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X-ray crystallography and computational studies of a variety of pyrrole derivatives obtained from mesoionic oxazoles and selected chromenones

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ABSTRACT

The molecular structure, packing properties, and intermolecular interactions of a series of pyrrole derivatives have been determined by single-crystal X-ray diffraction. They were efficiently synthesized from mesoionic oxazoles and selected chromenones via initial 1,3-dipolar cycloaddition followed by cascade transformations. Compounds **4**–**6** are described as three fused rings associated in the crystal lattice through H-bonding interactions. Besides the H-bonding interactions encountered in the crystal packing of **4**–**8**, a different strong centrosymmetric π-interaction has been found in **8**, involving the cyano group and the π-system of aromatic pyrrole ring. A density functional theory (DFT) study was carried out on the supramolecular dimer in order to understand the nature and role of this intermolecular force in driving the molecular packing.

1. Introduction

Pyrrole derivatives represent a class of compounds of great importance in heterocyclic chemistry. They can have intrinsic biological properties and also constitute the structural feature of many biologically active compounds. The synthetic approaches to pyrrole derivatives are mostly multistep and low yielding [1]. Thus, the development of new synthetic methods still remains an attractive goal. We have recently reported [2] the synthesis of various types of pyrrole derivatives starting from N-substituted and N-unsubstituted 1,3-oxazolium-5-olates and selected chromenones and thioanalogues. The isolated products show that these 1,3-dipolar cycloaddition reactions proceed differently from the classical behaviour. Their formation is consistent with the high levels of regiochemical control and by the *exo/endo* preference in the initial cycloaddition step. Scheme 1 summarizes the results of these investigations.

As shown in path (i) of the Scheme 1, starting from 4-methyl-2-phenyl-1,3-oxazolium-5-olate (MPO) **2** and 3-carboxymethylcoumarin **1a**, an unusual retention of the carboxylic function was observed, affording pyrrolocoumarin **4**, incorporating a stable α-aminoacid moiety; in path (ii) from MPO **2** and 3-acetylcoumarin **1b**, a similar aminoacid derivative was recovered and subsequently esterified with diazomethane into **5**. Paths (iii) and (iv) show that using 3,4-dimethyl-2-phenyl-1,3-oxazolium-5-olate (DMPO) **3** and 3-cyanocoumarin **1c** or 3-cyanochromone **1d**, compounds **7** and **8** respectively were obtained, as consequence of fragmentation and decarboxylative degradations of the corresponding *endo*-cycloadducts. Finally, in path (v), starting from DMPO **3** and 3-carboxymethylthiocoumarin **1e**, pyrrolothiocoumarin **6** was isolated and its formation is consistent with the standard decarboxylation of an initial 1,1-*exo* cycloadduct.

Despite the importance of the coumarin derivatives structural motifs occurring in many natural products and drugs [3], little is known in the literature about their crystallographic structures and intermolecular interactions that could be an aid in the elucidation of the molecular recognition processes involved in the biological activity. In this paper, we present the crystal structures both of the pyrrolocoumarin or pyrrolothiocoumarin derivatives **4**–**6** and of the fragmentation and decarboxilative degradation products **7**–**8** and an analysis of the corresponding molecular packing and intermolecular interactions involved in the crystal lattice. Although in pyrrolocoumarin and pyrrolothiocoumarin **4**–**6** and the pyrrole derivatives **7**–**8** the molecular structures are quite similar, respectively, the molecules pack in different ways. However, it has been observed that the hydrogen bonding pattern forms prevalently cyclic ring in the **4**–**7** molecular arrangements, whereas in **8** the intermolecular interactions not involve only classical H-bonding but also π-interactions.

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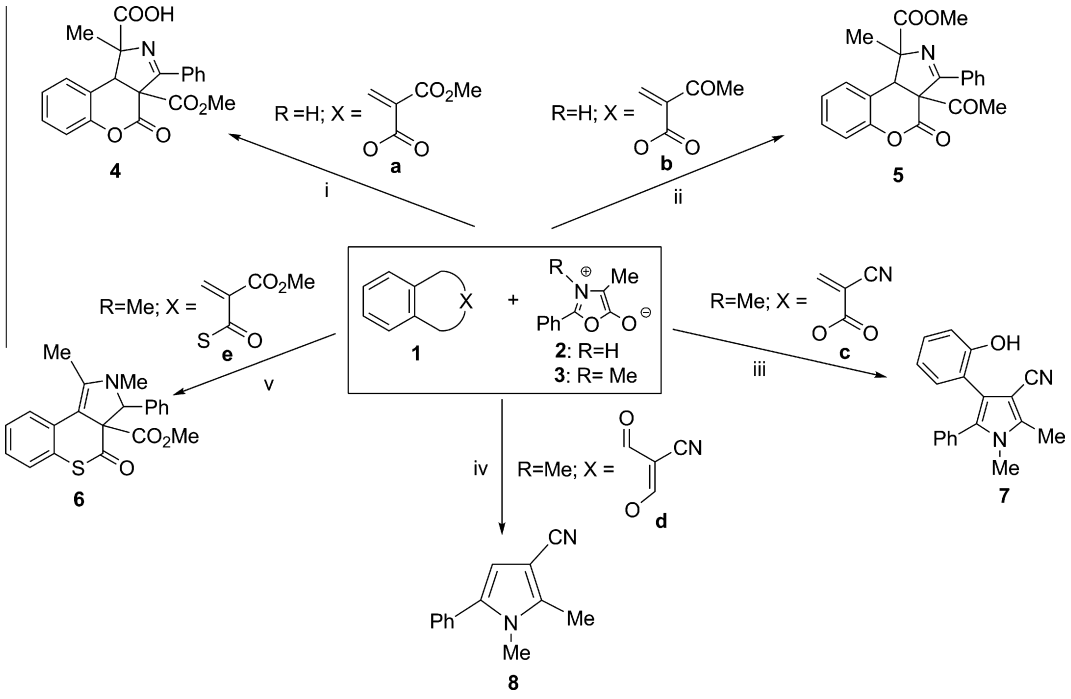
2. Results and discussion

The molecular structures of pyrrolocoumarin or pyrrolothiocoumarin derived compounds **4**–**6** and of the corresponding fragmentation and decarboxylative degradation products **7**–**8** are shown in Figs. 1a–5a with atomic numbering schemes. Summaries of selected bond lengths and angles and torsion angles are given in Tables 1 and 2, respectively. In Table 3, the geometric parameters



Scheme 1. Synthesis of pyrrole derivatives.

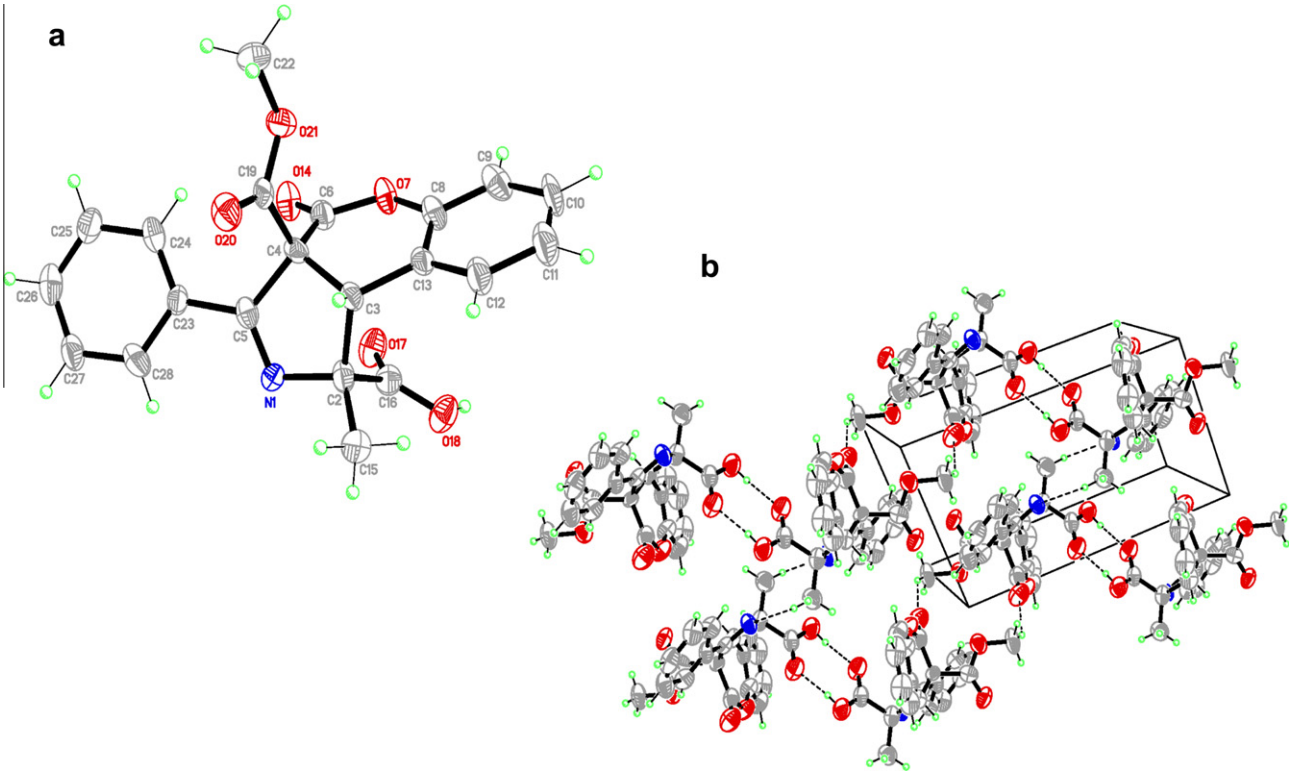


Fig. 1. (a) Ortep diagram of pyrrolcoumarin **4** with atomic numbering scheme and displacement ellipsoids drawn at the 30% probability level. (b) View of the molecular arrangement on the [010] crystallographic plane covered by supramolecular $R^2_2(8)$ and $R^2_2(14)$ synthons formed by H-bonds O(18)-H(18)...O(17)^{i}, C(15)-H(15A)...N(1)^{ii}, and C(22)-H(22C)...O(14)^{iii}, respectively for **4**. Dotted lines indicate C-H. . .O or C-H. . .N intermolecular contacts. Symmetry code: (i) –*x*, –*y*, –*z* + 1; (ii) –*x* – 1, –*y*, –*z* + 1; (iii) –*x*, –*y*,–*z*.