A specific intramolecular interaction in a bis(2-thienyl)maleimide derivative

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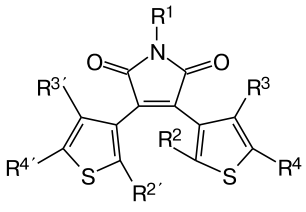
3,4-Bis(4-ethoxycarbonyl-3-hydroxy-5-methyl-2-thienyl)-1-phenyl-1*H*-pyrrole-2,5-dione shows no photochromism in the crystalline state, despite its typical "photochromic" structure (X-ray diffraction data): the *anti*-parallel orientation of the thienyl fragments relative to the plane of pyrrole-2,5-dione and a short distance between potential reactive sites (C(3′)...C(3′A), 3.27 Å). The absence of photochromism was explained by a specific attractive interaction between the O atoms of the maleimide ring and the thiophene S atoms, which can preclude UV-induced photocyclization.

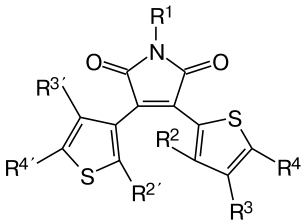
Key words: maleimide, dithienylethenes, X-ray diffraction analysis, molecular conformation, hydrogen bond, attractive interaction.

Dihetarylmaleimide derivatives occupy an important place among thermally irreversible photochromes promising for use in optoelectronics.[1—4] Recently discovered convenient routes to dihetarylmaleimides gave impetus to detailed investigations of their structures and physicochemical properties.[4—7] Bis(3-thienyl)ethenes with a maleimide bridge (**1**) are typical photochromes.[1,2] Replacement of one 3-thienyl fragment by a 2-thienyl fragment makes the photochromism much less pronounced: *e.g.*, the quantum yield of the photocyclization of compound **2** ($R^2 = R^3 = Me$, $R^4 = Ph$) is ~10 times lower than that for the corresponding bis(3-thienyl)ethene **1**.[3] No documented examples of the photochromism in bis(2-thienyl)-maleimide derivatives **3** have been furnished hitherto,[4] while structurally similar compounds with a perfluorocyclopentene bridge are good photochromes.[8—12] To better understand why compounds **3** are not photoactive, we studied the molecular structure of 3,4-bis(4-ethoxycarbonyl-3-hydroxy-5-methyl-2-thienyl)-1-phenyl-1*H*-pyrrole-2,5-dione (**3a**) using X-ray diffraction. The synthesis and spectroscopic characteristics of compound **3a** have been described earlier.[4]

The molecular structure of **3a** is shown in Fig. 1. The molecule has the axis of symmetry C_2 coinciding with an analogous axis of symmetry in the unit cell. The thiophene fragments make angles of 30.60° with the plane of the pyrrole-2,5-dione. The dihedral angle between the two thiophene rings is 31.81°. The alkoxycarbonyl fragments, except for the terminal methyl groups, are coplanar with the corresponding thiophene rings (to within ±0.1 Å). The hydroxy O(1′) and carbonyl O(2′) atoms are linked by an intramolecular hydrogen bond (O(1′)....O(2′), 2.62 Å; O(1′)—H...O(2′), 1.78 Å, O(1′)—H....O(2′) 147.16°). The angle between the phenyl substituent and the plane of the pyrrole ring is nearly the same (40.86°) as in other phenylpyrroles.[13,14] The thienyl fragments are *anti*-parallel relative to the pyrrole ring. The distance between the potential reactive sites C(3′)....C(3′A) (3.27 Å) is some-



1



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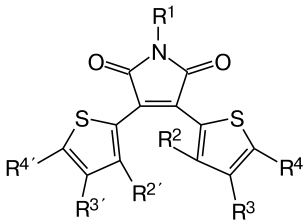

3, **3a**

1, **2**, **3:** R^1, R^2—$R^{4'}$ = Alk, Ar; **3a:** R^1 = Ph, $R^2 = R^{2'}$ = OH, $R^3 = R^{3'}$ = COOEt, $R^4 = R^{4'}$ = Me

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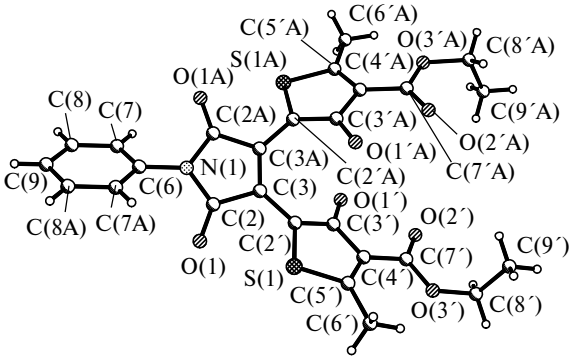
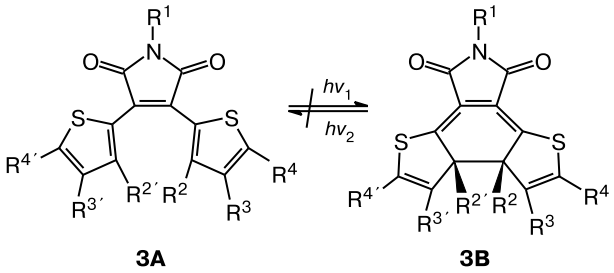


Fig. 1. The molecular structure **3a**.

what shorter than a normal van der Waals carbon—carbon contact (3.47 Å).[15] Thus, compound **3a** in the crystalline phase exists in an *anti*-parallel conformation with a distance ≤4.0 Å between the reactive sites, which is characteristic of photochromes.[16,17] However, irradiation with UV light did not result in the photochromic transition **3A** ⇄ **3B** (Scheme 1). Nor did variation of the substituents in the thiophene and maleimide rings give rise to photochromism either in the crystals or in solutions.[4]

Scheme 1



An analysis of the intramolecular distances in structure **3a** revealed some specificity of the O(1)...S(1) contact geometry: (1) the O(1)...S(1) distance is noticeably shorter (2.97 Å) than the sum of the van der Waals radii of the O and S atoms (3.32 Å),[15,18] (2) the S(1)...O(1) vector slightly deviates (by 19.7°) from the plane of the thiophene ring, and (3) this vector is virtually parallel to the S(1)—C(5´) bond (the angle O(1)—S(1)/S(1)—C(5´) is 156.37°). As shown earlier,[19] such a contact geometry is theoretically favorable for a specific nonbonding electron attractive interaction between the S and O= atoms, which can result from an orbital n—σ*-interaction of the lone electron pair of the carbonyl O atom with the antibonding orbital of the S—C bond. Such shortened intramolecular nonbonding contacts in crystal structures have been observed experimentally. An analysis of their nature[20—22] has revealed that the S...O interaction energy is mainly contributed by the electrostatic (Coulomb) component. For instance, according to the RHF/AM1 quantum-chemical calculations with the Fletcher—Reeves optimization, the energy of this interaction in 3-amino-β-mercaptoacrolein is estimated at −6.5 kcal mol^{-1}, which is comparable with a hydrogen bonding energy.[22]

Bithiophene ester derivatives provide another example of the attractive electron interaction. As shown earlier,[23,24] these structures are stabilized by the intramolecular attractive interaction S...O= even in a distorted conformation.

Apparently, structure **3a** can also show a strong intramolecular nonbonding attractive interaction between the O atoms of the maleimide bridge and the thiophene S atoms, which stabilizes its conformation and precludes any structural rearrangement during photocyclization. Such an attractive interaction seems to be characteristic of all bis(2-thienyl)maleimides **3** and accounts for their inertness in UV-induced photocyclization.

Experimental

X-ray diffraction study of compound 3a. Ruby-colored prismatic single crystals of compound **3a** ($C_{26}H_{23}NO_8S_2$) suitable for X-ray diffraction analysis were grown from light petroleum—ethyl acetate (3 : 1). The unit cell parameters and the intensities of 2386 independent reflections were measured on a Syntex P2/1 diffractometer at 193 K (λ(Mo-Kα) radiation, graphite monochromator, ω scan mode, 3.39° ≥ θ ≤ 25.99°). The crystals are monoclinic, space group *C*2/*c*, a = 17.430(5) Å, b = 16.507(4) Å, c = 10.038(3) Å, β = 118.855(18)°, V = 2529.5(12) Å^3, Z = 4, d_{calc} = 1.422 g cm^{-3}, m.p. 466—468 K, M = 541.57. The structure was solved by the direct method and refined by the full-matrix least-squares method on F in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were located geometrically and refined isotropically using a riding model. The final R-factors: R_1 = 0.048 and wR_2 = 0.098 for 1916 reflections with $I > 2\sigma(I)$ and R_1 = 0.063 and wR_2 = 0.102 for all independent reflections. All calculations were performed with the Siemens[25] and SHELXTL PLUS 5 program packages.[26] The atomic coordinates and thermal and geometrical parameters of structure **3a** have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 796 863).

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