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PHOTO- AND THERMOCHROMIC SPIRANES 26*. COMPARATIVE STUDY OF THE STRUCTURE OF BENZOXAZINONE SERIES SPIROPYRANS USING X-RAY ANALYSIS

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X-Ray analysis has been used to study the structure of a spiropyran in the series 4-oxodihydro-2H-1,3-benzoxazine with the molecular formula $C_{27}H_{23}N_3O_5$. The structural parameters for this spiropyran, which contains a phenoxyacetic acid hydrazide substituent, have been compared with those of other spiropyrans in this series.

Keywords: benzoxazinone, hydrazides, spiropyran, X-ray analysis, photochromism

The work concerns the X-ray analysis and photochemical investigation of the spiropyran **1** and continues a comparative study of the structure of 3,6'-dimethylspiro(4-oxodihydro-2H-1,3-benzoxazine-2,2'-[2H]chromenes) [1]. Compound **1** [2] was prepared by condensation of spiropyran **2** [3] with phenoxyacetic acid hydrazide. This compound is of obvious interest since it gives the potential for stabilizing open colored forms *via* the chelation of metal ions to give complexes of type **4** [4] and can be used as a promising precursor of compounds with regulating magnetic and photochemical parameters.

As we have shown in preceding experiments the UV light irradiation of spiropyran **2** in the steady state mode reveals photochromic properties in solutions at low temperatures and in the solid phase as thin films prepared by vacuum thermal spray coating on glass or quartz backings [2]. By contrast with compound **2**, the spiropyran **3** shows photochromic properties only in solution under the same conditions [5]. Spiropyran **1** is not a photoactive compound [2], i.e. exchange of a formyl group for a hydrazone leads to the disappearance of the photochromic properties in the solid phase and in solutions in the range from -196°C to room temperature under UV light irradiation in the steady state mode.

* Dedicated to Edmund Lukevics on his 70th birthday

* For Communication 25 see [1].

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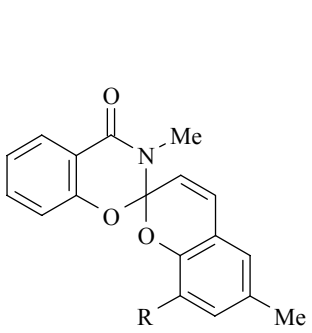

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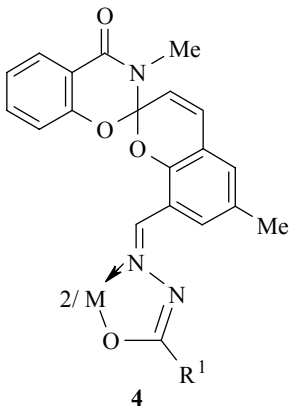

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1 R = CH=NNHCOCH$_2$OPh; **2** R = CHO; **3** R = H;
4 R^1 = *p*-C$_6$H$_4$Me, *p*-C$_6$H$_4$NO$_2$, *m*-C$_6$H$_4$Br; M = Co, Ni, Zn, Cu

In order to account for the effect of the structure of spiropyran **1** on the photochromic properties an X-ray analysis of its monocrystal was carried out.

In molecule **1** (Fig. 1) the benzopyran and benzoxazine fragments are approximately orthogonal to one another and individually nonplanar. The benzoxazine fragment has a twist along the O$_{(1)}$…N$_{(3)}$ axis of 38.1° and the benzopyran fragment twists of 20.2 and 11.4° around O$_{(1')}$…C$_{(3')}$ and O$_{(1')}$…C$_{(4')}$ respectively.

The substituent at position 8' does not lie in the plane of the benzopyran fragment as a result of rotation of the phenol fragment by 15.8° along the C$_{(17)}$–C$_{(19)}$ bond (Fig. 1). The deviation of atom N$_{(3)}$ from the plane through atoms C$_{(4)}$, C$_{(2'2)}$, C$_{(12)}$ is 0.15 Å (for compound **2** – 0.006 Å) and occurs in the lower end of the range of similar values (0.34-0.12 Å) for previously studied [4] indoline spiropyrans with a methyl substituent on the nitrogen atom. The overall valence angles at the N$_{(3)}$ nitrogen atom come to 356.8° (355.8° in compound **3**). These values point to a small pyramidalization of configuration for the nitrogen atom and a smaller *sp*^{3}-character of its unshared electron pair when compared with indoline spiropyrans. The unshared electron pair on the nitrogen atom is found in a *syn* orientation to the σ*-orbital of the C$_{(2'2)}$–O$_{(1')}$ bond.

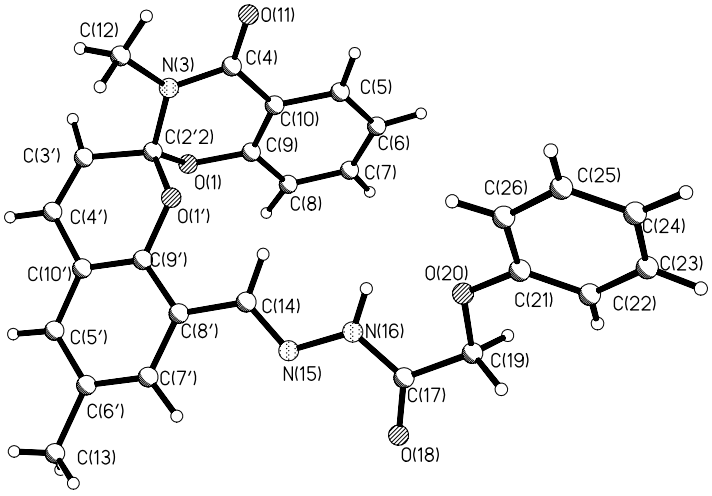

Figure 1. Structure of the spiropyran **1** from X-ray data

Introduction of a bulky substituent does not lead to a major change in the molecular structure of the central fragment. When comparing the molecular structures of compounds **1** and **3** by superimposing along the $C_{(2'2)}$, $N_{(3)}$, $O_{(1)}$ atoms (Fig. 2) the deviation of the atoms is small and does not exceed 0.5 Å.

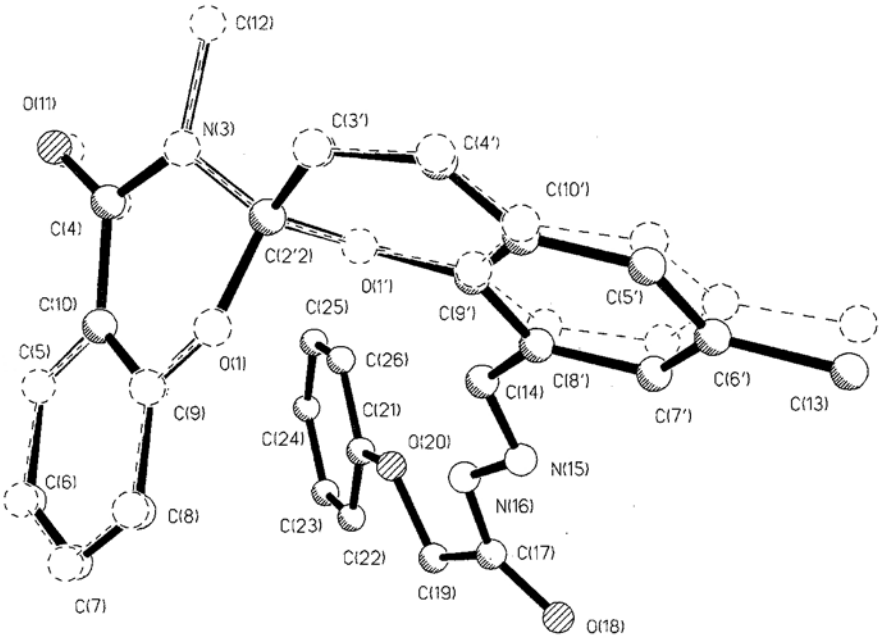

Figure 2. Comparative molecular structures of the spiropyrans **1** and **3** by the superposition method (dotted lines for molecule **3**)

In compound **1** the $N_{(3)}$ atom takes part in amide conjugation with the $C_{(4)}$=$O_{(11)}$ carbonyl group and this leads to shortening of the $N_{(3)}$–$C_{(4)}$ bond to 1.370(4) Å (in compound **2** the $N_{(3)}$–$C_{(4)}$ bond length is also 1.370(3) Å) and to a decrease in the efficiency of the *n*-σ^* interaction of the nitrogen atom unshared electron pair and the σ^*-orbital of the $C_{(2'2)}$–$O_{(1)}$ bond in the molecule **1** when compared with indoline analogs [4].

In molecule **1** the $N_{(16)}$ atom can also take part in amide conjugation with the $C_{(17)}$=$O_{(18)}$ carbonyl group. The overall angles at the $N_{(16)}$ atom are 360° and the bonds length are 1.348(3) for $N_{(16)}$–$C_{17)}$ and 1.220(3) Å for $C_{(17)}$=$O_{(18)}$. The length of this bond is less than the analogous $C_{(14)}$=$O_{11)}$ and this points to a participation of the $O_{(11)}$ atom in an intermolecular hydrogen bond while the $O_{(18)}$ does not form such an intermolecular hydrogen bond.

Judged by the $O_{(1)}$–$C_{(9)}$ bond length of 1.385(4) (1.370(3) in compound **2**) and $O_{(1')}$–$C_{(9')}$ of 1.391(4) (1.375(3) Å in compound **2**) the participation of an unshared electron pair of the $O_{(1)}$ and $O_{(1')}$ atoms in conjugation with the benzene rings is the same and hence the polarity of these bonds is the same. However, these bonds are longer in compound **1** than **3** and this is probably a result of forming an intramolecular and intermolecular hydrogen bond (Fig. 1). The lengths of the $O_{(1)}$–$C_{(2'2)}$ and $O_{(1')}$–$C_{(2'2)}$ bonds of 1.423(4) and 1.433(4) Å (1.423(3) and 1.424(3) Å in compound **3**) are the same within 3σ limits but are outside the range of analogous C_{spiro}–O bond lengths in indoline spiropyrans (1.485-1.492 Å). The bond length for $N_{(3)}$–$C_{(2'2)}$ is 1.455(4) Å (1.444(3) Å in compound **3**) and it is found within the range of analogous values for indoline spiropyrans (1.438-1.497 Å [4]). This evidently explains the absence of photochromic effects for compound **1** in the solid phase, similarly to compound **3**, in contrast to compound **2** with a formyl substituent in position 8' [5].

It was expected that the introduction of a bulky substituent at the 8' position would lead to a looser molecular packing in the crystal and, in turn, favorably affect the photochromic properties of the crystal. The overall energy of the crystal lattice for compound **1** is -39.7 kcal/mol (-32.0 kcal/mol in compound **3**).

An intermolecular N–H···O=C type hydrogen bond is achieved with the parameters: $O_{(11a)}\cdots N_{(16b)}$ 2.961(4), $O_{(11a)}\cdots H_{(16b)}$ 2.13(4) Å, and $O_{(11a)}H_{(16b)}N_{(16b)}$ 146.5°. Hence the spiropyran molecule **1** forms dimer associates (Fig. 3) with an energy of pairwise intermolecular interaction of -13.5 kcal/mol.

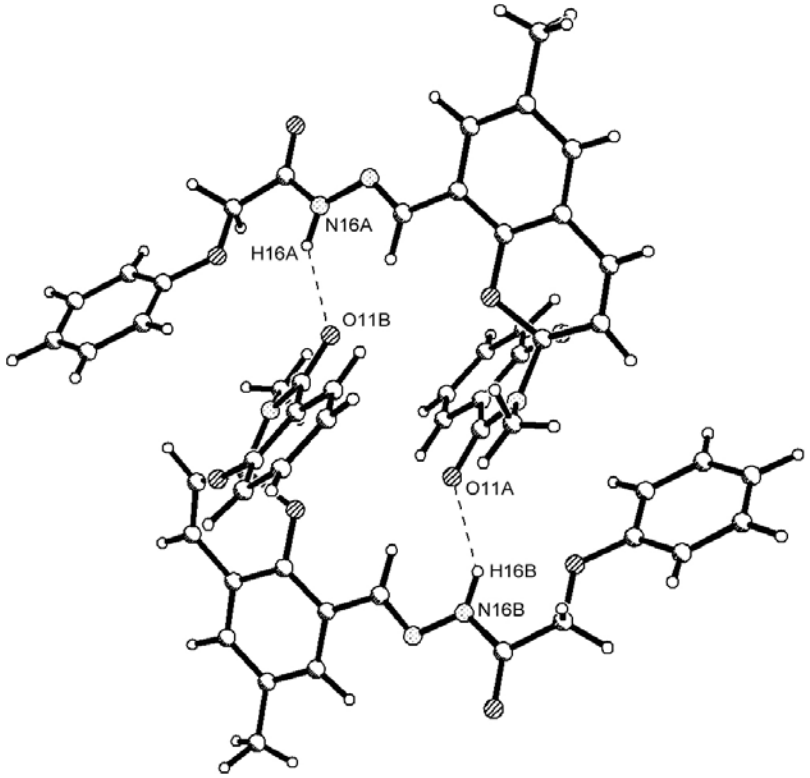

Figure 3. Representation of the dimer associates in the spiropyran 1crystal

It should be noted that the substituent does not have a fully conjugated system and has a degree of rotation around the single bonds $C_{(17)}$–$C_{(19)}$, $O_{(20)}$–$C_{(19)}$, and $O_{(20)}$–$C_{(21)}$ of 21.2, -14.6, and 17.3° respectively. In the crystal, molecule **1** occupies a conformation with a minimal volume: the phenol fragment is turned in such a way that an intramolecular hydrogen bond with the parameters $O_{(20)}\cdots N_{(16)}$ 2.618(4) and $O_{(20)}\cdots H_{(16)}$ 2.13(4) Å becomes possible (Fig. 1).

Hence the introduction of a bulky substituent in molecule **1** does not lead to a marked change in the molecule structure and it is similar to the structure of compound **2**.

EXPERIMENTAL

Compound **1** ($C_{27}H_{23}N_3O_5$) crystallized from methanol in the monoclinic system and its basic crystallographic parameters are: a = 13.842(2), b = 15.945(3), c = 11.098(3) Å, β = 101.00(3) °, V = 2404.4(9) $Å^3$, d_{calc} = 1.297 g/cm^3, M = 469.48, space group $P2_1/c$, Z = 4. A set of the intensities of 4533 reflections was obtained on a *KUMA*-4 four circle diffractometer (Mo$K\alpha$ radiation) at T = 293°K and $2\theta_{max}$ = 54°). The structure was solved by a direct method and refined in full matrix least squares analysis in the anisotropic

approximation for non-hydrogen atoms using the *SHELXL*-97 program package [7]. Hydrogen atoms were calculated geometrically. The final refinement parameters were: $R = 0.051$, GOF = 0.749, $F(000) = 984$ for 1347 reflections with $I > 2\sigma(I)$.

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