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SCIENCE DIRECT
Tetrahedron 62 (2006) 586–593
Tetrahedron

Synthesis, properties and molecular structure of a novel dicyanoheptafulvene derivative, 4′-dicyanomethylidenedispiro[cyclohexane-1, 1′-(1′,4′,7′-trihydrocyclopenta[*f*]azulene)-7′,1″-cyclohexane]

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Received 24 August 2005; accepted 6 October 2005

Available online 2 November 2005

Abstract—A novel dicyanoheptafulvene **9** annulated by two spiro[4,5]deca-1,3-dienes was synthesized by the reaction of dispirocyclopentaazulenium cation **8** with bromomalononitrile. Although **9** was found to have a nonplanar heptafulvene structure by its X-ray crystallographic analysis, it is still capable of π-conjugation and thus shows appreciable contribution of the dipolar resonance form **9B** based on its spectroscopic data. The degree of the contribution was further evaluated for various dicyanoheptafulvenes in terms of the partial sum of atomic charges of the dicyanomethylene group in the calculated structures besides the interplanar angles of the heptafulvene part and the length of the exocyclic double bond in the crystal structures.

1. Introduction

Heptafulvene (**1**) having a typical cross-conjugated system belongs to a non-alternant hydrocarbon and appears red in color because of it relatively narrow HOMO–LUMO gap.[1] For more than four decades since its first synthesis continuous attention is still drawn not only to the ground and excited state structures[2] and its derivatives towards understanding their stability in respect to aromaticity but also to their application to colorants and optical materials.[3] While **1** shows a polyolefinic nature and is reactive,[1] 8,8-dicyanoheptafulvene (**2**) is relatively stable[4] and reluctant to electrophilic substitution and cycloaddition reactions.[5] The planar structure of **2**, revealed by X-ray crystallographic analysis,[6] and its large dipole moment (7.49 D)[7] indicate a significant contribution of the resonance form **2B**. On the other hand, 8,8-dicycano-2,6-dimethylheptafulvene (**3**)[8] shows smaller dipole moment than the value expected by regarding its seven-membered ring as a planar and regular heptagonal, and its X-ray analysis[9] revealed that **3** has a boat form like 1,3,5-cycloheptatriene[10] due to steric hindrance between the methyl and cyano groups. Feasibility of the dipolar contribution of dicyanoheptafulvenes should be dependent on its molecular planarity and also on the relative thermodynamic stability of the tropylium cation part in the polar canonical form; that is, it is expected that a dicyanoheptafulvene derivative with the more stable cationic part in the form shows the more significant dipolar contribution. Although there have been known many tropylium cation derivatives more stable than the parent tropylium ion **4**, only a few of the corresponding dicycanoheptafulvene derivatives have appeared in the literature. Mori and Takeshita et al. synthesized dithiin-annulated dicyanoheptafulvenes, **5** and **6**, from the tropylium cation **7**, and clarified their crystal structures;[11,12] the heptafulvene **5** has a nonplanar structure and **6** has a nearly planar structure. While **6** shows almost the same degree of contribution of the polar canonical form to that of **2**, **5** indicates diminished contribution compared with those of **2** and **6** based on the spectroscopic data (Chart 1).

In the meantime, we have recently reported a new, highly stable hydrocarbon cation, dispiro[cyclohexane-1,1′-(1′,7′-dihydrocyclopenta[*f*]azulenium)-7′,1″-cyclohexane] ion (**8**),[13] whose pK_R+value (13.2) is greater by 9.3 pK_R+ unit than that of the tropylium cation **4**.[14] Thus, 4′-dicyanomethylidenedispiro[cyclohexane-1, 1′-(1′, 4′, 7′-trihydrocyclopenta-[*f*]azulene)-7′,1″-cyclohexane] (**9**)

Keywords: Heptafulvene; Carbenium ions; Cyclopenta[*f*]azulenes; Density functional calculation; X-ray crystal structures.
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doi:10.1016/j.tet.2005.10.015

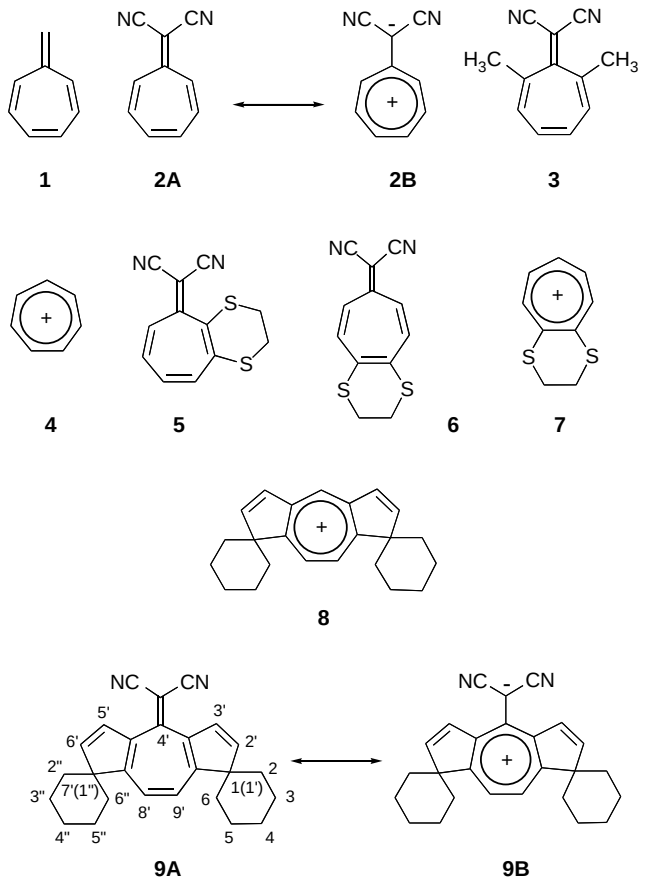


Chart 1.

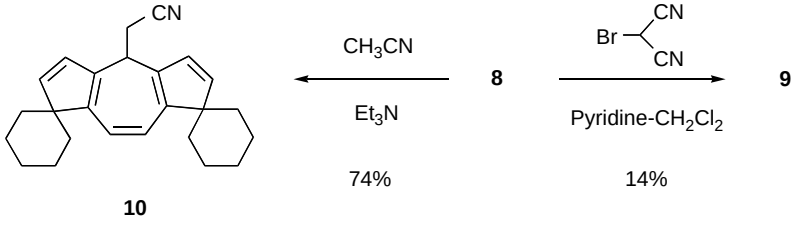
derived from carbocation **8** is expected to indicate great contribution of the resonance form **9B**. Herein we describe the synthesis, spectroscopic properties and molecular structure of **9**, which indicate that compound **9** is a unique example of 8,8-dicyanoheptafulvene derivatives having appreciable contribution of its dipolar resonance form despite its nonplanar structure. We also discuss the degree of the contribution for various 8,8-dicyanoheptafulvenes based on their structural features both in the crystal and calculated structures.

2. Results and discussion

2.1. Synthesis and spectroscopic properties of 9

The reaction of **8** in acetonitrile in the presence of triethylamine as a base gave the acetonitrile adduct **10** in 74% yield. This result encouraged us to synthesize the desired dicyanoheptafulvene **9** from **8** by the Mori–Takeshita method, which is a procedure for preparing **2** directly from a tropylium salt.[15] The reaction of **8** with bromomalononitrile in the presence of pyridine as a base in dichloromethane gave **9** as orange-red microcrystals in 14% yield, accompanied with some unidentified minor products (Scheme 1). Under similar conditions with other bases, such as triethylamine or DBU, the yield of **9** was less than 6%.

The structure of **9** was fully characterized by spectroscopic and elemental analyses. The assignments of proton signals of **9** in the ^{1}H NMR spectrum, summarized in Figure 1 with those of **8** and the corresponding hydrocarbon **11**, were based on the relationships in H–H COSY and DFNOE experiments (Fig. 2). The average proton chemical shift (δ_{av}=7.18 ppm in $CDCl_3$, δ_{av}=7.35 ppm in DMSO-d_6) of the olefinic protons of **9** was found to be close to the middle value between those of **11** (δ_{av}=6.48 ppm in $CDCl_3$) and **8** (δ_{av}=8.26 ppm in $CDCl_3$). The δ_{av} value of **9** shows downfield shift of 0.17 ppm in the aprotic dipolar solvent of DMSO-d_6 compared with that in $CDCl_3$. It is noteworthy that the field shift by solvent polarity also changes the signal line-up of the hydrogens at the 2′(6′) and 3′(5′) positions in the spectra; that is, while in $CDCl_3$ the 2′(6′) hydrogen in **9** resonates at higher field than the 3′(5′) hydrogen similarly to the case of **11**, in DMSO-d_6 the 2′(6′) hydrogen resonates at lower field than the 3′(5′) hydrogen similarly to the case of **8**. These results clearly show that contribution of the resonance form **9B** enhances in a polar solvent. The aliphatic methylene protons at the 2 (6, 2″, and 6″) position in NMR shift to down field in the series **11**→**9**→**8**, indicating that the anisotropic deshielding effect of the seven-membered ring part ascends in this order. Under the acidic conditions with a mixture of CF_3CO_2D and DMSO-d_6, the protonated species **12** was observed in the ^{1}H NMR spectrum and **9** was recovered quantitatively by alkaline work-up (Scheme 2). In the ^{13}C NMR spectra, the cyano-substituted carbon atom of **2**, **6** and **9** resonates at δ 70.1, 68.7 and 68.9 ppm, respectively, (Table 1). The high-field shift of the carbon can be explained by a shielding effect of the anion charge localized at the dicyanomethylene group in the polar canonical form. On the other hand, the carbon of dimethyl derivative **3** appears at relatively lower field of δ 81.6 ppm and that of **5** at δ 80.1 ppm. From these NMR spectroscopic data, it is strongly suggested that contribution of the resonance form **9B** is very important in **9**. Particularly, comparison of the ^{13}C chemical shifts between **9** and **2** indicates that **9** has a large degree of the contribution the same as **2** and **6** have. Furthermore, the IR spectra of these dicyanoheptafulvenes show characteristic features. The stretching frequency (ν_{CN}) of dicyanoheptafulvenes is well-known to be denotive of the resonance contribution. The frequency data of **2**, **3**, **5**, **6** and **9** are



Scheme 1.