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Unequivocal existence of a centrosymmetric associated dimer of 4-(4-azuleno[1,2-*b*]thienyl)but-3-en-2-one formed by C–H···O=C hydrogen bonds in the crystals

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Abstract

Unequivocal existence of a centrosymmetric associated dimer of the title compound **1** formed by C–H···O=C hydrogen bonds was found by X-ray crystallography. The occurrence of this hydrogen bond, as well as the observed reduction of the bond-length alternation in the seven-membered ring of **1**, is understandable by the dipole resonance structures of the compound. © 1999 Elsevier Science Ltd. All rights reserved.

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Azulene and its derivatives are a well-known class of polycyclic nonbenzenoid aromatic compounds, and have been a fascinating target for research due to their unusual electronic structure and remarkable color. One point of interest in azulene derivatives has been the bond-length alternation in the seven-membered ring. The C–C bond lengths in simply substituted azulenes are relatively equivalent due to the peripheral delocalized aromatic carbon system.[1] On the other hand, the annelation of an aromatic ring onto the five-membered ring of azulenes causes bond-length alternation in the seven-membered ring. That is, for benz[*a*]azulelne,[2] azuleno[2,1-*a*]3,8-methano[10]annulene,[3] azuleno[1,2-*b*]thiophene,[4] azuleno[2,1-*d*]pyrrole,[5] and azuleno[2,1-*d*]tropone,[5] a high degree of bond-length alternation was suggested by their ^{1}H NMR analyses, and the X-ray structures of 9-phenylbenz[*a*]azulene[1c] and azuleno[1,2-*b*]thiophene[6] indicated clearly alternating carbon–carbon bond lengths.

Introduction of an α,β-unsaturated carbonyl group into the five-membered ring of annelated azulenes seems very interesting: first, the bond-length alternation in the seven-membered ring is expected to be reduced owing to a contribution of the dipole resonance structure shown in Scheme 1; second, this dipole resonance structure contributes to increase the acidity of the H atoms on the seven-membered ring and at the same time the negative charge on the carbonyl oxygen atom to enhance the potential ability of the atoms to participate in C–H···O=C hydrogen bonds.[7,8] We studied the X-ray structures of 4-(4-

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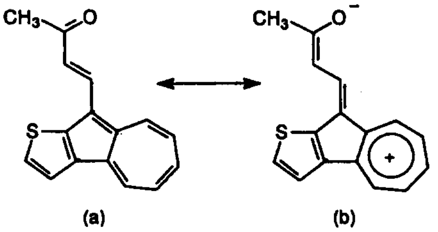
azuleno[1,2-*b*]thienyl)but-3-en-2-one (1),[9] 4-(4-azuleno[2,1-*b*]thienyl)but-3-en-2-one,[10] 1-phenyl-3-(4-azuleno[2,1-*b*]thienyl)prop-2-en-1-one[10] and 1,1,1-triphenyl-4-(10-benz[*a*]azulenyl)-3-buten-2-one[11] in order to investigate the bond-length alternation and the possibility of a C–H···O=C hydrogen bond in their crystals. In this paper we will report the unequivocal presence of the C–H···O=C hydrogen bond, as well as the reduction of the bond-length alternation, found for compound **1**.



Scheme 1. Dipole resonance structure of **1**

Fig. 1 shows a pair of two molecules of **1** related by the center of symmetry determined by X-ray crystallography.[12] The thienoazulene ring of **1** is planar: the mean and maximum deviations of the atoms from the least-squares mean plane of the ring are ca. 0.014 and 0.034 Å (for C(6)), respectively. The molecule as a whole (except for the methyl hydrogen atoms) is also approximately planar, although C(13) and the carbonyl oxygen atom deviate from the mean plane by ca. 0.20 and 0.34 Å, respectively.

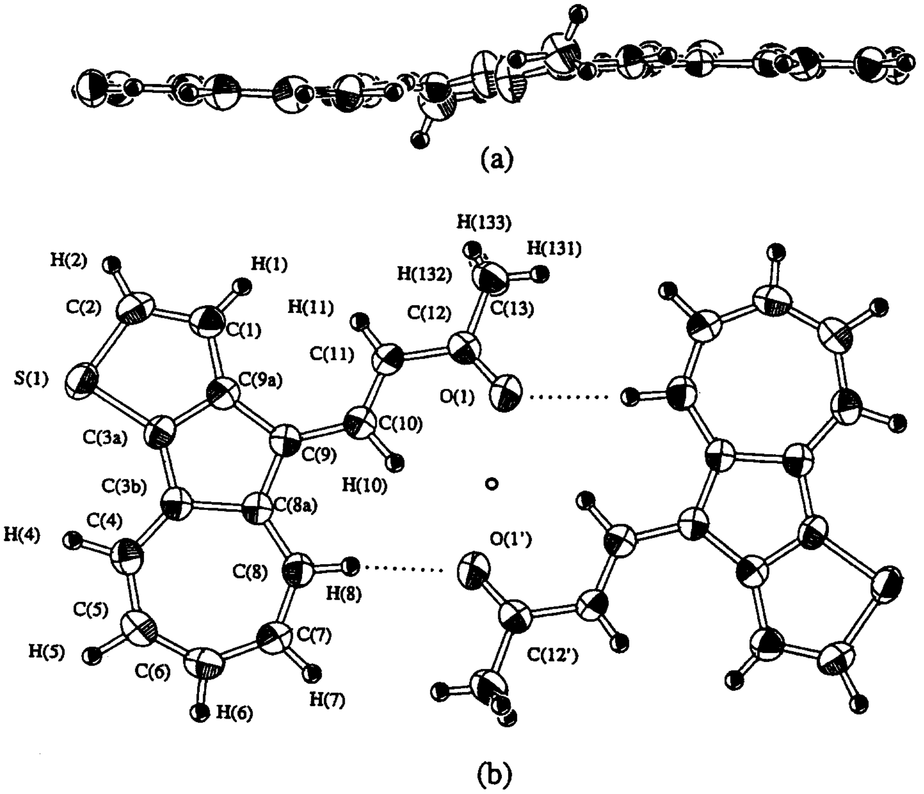


Figure 1. Two molecules of **1** related by a center of symmetry: (a) and (b) are side and top views, respectively. Broken lines indicate C–H···O=C hydrogen bonds. The numbering scheme of the atoms is a convenient one and it is not in accord with the rigorous nomenclature. C(3b)–C(4)=1.378(2), C(4)–C(5)=1.394(2), C(5)–C(6)=1.371(2), C(6)–C(7)=1.394(2), C(7)–C(8)=1.377(2), C(8)–C(8a)=1.392(2) and C(3b)–C(8a)=1.493(2) Å

As can be seen in the caption of Fig. 1, the maximum difference between the longest and the shortest C–C bond lengths in the seven-membered ring of **1** is 0.023(2) Å, being smaller than the corresponding one (ca. 0.08 Å) observed for 4-phenylazulene, for which the absence of bond-length alternation has been reported.[1c] Thus, the bond-length alternation of the seven-membered ring of **1** almost disappears, although very slight alternation still remains.[13] The average chemical shift (δ_{av}=7.78 ppm) of the protons at the seven-membered rings of **1** is greater than that (δ_{av}=7.65 ppm) of the unsubstituted azuleno[1,2-*b*]thiophene[4] and the C=O stretching frequency of **1** (1667 cm^{-1}) is lower than that (1684 cm^{-1}) of benzylideneacetone. These facts indicate a considerable contribution of the dipole resonance structure (b) in Scheme 1.

For the pair of molecules shown in Fig. 1, the C(8)···O(1′) and H(8)···O(1′) distances (3.332(2) and 2.36(1) Å, respectively) and C(8)–H(8)···O(1′) and C(12′)–O(1′)···H(8) angles (172.0(10) and 133.2(4)°, respectively) satisfy the following geometrical criteria reported for the general C–H···O hydrogen bond;[7,8] i.e. the C···O and H···O distances are 3.0–4.0 and 2.4–3.0 Å, respectively; the C–H···O angle is within 90–180°; when the acceptor is a carbonyl group, the H···C=O angle is distributed around 120° and the C–H group lies in the plane defined by the O lone pairs. The pair of molecules in Fig. 1 is, therefore, a centrosymmetric associated dimer, just like the molecules of carboxylic acid, formed by C–H···O=C hydrogen bonds. This hydrogen bond would be responsible for the stabilization of the unusual *s-cis* form of the α,β-unsaturated carbonyl group found for **1**.

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12. Crystal data for **1**: $C_{16}H_{12}OS$, M=252.3, monoclinic, $P2_1/n$ (no.14), a=14.003(3), b=5.251(2), c=17.362(2) Å, β=106.85(1)°, V=1221.7(4) $Å^3$, Z=4, D_c=1.372 g cm^{-3}, μ(Mo-Kα)=2.474 cm^{-1}, F(000)=528. Independent reflections (3117, R_{int}=0.016) were measured on a Rigaku AFC5R diffractometer with Mo-Kα radiation using a θ–2θ scan. The structure was solved by direct method and non-hydrogen atoms (H atoms except for those in the methyl group) were refined with anisotropic (isotropic) thermal factors, respectively, using full-matrix least-squares based on F^2 with absorption corrected data to give R_1=0.049, wR_2=0.056 for 2810 independent observed reflections (all reflections), 2θ≤55° and 200 parameters. Program teXsan was used.
13. The reduction of the bond-length alternation was also found in 4-(4-azuleno[2,1-*b*]thienyl)but-3-en-2-one, 1-phenyl-3-(4-azuleno[2,1-*b*]thienyl)prop-2-en-1-one and 1,1,1-triphenyl-4-(10-benz[*a*]azulenyl)-3-buten-2-one.