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Reactions of guaiazulene with thiophene-2,5-dicarbaldehyde and furan-2,5-dicarbaldehyde in methanol in the presence of hexafluorophosphoric acid: a facile preparation and properties of delocalized dicarbenium-ion compounds stabilized by two 3-guaiazulenyl groups and a thiophene (or furan) ring

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Abstract—Reaction of guaiazulene (**1**) with thiophene-2,5-dicarbaldehyde (**2**) in methanol in the presence of hexafluorophosphoric acid at 25 °C for 3 h gives as high as 90% isolated yield of the delocalized dicarbenium-ion compound, 2,5-thienylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**3**). Similarly, reaction of **1** with furan-2,5-dicarbaldehyde (**4**) under the same conditions as the above reaction affords the corresponding dicarbenium-ion compound, 2,5-furylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**5**), in 84% isolated yield. Along with a facile preparation and the spectroscopic and electrochemical properties of **3** and **5**, comparative studies on the ^{1}H and ^{13}C NMR spectral and chemical properties of **3** and **5** with those of the delocalized mono- and dicarbenium-ion compounds [i.e., (3-guaiazulenyl)(2-thienyl)methylium hexafluorophosphate (**7**), (2-furyl)(3-guaiazulenyl)methylium hexafluorophosphate (**9**), α,α'-bis(3-guaiazulenylmethylium) bis(tetrafluoroborate) (**10**), 1,2-phenylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**11**), and 1,4-phenylenebis(3-guaiazulenylmethylium) bis(tetrafluoroborate) (**12**)] are reported. Moreover, referring to the results of the X-ray crystallographic analyses of **7**, **9**, **11**, and **12**, the optimized 2,5-thienylenebis(3-guaiazulenylmethylium)- and 2,5-furylenebis(3-guaiazulenylmethylium)-ion structures for **3** and **5**, calculated by a WinMOPAC (version 3.0) program using PM3 as a semiempirical Hamiltonian, are described.

1. Introduction

In the previous papers,[1–13] we reported a facile preparation and the crystal structures as well as the spectroscopic, chemical, and electrochemical properties of the delocalized mono- and dicarbenium-ion compounds stabilized by the expanded π-electron systems with a 3-guaiazulenyl group. In relation to our basic studies, the synthesis, stability, spectroscopic and chemical properties, crystal structures, electrochemical behavior, and theoretical study (e.g., ab initio calculations, DFT, GIAO-NMR, and NICS) of the azulenium-,[14–16] azulenylium- (and azulenylmethylium-)[17–27] ions and the azulen-1-yl-substituted cations[17c,28–30] have been studied to a considerable extent, and a large number of the results and discussion regarding those delocalized cations have been well documented. During the course of our systematic investigations on the delocalized 3-guaiazulenyl-substituted carbenium-ion compounds derived from naturally occurring guaiazulene[31] (**1**), we have recently found (i) that the reactions of **1** with thiophene-2-carbaldehyde (**6**) and 2-furaldehyde (**8**) in methanol in the presence of hexafluorophosphoric acid at 25 °C for 30 min gave the corresponding monocarbenium-ion compounds, (3-guaiazulenyl)(2-thienyl)methylium hexafluorophosphate (**7**) and (2-furyl)(3-guaiazulenyl)methylium hexafluorophosphate (**9**) with the representative two resonance forms [i.e., the 3-guaiazulenylium- and 2-thienylium- (or 2-furylium-) ion

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structures (**A** and **B**)] (see Chart 1), respectively, in 98 and 93% isolated yields;[10] and (ii) that the crystal structures of **7** and **9** could be determined by means of the X-ray diffraction (see Fig. 1),[10] and from the dihedral angles between the least-squares planes, it was found that the plane of the 2-thienyl group of **7** was twisted by 13.7° from the plane of the 3-guaiazulenyl group, owing to the influence of steric hindrance and repulsion between the sulfur atom of the 2-thienyl group and the H-2′ hydrogen atom of the 3-guaiazulenyl group, whose twist was larger than that between the planes of the 2-furyl and 3-guaiazulenyl groups of **9** (7.2°).[10] Moreover, from the bond lengths of **7** and **9**, it could be inferred that, although the positive charge of **7** in the single crystal was mainly localized at the C-α carbon atom, forming the 3-guaiazulenylmethylium-ion structure, the positive charge apparently was transferred to the seven-membered ring or the 2-thienyl group, forming the 3-guaiazulenylium- or 2-thienylium-ion structure and, further, the same result could be inferred for **9** (see Chart 1). As a systematic investigation on the above chemistry, our interest has quite recently been focused on a facile preparation, the molecular structures, and properties of the following dicarbenium-ion compounds, i.e., 2,5-thienylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**3**) and 2,5-furylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**5**), with the representative four resonance forms of **C**–**F** (see Chart 2), with a view to a comparative study on those of **7** and **9**. In relation to these studies, in 2001 Ito et al. reported the synthesis, properties, and redox behavior of 2,5-thiophenediylbis[bis(3-methyl-1-azulenyl)methylium] bis(hexafluorophosphate) and 2,5-thiophenediylbis[bis(3,6-di-*tert*-butyl-1-azulenyl)methylium] bis(hexafluorophosphate),

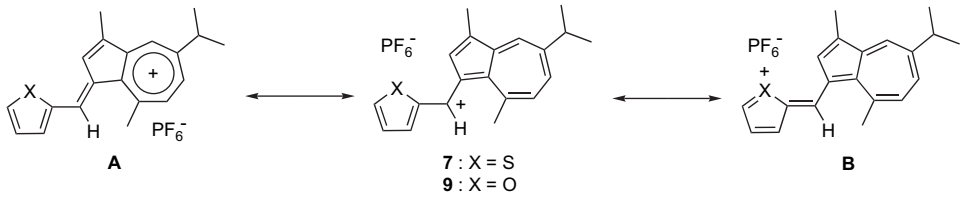

Chart 1.

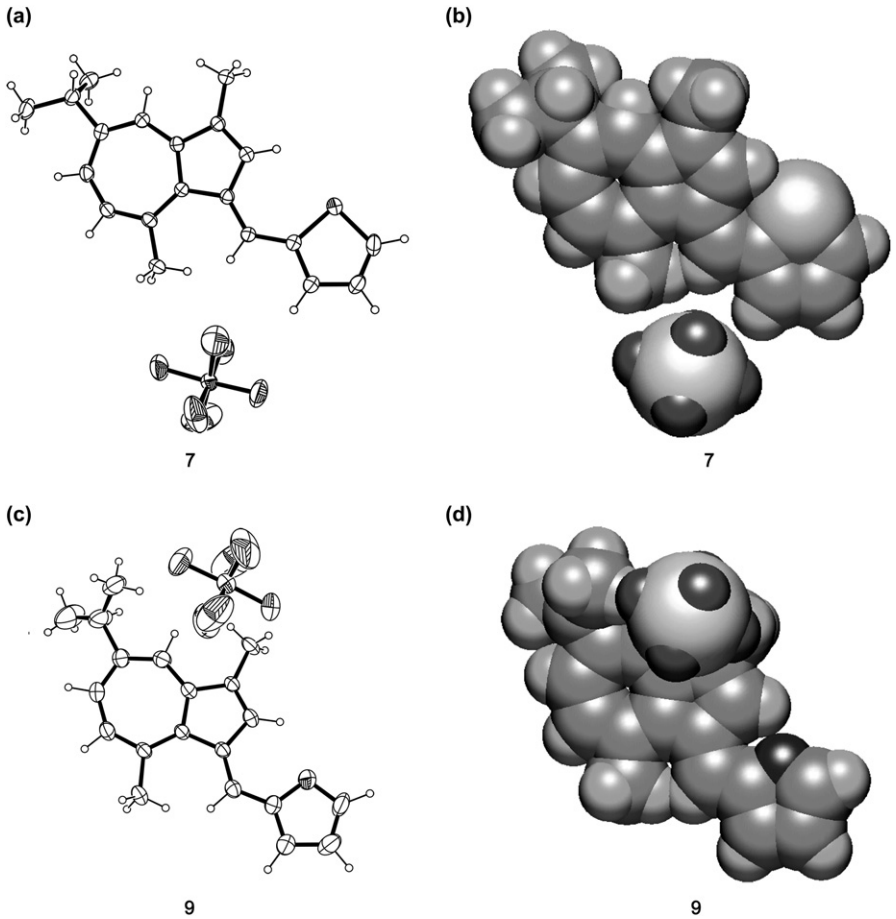

Figure 1. (a) The ORTEP drawing of **7** (30% probability thermal ellipsoids).[10] (b) The crystal structure of **7** shown using a space-filling mode. (c) The ORTEP drawing of **9** (30% probability thermal ellipsoids).[10] (d) The crystal structure of **9** shown using a space-filling mode.