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Reaction of guaiazulene with *o*-formylbenzoic acid in diethyl ether (or methanol) in the presence of hexafluorophosphoric acid: comparative studies on ^{1}H and ^{13}C NMR spectral properties of 3-guaiazulenylmethylium- and 3-guaiazulenium-ion structures

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Abstract—Reaction of guaiazulene (**1**) with *o*-formylbenzoic acid (**2**) in diethyl ether in the presence of hexafluorophosphoric acid at 25 °C for 90 min gives the corresponding monocarbenium-ion compound, [2-(carboxy)phenyl](3-guaiazulenyl)methylium hexafluorophosphate (**3**), quantitatively, which upon treatment with aq $NaHCO_3$ leads to 3-(3-guaiazulenyl)-2-benzofuran-1(3*H*)-one (**5**) in 96% isolated yield. Similarly, reaction of **1** with **2** in methanol under the same conditions as the above reaction affords two kinds of inseparable monocarbenium-ion compounds, **3** and (3-guaiazulenyl)[2-(methoxycarbonyl)phenyl]methylium hexafluorophosphate (**4**) with an equilibrium between them, which upon reaction with a solution of $NaBH_4$ in ethanol at 25 °C for 30 min leads to **5** in 46% isolated yield and (3-guaiazulenyl)-[2-(methoxycarbonyl)phenyl]methane (**6**) in 37% isolated yield. Along with the ^{1}H and ^{13}C NMR spectral properties of a solution of **5** in trifluoroacetic acid-d_1 at 25 °C, whose molecular structure is converted to a ca. 1:1 equilibrium mixture of **7** possessing a partial structure of the 3-guaiazulenylmethylium-ion and **8** possessing a partial structure of the 3-guaiazulenium-ion, comparative studies on the ^{1}H and ^{13}C NMR spectral properties of **7** and **8** with those of the monocarbenium-ion compound, (3-guaiazulenyl)[4-(methoxycarbonyl)phenyl]methylium hexafluorophosphate (**A**), **5**, and **6** are reported. From these NMR studies, it can be inferred that the positive charge of the 3-guaiazulenylmethylium-ion part of **7** apparently is transferred to the seven-membered ring, generating a resonance form of the 3-guaiazulenylium-ion structure η′, and the same result can be inferred for the previously documented monocarbenium-ion compounds **A**–**I**. Moreover, referring to a comparative study on the C–C bond lengths of **A** observed by the X-ray crystallographic analysis with those of the optimized (3-guaiazulenyl)[4-(methoxycarbonyl)phenyl]methylium-ion structure for **A** calculated by a WinMOPAC (Ver. 3.0) program using PM3, AM1, or MNDOD as a semiempirical Hamiltonian, the optimized [2-(carboxy)phenyl](3-guaiazulenyl)methylium-ion structure for **3** calculated using PM3 is described.

1. Introduction

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-,[1–3] azulenylium-, and azulenylmethylium-ion structures[4–14] have been studied to a considerable extent, and a large number of the results and discussion regarding those delocalized carbocation compounds have been well documented. In relation to those basic studies, we previously 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.[15–28] During the course of our systematic investigations on the delocalized 3-guaiazulenyl-substituted carbenium-ion compounds derived from naturally occurring guaiazulene[29] (**1**), we have recently found (i) that the reaction of **1** with methyl terephthalaldehydate in methanol in the presence of hexafluorophosphoric acid at 25 °C for 2 h gave the corresponding monocarbenium-ion compound, (3-guaiazulenyl)[4-(methoxycarbonyl)phenyl]methylium hexafluorophosphate (**A**), in 94% isolated yield; (ii) that the spectroscopic data of **A** led to the molecular structure with a resonance form of the 3-guaiazulenylium-ion structure **A′** in acetonitrile (see Chart 1);[23] and (iii) that along with the spectroscopic data for **A** in acetonitrile, the X-ray crystallographic analysis for **A** (see Fig. 1a,b) also led to the crystal structure with a resonance

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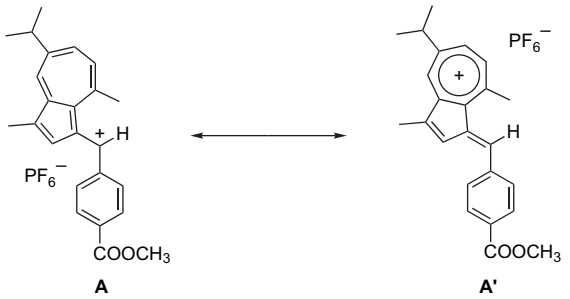

Chart 1.

form of **A′**. As a systematic investigation on the above chemistry, our interest has quite recently been focused on a facile preparation, the molecular structure, and properties of the delocalized monocarbenium-ion compound, [2-(carboxy)-phenyl](3-guaiazulenyl)methylium hexafluorophosphate (**3**), which upon treatment with aq $NaHCO_3$ leads to the formation of 3-(3-guaiazulenyl)-2-benzofuran-1(3*H*)-one (**5**). We now wish to report the detailed studies on the reaction of **1** with *o*-formylbenzoic acid (**2**) in diethyl ether (or methanol) in the presence of hexafluorophosphoric acid affording **3** and (3-guaiazulenyl)[2-(methoxycarbonyl)phenyl]methylium hexafluorophosphate (**4**), whose compounds can be led to **5** and (3-guaiazulenyl)[2-(methoxycarbonyl)phenyl]methane (**6**), respectively, and comparative studies on the ^{1}H and ^{13}C NMR spectral properties of **7** possessing a partial structure of the 3-guaiazulenylmethylium-ion and **8** possessing a partial structure of the 3-guaiazulenium-ion, with an equilibrium between them, yielded from **5** dissolved in trifluoroacetic acid-d_1 at 25 °C (see Fig. 2) with those of **A**, **5**, **6**, and the previously documented monocarbenium-ion

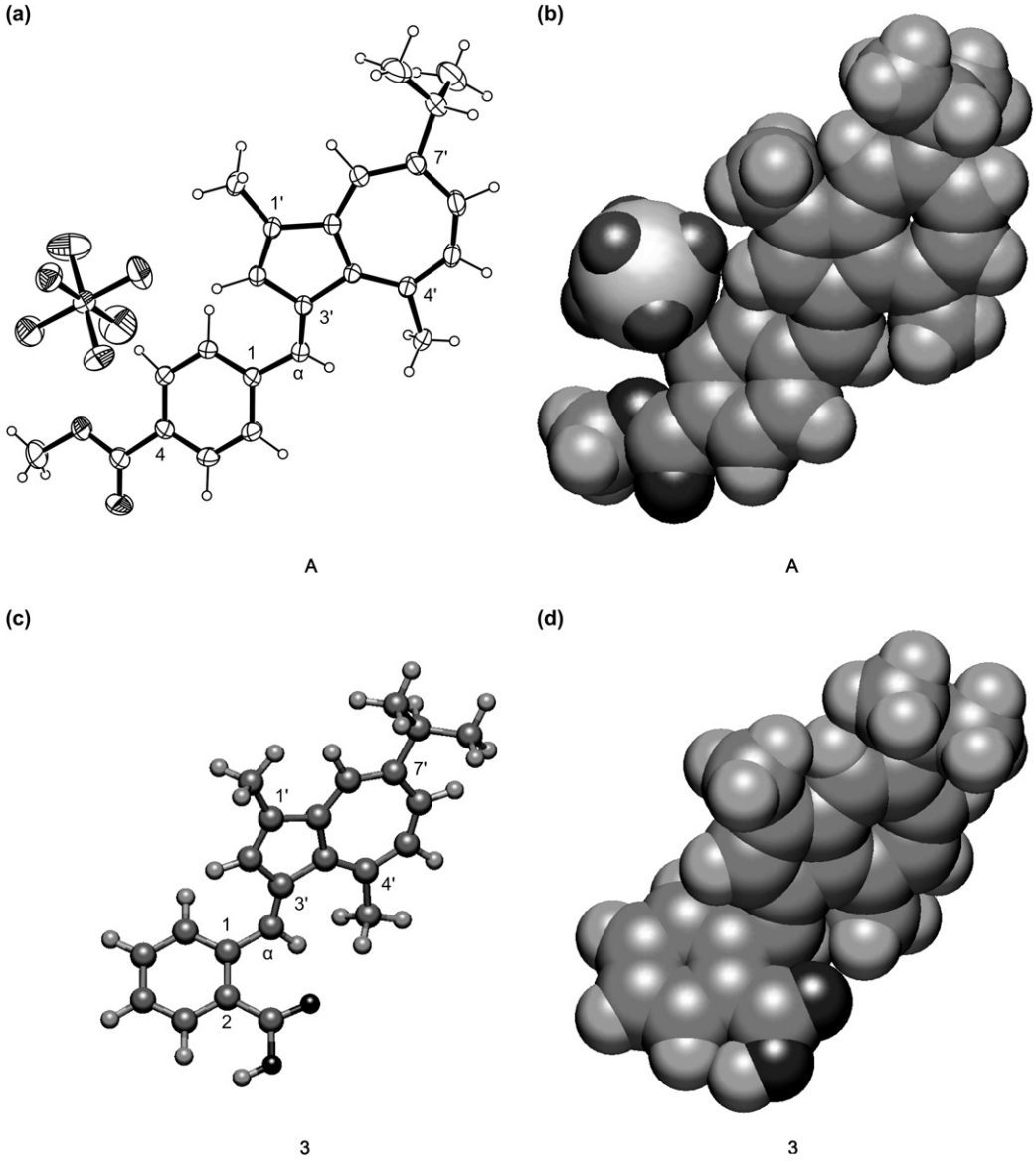

Figure 1. (a) The ORTEP drawing of **A** (30% probability thermal ellipsoids).[23] (b) The crystal structure of **A** shown using a space-filling mode. (c) The optimized [2-(carboxy)phenyl](3-guaiazulenyl)methylium-ion structure for **3**[33] shown using a ball-and-stick mode. The selected bond lengths (Å): C1–C2: 1.405, C2–C3: 1.398, C3–C4: 1.389, C4–C5: 1.391, C5–C6: 1.390, C6–C1: 1.398, C1–Cα: 1.462, C1′–C2′: 1.361, C2′–C3′: 1.465, C3′–C3a′: 1.479, C3a′–C4′: 1.390, C4′–C5′: 1.408, C5′–C6′: 1.373, C6′–C7′: 1.405, C7′–C8′: 1.387, C8′–C8a′: 1.389, C8a′–C1′: 1.466, C8a′–C3a′: 1.434, C3′–Cα: 1.349. (d) The optimized [2-(carboxy)phenyl](3-guaiazulenyl)methylium-ion structure for **3**[33] shown using a space-filling mode.