochromic shift of absorption spectrum maximum is observed for this compound. It indicates the forma-
tion of spatially extended conjugated system.

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