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A NEW SULFUR-CONTAINING AZULENE

3,5,8-TRIMETHYLAZULENO[6,5-b]THIOPHENE

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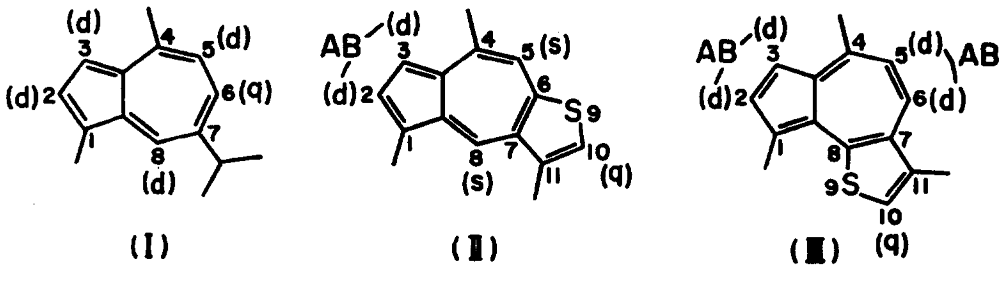
By the action of sulfur on S-guaiazulene (I) at 200°C, a dark violet crystalline substance, m.p. 116.0 - 116.5°C, was obtained, which produced a picrate, m.p.$>$300°C, and exhibited a NMR spectrum shown in Fig. 2-a, and its structure was elucidated to be 3,5,8-trimethylazuleno[6,5-b]thiophene (II). The compound is the first example which has a thiophene ring fused to the seven-membered ring of an azulene nucleus.

On the basis of the elementary analysis and the molecular weight determination, the molecular formula of this compound was $C_{15}H_{14}S$. When the compound was subjected to the reductive desulfurization by Raney Ni (1) at room temperature, and then the reaction product was dehydrogenated with sulfur, S-guaiazulene was obtained in good yield. In the NMR spectrum of the present sulfur-containing compound (Fig. 2-a), disappears the signal of the isopropyl group which clearly presented in case of S-guaiazulene, and three signals of aromatic methyl groups appear. Hence, it is expected that this compound can be represented by either of structure (II) or (III).



(I) (II) (III)

Fig. 1 Expected NMR splitting patterns of aromatic protons.

In the NMR spectrum of the present compound (Fig. 2-a) a sharp singlet (1H) appears at 8.20 ppm in the aromatic proton region. On the other hand, the expected splitting patterns concerning the aromatic protons of structural formulae (II) and (III) are shown in Fig. 1*.

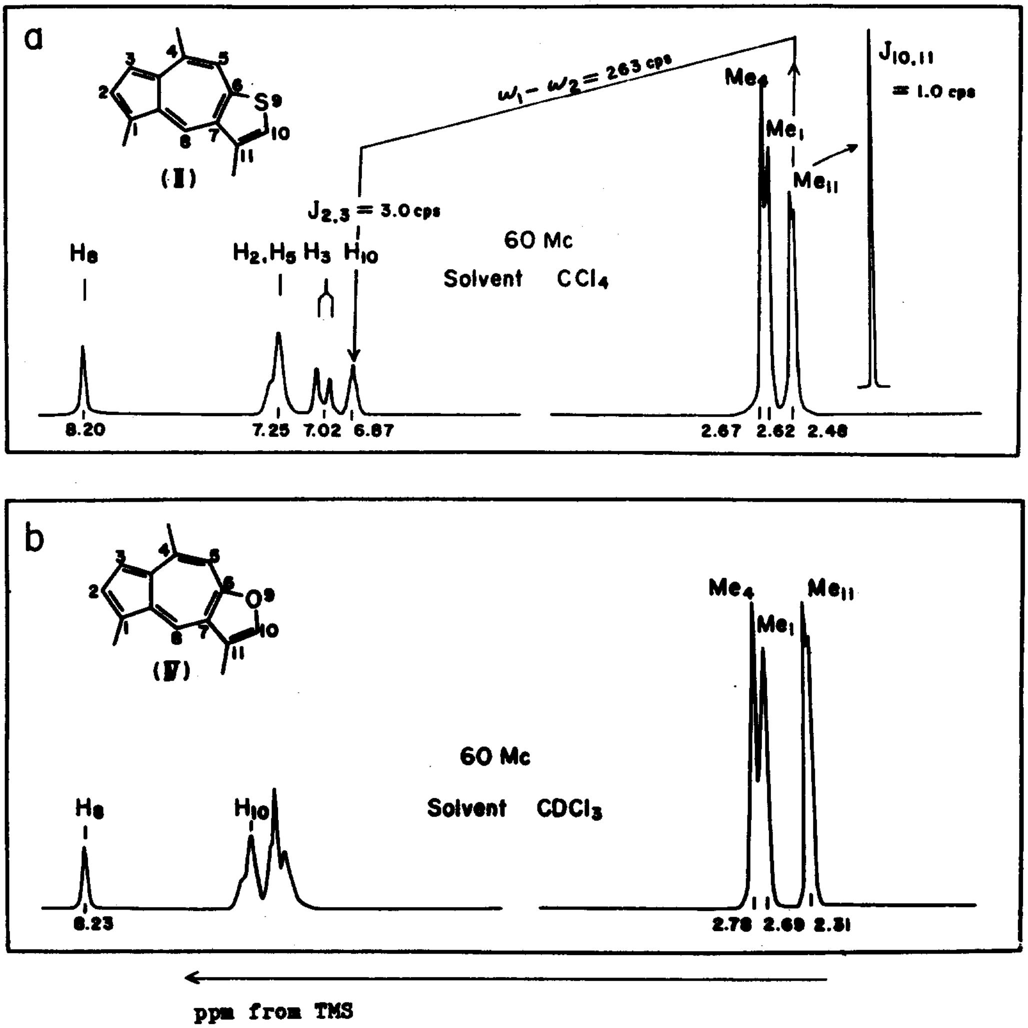


Fig. 2 NMR spectra of S-containing compound (a) and linderazulene (b).

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* In the subsequent discussion, the authors adopt the numbering system corresponding to that of azulenes for the convenience of comparison.

As a spin coupling has been observed between α-H and β-Me in 3-methylbenz(b)thiophene (2), it is not likely to expect a singlet of H_{10} in the thiophene moiety of the formulae (II) and (III). Hence, the sharp singlet mentioned above is expected merely from H_5 or H_8 of the structure (II).

The NMR spectrum of the sulfur-containing compound can be reasonably explained by the formula (II) as follows. Two aromatic proton signals of 8.20 (singlet, 1H) and 7.02 ppm (doublet, 1H), and two methyl signals of 2.67 (singlet, 3H) and 2.62 ppm (singlet, 3H) (Fig. 2-a) can be easily assigned to H_8, H_3, Me_4 and Me_1 of the formula (II) respectively, by comparing with the spectrum of S-guaiazulene which has been thoroughly interpreted by D. Meuche et al. (3). The aromatic proton of 6.87 ppm (quartet, 1H, J = ca. 1.0 cps) and methyl protons of 2.48 ppm (doublet, 3H, J = 1.0 cps) can be also assigned to H_{10} and Me_{11} on reference to the spectrum of 3-methylbenz(b)thiophene (2), and this assignment was confirmed by a double resonance experement, which is shown additionally in Fig. 2-a. The broad signal of 7.25 ppm (multiplet, 2H) still existing in the aromatic proton region may be well understood as the overlap of H_2 and H_5 signals, which occured owing to the paramagnetic shift of H_5 under the deshielding effect of the sulfur atom.

The considerable resemblance is recognized between the NMR spectra of the sulfur-containing compound and linderazulene (Fig. 2-b) (4), whose molecular structure is the same as that of the formula (II) except a heteroatom. Besides the discrepancy between both spectra is well understood by the difference of the deshielding effect in sulfur and oxygen. This fact is also a support for the formula (II).

The spectrum of this compound (Fig. 3-b) taken in a trifluoroacetic acid solution is easily interpreted as the conjugate acid form (VI) of the formula (II) on comparison with the well interpreted spectrum of S-guaiazulenium cation (Fig. 3-a) and the above discussed spectrum of the present compound (Fig. 2-a). By a double resonance experiment in the trifluoroacetic acid solution (Fig. 4), furthermore, it was confirmed that the protons of the five-membered moiety, H_2, $2H_3$ and Me_1, were spin-coupled to produce an AX_2Y_3 system which is identical with that of the five-membered moiety of S-guaiazlene (3) in the same

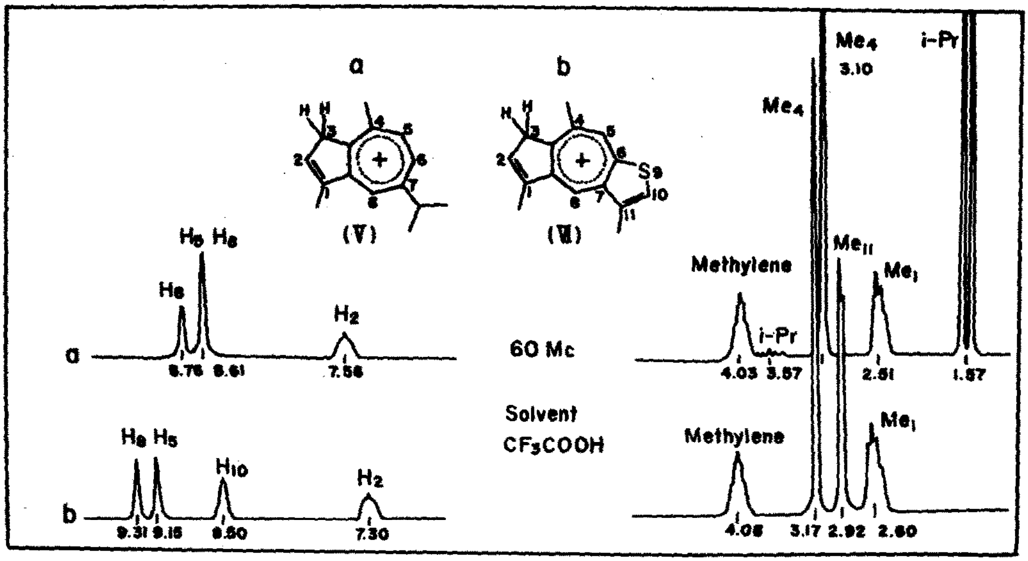

Fig. 3 NMR spectra of conjugate acid of S-guaiazulene (a) and S-containing compound (b).

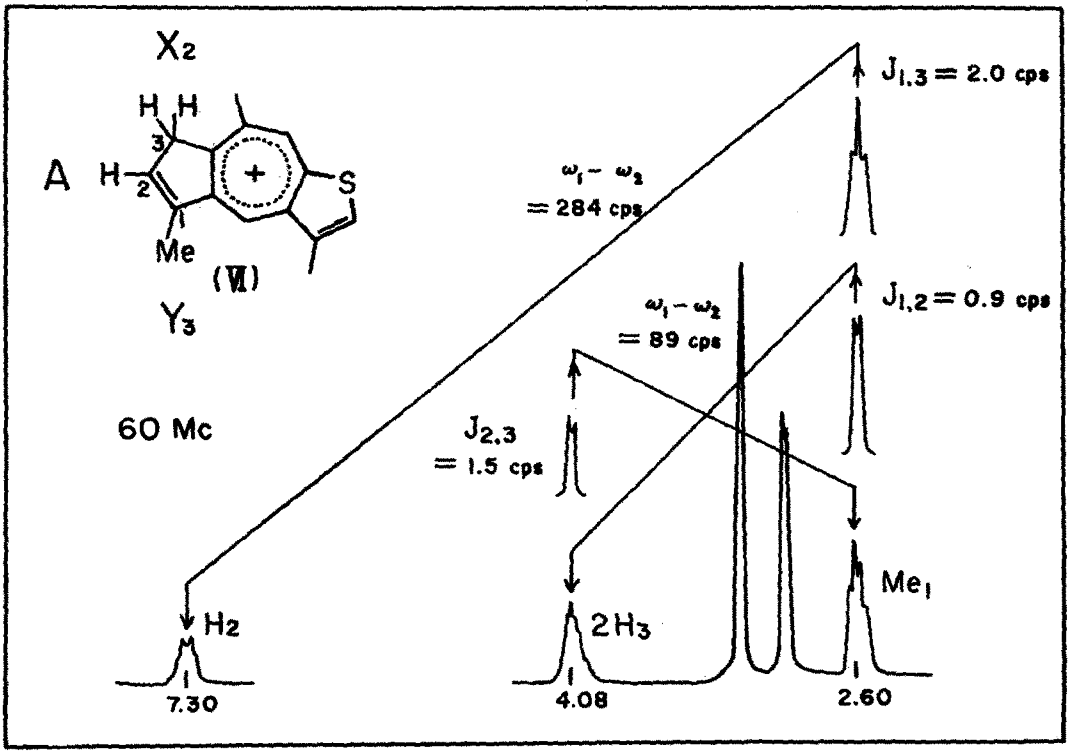

Fig. 4 Spin decoupling experiments of conjugate acid.

condition. Therefore, it is certain that the reaction of S-guaiazulene with sulfur did not occur in any position of its five-membered moiety. UV, visible, IR and mass spectra of this compound also afforded the additional supporting evidence for the formula (II) (5).

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