# Photochromic dihetarylethenes 9.* Dithienylperfluorocyclopentenes: a quantum-chemical study

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MNDO calculations of the open and cyclic forms of the molecules of three photochromic 1,2-di(3-thienyl)perfluorocyclopentene derivatives were carried out. Structural parameters as well as electronic and thermodynamic characteristics of the compounds studied were analyzed. The optimized geometric parameters of the open forms of the three molecules under study are in satisfactory agreement with the results of X-ray diffraction studies. Analysis of the effect of substituents on the electronic characteristics of the central fragment and on the composition of the frontier MOs suggests that it is more appropriate to use cyclic rather than open forms of the molecules for correlation analysis and for prediction of photochromism of dithienylperfluorocyclopentenes.

**Key words:** dithienylperfluorocyclopentenes, photochromic compounds, quantum-chemical calculations, MNDO approximation, molecular structure, photochromism.

Recent experimental[2,3] and theoretical[4] studies showed that photochromism of most of dithienylethenes is thermally irreversible. This dictates an increasing interest in this class of photochromes owing to the perspectives of their use as elements of optical memory devices, switching devices,[5—7] *etc.*

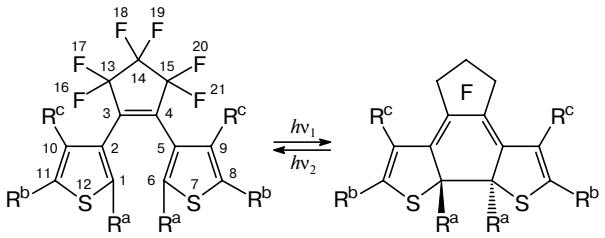
However, the synthesis of these promising products faces considerable difficulties.[8,9] In addition, a number of dithienylethenes is known to exist only in the open form;[10] in other words, these compounds do not undergo cyclization by UV light.

Recently, we have first synthesized ten thermally irreversible dithienylperfluorocyclopentenes including those (i) with heterocyclic substituents in the thiophene ring and (ii) substituted at position 4 of the thiophene ring and studied photochromic properties of these compounds.[3,11—13] The molecular structures of the open forms of three out of the ten photochromes were established by X-ray diffraction analysis. These are 1,2-bis(2-ethyl-5-ethylsulfonyl-3-thienyl)perfluorocyclopentene[12] (**1A**), 1,2-bis(2-methyl-5-benzooxazol-2-yl-3-thienyl)hexafluorocyclopentene[13] (**2A**) and 1,2-bis[4-methoxycarbonyl-2-ethyl-5-(ethylthio)-3-thienyl]perfluorocyclopentene[1] (**3A**). UV-Irradiation of **1A—3A** leads to their cyclization (Scheme 1) to give the cyclic forms **1B—3B**. Exposure of the forms **1B—3B** to visible light leads to the ring opening and recovery of the initial forms **1A—3A**.

Since the synthesis of dithienylethenes is labor-consuming, the development of simple methods for prediction of their photochromic properties based on correlation analysis using, in particular, the results of semiempirical quantum-chemical calculations, acquires particular significance. Unfortunately, only a few studies on the quantum-chemical calculations of the electronic structure and reactivities of photochromic diarylethenes have been reported. Band assignment in the electronic spectrum of only one compound, 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene, has been proposed.[14] A theoretical study[4] of diarylethenes including dihetarylethenes with different aryl fragments showed that, in accord with the Woodward—Hoffmann rule, the corotatory cyclization is allowed for the hexatriene system.

The stability of photochromic forms (*i.e.*, thermal irreversibility of photocyclization) depends on the height of the barrier to transition between the structures **A** and **B**. It is believed[4] that the barrier height correlates with

**Scheme 1**




| | | | |
|---|---|---|---|
| **1—4** | $R^a$ | $R^b$ | $R^c$ |
| **1A, 1B** | Et | $SO_2Et$ | H |
| **2A, 2B** | Me | benzooxazol-2-yl | H |
| **3A, 3B** | Et | SEt | COOMe |
| **4A** | H | H | H |

* For Part 8, see Ref. 1.

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the difference between the heats of formation of the cyclic and open forms in the ground state and that this difference is in turn determined by the aromaticity degree of the aryl ring. The so-called "aromatization energy" was proposed to be a quantitative indicator of the aromaticity. It was also reasonable to assume that the lower the "aromatization energy," the lower the difference between the heats of formation of the photochromic forms **A** and **B** and the higher the corresponding activation barrier. According to recent MNDO calculations,[4] the "aromatization energies" of phenyl, pyrrol-3-yl, 3-furyl, and 3-thienyl are 27.7, 13.8, 9.1, and 4.7 kcal $mol^{-1}$, respectively. It is noteworthy that, in contrast to the results of these calculations,[4] thiophene is usually thought to have a greater aromaticity than furan.[15] Nevertheless, based on these values of "aromatization energies," it was concluded[4] that thermal irreversibility of photocyclization should be expected for the compounds with the 3-thienyl aryl fragments, *i.e.*, for dithienylethenes.

In this work, we carried out a quantum-chemical study of (i) three open structures **1A—3A** with the known molecular geometries and (ii) corresponding cyclic forms **1B—3B**. Particular attention was paid to the central structural fragment, which is common to all structures and comprises the atoms labeled from 1 to 12 (the numbering of atoms is shown in Scheme 1). All calculations were carried out in the MNDO approximation using the MOPAC program package.[16]

## Results and Discussion

Comparison of the calculated bond lengths and bond angles in molecules **1A—3A** with the experimental results obtained from X-ray studies of these compounds showed that almost all of them are in good agreement (in most cases, the differences did not exceed 4%). The largest deviations (up to 18%) were found for the C—C bonds of the perfluorocyclopentene ring. The reason is likely that the parametrization of the MNDO approximation is inadequate for the calculations of structural fragments with a large number of fluorine atoms. For all the three compounds, the calculated bond angles differ from the experimental values by at most 3%.

Particularly large are the differences between the calculated and averaged experimental values for the C(14)—C(15) bond length and the C(13)—C(14)—C(15) bond angle in molecule **3A** (~18% and ~8%, respectively). The reason is that the lengths of symmetric bonds C(13)—C(14) and C(14)—C(15) determined by X-ray analysis differ appreciably, which is likely due to the inaccuracy of determination of the atomic coordinates of C(14) owing to partial statistical disorder and large amplitudes of thermal vibrations. For our purposes, the most important is that almost all calculated geometric parameters of molecules **1A—3A** and first of all those of the central structural fragment comprising the atoms from C(1) to S(12) are in reasonable agreement with the averaged data of X-ray diffraction study. Therefore, structural characteristics of these and related molecules optimized in the MNDO approximation must be well suited for correlation analysis of their electronic structure and photochromic properties.

Table 1 lists the heats of formation ($\Delta H_f$), dipole moments ($\mu$), frontier MO energies ($\varepsilon_f$, $\varepsilon_v$) and their differences, as well as the calculated in the conventional MNDO approximation atomic charges ($Q$). Changes in the strength of X—Y bonds in the central fragments of the molecules of compounds **1—3** as compared to structure **4A** (a reference structure) are characterized by the $i_{XY}$ indices[17] listed in Table 2. All the data listed in Tables 1 and 2 refer to the molecular structures optimized in the MNDO approximation. The results of calculations for the experimental structures are virtually the same as those listed in Tables 1 and 2.

Comparison of the $\Delta H_f$ values for the open and cyclic forms of molecules **1—3** shows that the former are 31.1 (**1A**), 20.9 (**2A**), and 29.7 kcal $mol^{-1}$ (**3A**) more thermodynamically stable than the latter. According to the published data,[4] the differences between the heats of formation of the open and cyclic forms of diphenylethene and dipyrrolylethene with thermally unstable cyclic structures are 23.7 and 15.5 kcal $mol^{-1}$, respectively. The $\Delta H_f$ values for difurylethene and dithienylethene, which undergo a thermally irreversible photocyclization, are 9.2 and −3.3 kcal $mol^{-1}$, respectively.[4] As can be seen, the "gas-phase" differences between the $\Delta H_f$ values for the cyclic and open forms of typical photochromes **1—3** and those of non-photochromic diphenylethene lie in the

**Table 1.** Characteristics of the open and cyclic forms of compounds **1—3** calculated in the MNDO approximation

| Compound | $\Delta H_f$ /kcal $mol^{-1}$ | $\mu$ /D | $\varepsilon_f$ | $\varepsilon_v$ | $\varepsilon_v - \varepsilon_f$ | $Q$ (au) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | eV | | | C(1), C(6) | C(2), C(5) | C(3), C(4) | S(7), S(12) | C(8), C(11) | C(9), C(10) |
| **1A** | −107.5 | 5.6 | −11.0 | −2.2 | 8.8 | −0.20 | −0.11 | −0.03 | 0.49 | −0.66 | 0.08 |
| **1B** | −76.4 | 4.4 | −10.0 | −2.9 | 7.1 | −0.11 | 0.00 | −0.11 | 0.26 | −0.54 | 0.06 |
| **2A** | −207.1 | 5.8 | −9.1 | −1.4 | 7.7 | −0.22 | −0.10 | −0.02 | 0.41 | −0.24 | 0.02 |
| **2B** | −186.2 | 6.5 | −9.0 | −2.3 | 6.7 | −0.13 | 0.02 | −0.12 | 0.23 | −0.13 | −0.03 |
| **3A** | −402.7 | 4.1 | −9.7 | −1.3 | 8.4 | −0.20 | −0.07 | −0.01 | 0.41 | −0.38 | −0.03 |
| **3B** | −373.0 | 8.8 | −9.2 | −2.2 | 7.0 | −0.11 | 0.06 | −0.13 | 0.20 | −0.26 | −0.10 |

*Note.* $\Delta H_f$ is the heat of formation, $\mu$ is the dipole moment, $\varepsilon_f$ is the HOMO energy, $\varepsilon_v$ is the LUMO energy, $Q$ is the atomic charge.

**Table 2.** $X_j$—$Y_k$ bond strength indices ($i_{XY}$) for the open and cyclic forms of compounds **1—3** calculated in the MNDO approximation

| Compound | $i_{XY}$ (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | C(1)C(2), C(5)C(6) | C(2)C(3), C(4)C(5) | C(3)C(4) | C(6)S(7), S(12)C(1) | S(7)C(8), C(11)S(12) | C(8)C(9), C(10)C(11) | C(9)C(5), C(10)C(2) |
| **1A** | −2.7 | 0.1 | 0.1 | 2.2 | 13.7 | −0.2 | 2.6 |
| **1B** | −33.5 | 40.8 | −30.4 | −19.3 | 0.1 | 5.0 | −6.3 |
| **2A** | −1.7 | 0.1 | 0.1 | 0.8 | 0.1 | −2.3 | 1.6 |
| **2B** | −33.4 | 40.3 | −30.2 | −19.2 | −8.0 | 1.9 | −4.7 |
| **3A** | −1.7 | −0.1 | −0.1 | 0.6 | 4.6 | −3.0 | 1.5 |
| **3B** | −33.8 | 40.4 | −31.0 | −19.0 | −5.5 | 0.5 | −4.5 |

same range (~20—30 kcal $mol^{-1}$) and cannot therefore serve as a criterion for the presence or absence of photochromism of a particular compound.

The dipole moment of molecule **1A** is larger than that of the cyclic molecule **1B**. The reverse is observed for the other two compounds. Ignoring the changes in the size and polarizabilities of molecules **1—3** upon photochromic transition, one can expect in accord with Onsager's solvation model for spherical electrically neutral systems[18] that the cyclic structures **2B** and **3B** will be much more stable in polar solvents. Therefore, solvation is thought to favor photochromism of compounds **2** and **3**. As to system **1**, the effect of solvation must be opposite in sign. It is likely that the change in the molecular dipole moment upon photochromic transition is first of all due to the nature and positions of substituents rather than the electron density distribution over the atoms of the central fragment.

According to Koopmans' theorem,[19] the HOMO and LUMO energies are related to the ionization potential and electron affinity. These energies are high in absolute values. Their maximum values were found for the open form **1A**. According to calculations, for all the three systems cyclization must lead to a decrease in the ionization potentials, an increase in the electron affinities, and a narrowing of the energy gap between the frontier MOs. It is noteworthy that the energy gap width changes in parallel with the bathochromic shift of the long-wavelength absorption band in electronic spectra.[1,12,13]

Since the atoms S(7) and S(12) carry large positive charges while the atoms C(1), C(6), C(8), and C(11) are negatively charged, the C(6)—S(7), C(8)—S(7), C(1)—S(12), and C(11)—S(12) bonds are strongly polarized. Cyclization of the photochromes leads to a decrease in the atomic charges of (i) C(1), C(2), C(5), C(6), C(8), and C(11) by ~0.1 au in absolute value and (ii) S(7) and S(12) by ~0.2 au in structures **1B—3B**. The negative charges of the C(3) and C(4) atoms in the perfluorocyclopentene fragment increase.

The $i_{XY}$ values[17] listed in Table 2 indicate that for all compounds studied in this work the strengths of the C(1)=C(2), C(3)=C(4), and C(5)=C(6) double bonds decrease by more than 30%, while those of the C(2)—C(3) and C(4)—C(5) ordinary bonds increase by more than 40% on going from the open form to the corresponding cyclic form. This is due to the fact that the corresponding bond orders in structures **A** and **B** (see Scheme 1) differ by a unity. Mention can also be made of a substantial weakening of the C(6)—S(7) and C(1)—S(12) bonds (by ~20%) and appreciable weakening of the C(8)—S(7) and C(11)—S(12) bonds (by ~8—14%). This is accompanied by the above-mentioned decrease in absolute values of the atomic charges of C(1), C(6), C(8), C(11), S(7), and S(12) and, correspondingly, by a decrease in the polarization of these bonds.

As should be expected, substituent effects are particularly pronounced for the ring atoms involved in the corresponding chemical bonds, the S(7) and S(12) atoms, and, of course, the chemical bonds in which these atoms are involved. The most pronounced is the effect of sulfonyl groups in position 5 of the thiophene rings (compounds **1A** and **1B**). By and large, it is noteworthy that the structural and electronic characteristics of the C(1)—C(6) fragment involved in the rearrangement (see Scheme 1) are nearly identical for each group of three structurally similar forms (**1A—3A** and **1B—3B**).

Table 3 lists the compositions of the frontier MOs of compounds **1—3**. We present here only those contributions of different C, S, and other atoms that are at least 0.25%, so that their sum in each case is at least 95%. The contributions of the AOs of F and H were found to be negligibly small. As can be seen from the data listed in Table 3, the common rule for the three compounds studied is that both frontier MOs in their cyclic forms (in contrast to the open forms) are localized on the central fragment. This means that transition to the excited state in cyclic structures must be accompanied by redistribution of the electron density over this fragment rather than by transfer of an electron between this fragment and substituents, as is the case of the open forms. It is noteworthy that the atoms C(1) and C(6) are almost not involved in this redistribution (the contributions of the AOs of C(1) and C(6) to the HOMOs and LUMOs of molecules **1B—3B** in most cases do not exceed 0.5%).

Thus, the results of our quantum-chemical calculations indicate that the molecular structures of this type

**Table 3.** Composition of the frontier MOs of compounds **1—3**

| Compound | HOMO / LUMO (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | C(1), C(6) | C(2), C(5) | C(3), C(4) | S(7), S(12) | C(8), C(11) | C(9), C(10) | C(13), C(15) | C(14) | Atoms of substituents $R^a$, $R^b$, and $R^c$ |
| **1A** | 2.9 | 17.6 | 0.6 | 19.8 | 3.2 | 4.2 | 0.8 | ≤0.25 | ≤0.25 |
| | 2.0 | <0.25 | 1.6 | 1.0 | 7.3 | 1.1 | <0.25 | <0.25 | 69.6 |
| **1B** | 1.1 | 5.4 | 7.9 | 19.8 | 6.5 | 6.5 | ≤0.25 | ≤0.25 | 1.9 |
| | <0.25 | 18.5 | 11.8 | 1.2 | 10.3 | 4.9 | <0.25 | <0.25 | 2.1 |
| **2A** | 3.0 | 0.8 | ≤0.25 | ≤0.25 | 3.5 | 3.2 | ≤0.25 | ≤0.25 | 77.1 |
| | 12.0 | 2.9 | <0.25 | 4.8 | 7.7 | 6.7 | <0.25 | <0.25 | 27.7 |
| **2B** | 0.3 | 3.4 | 6.4 | 6.7 | 5.1 | 7.8 | ≤0.25 | ≤0.25 | 36.2 |
| | <0.25 | 17.2 | 10.5 | 1.3 | 9.9 | 3.8 | <0.25 | <0.25 | 10.5 |
| **3A** | 6.9 | 3.4 | ≤0.25 | 0.6 | 6.8 | 4.3 | ≤0.25 | ≤0.25 | 51.4 |
| | 4.0 | 0.8 | 38.2 | 1.2 | 1.6 | 1.0 | 0.4 | 0.3 | <0.25 |
| **3B** | 0.3 | 5.6 | 9.5 | 6.8 | 5.5 | 11.3 | ≤0.25 | ≤0.25 | 18.0 |
| | <0.25 | 18.4 | 10.9 | 1.2 | 12.8 | 2.8 | <0.25 | <0.25 | 3.0 |

of dithienylethenes can be satisfactorily described in the conventional MNDO approximation. Though the $\Delta H_f$, $\mu$, $\varepsilon_f$, $\varepsilon_v$, and $\varepsilon_v - \varepsilon_f$ parameters related to some experimentally measured values are strongly dependent on the chemical nature of substituents in the thiophene rings, these substituents have little effect on the atomic charges and bond strength indices of the C(1)—C(6) fragment involved in the rearrangement, which accompanies the photochromic transition. In the open forms **1A—3A**, the frontier MOs are composed mainly of the orbitals of the atoms constituting the substituents. Unlike this, in cyclic structures **1B—3B** these MOs are composed mainly of the orbitals of the atoms constituting the common (central) structural fragment comprising the thiophene rings and C atoms of the perfluoropentene ring involved in the ethylene bond. Because of this, it is experimental and theoretical studies of cyclic forms that seem to be more promising from the standpoint of correlation analysis and prediction of photochromic properties of dithienylperfluorocyclopentenes.

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