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AZULENOPHANE IV. [2.2](2,6)AZULENOPHANE II.
ISOLATION OF syn- AND anti-ISOMERS AND THEIR PHYSICAL PROPERTIES

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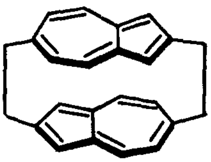
[2.2](2,6)Azulenophane, the first azulenophane synthesized, was found to be a 5:4 mixture of anti- and syn-isomers, which were separated successfully by low-temperature column chromatography on H_3PO_4-impregnated SiO_2. Physical properties of the isomers including PMR, CMR and electronic spectra are very similar with each other, suggesting major contribution of peripheral 10π-structure for azulene.

In 1976, two groups1,2) including us reported the synthesis of [2.2](2,6)azulenophane, the first azulenophane, by the Hofmann-type pyrolysis of N(2-methyl-6-azulenylmethyl)trimethylammonium hydroxide. Anti-configuration was assigned on the basis of PMR evidence and consideration of by-products in the pyrolysis2). Thus, in spite of the correct MS pattern and reasonable UV and IR spectra, there is no rigorous proof on the homogeneity of the substance because of poor solubility (and lack of clear melting point) nor on the orientation of two azulene rings (due to disorder in crystals). However, slight deviation from symmetrical AA'BB' pattern of bridge protons and a quartet nature of H_4 in PMR spectra measured in $CDCl_3$ and C_6D_6 led us, after synthesis of two deuterated compounds, to believe the substance to be a mixture of two components. We have now separated it into anti- (**1**) and syn-[2.2](2,6)azulenophane (**2**) and examined their physical properties.



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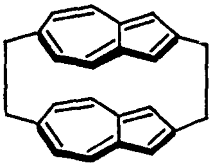


2

Separation Although the pyrolysis product3) shows a clear, round spot on TLC (Al_2O_3, SiO_2), it gives two spots on phosphoric acid-SiO_2 system. Column chromatography at -30°4) on SiO_2 impregnated with

0.4 % phosphoric acid (toluene-CH_2Cl_2) afforded, in the order of elution, compounds **1** and **2** in 55% and 41% yield, respectively. Although both of them are dark greenish blue prisms with m.p. >300°(gradual decomposition) and hardly soluble in almost all organic solvents, their structures are assigned unambiguously on the spectral basis described below.

Spectra Mass spectra of **1** and **2** are indistinguishable, showing peaks at m/e 308 (M^+) and 154 (base peak, 1/2 M^+). IR spectra are also very similar, but **1** can be identified by a medium band at 1335 cm^{-1}, which is absent in the spectrum of **2**.

Despite of their limited solubilities, PMR spectra, especially signals due to the bridge hydrogens, have diagnostic value (Fig. 1): While **1** shows complex AA'BB' pattern centered at 3.23 ppm, **2** exhibits two singlets at 3.15 and 3.28 ppm. Azulenic protons also have slight difference in chemical shift (shown in Fig. 1)[5]. All the azulenic protons of **1** and **2** show considerable up-field shifts when compared with those

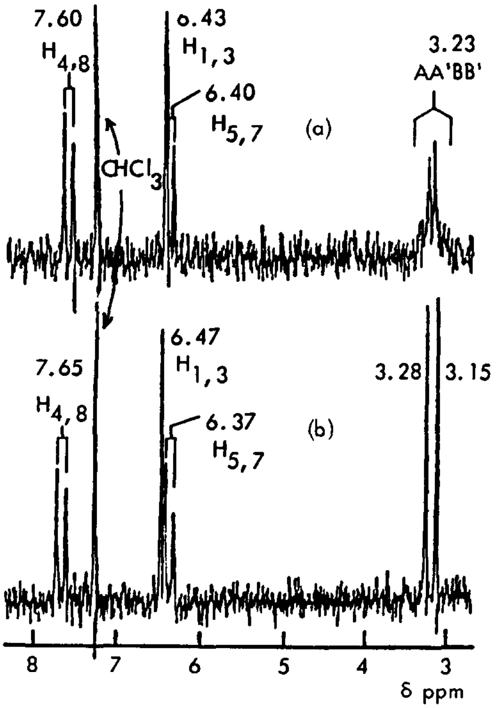


Fig. 1 PMR spectra of **1** (a) and **2** (b) in $CDCl_3$

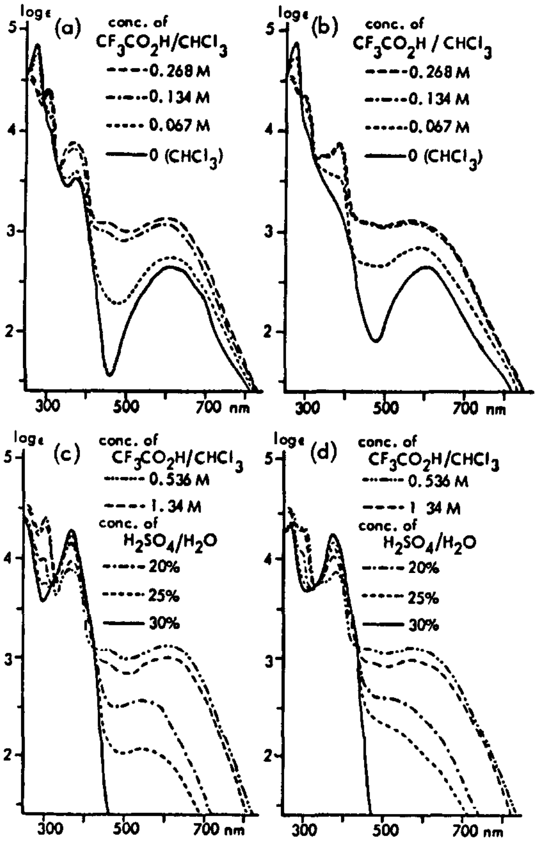


Fig. 2 Electronic spectra of **1** (a, c) and **2** (b, d) in neutral and acidic media

of 2,6-dimethylazulene **3**[2], [Δδ: 0.71 and 0.67 ppm for $H_{1,3}$, 0.47 and 0.42 ppm for $H_{4,8}$, 0.68 and 0.71 ppm for $H_{5,7}$, respectively, for **1** and **2**]. The smaller Δδ value of H_4 (H_8) compared with those of the other protons, the fact responsible for the previous erroneous assignment of configuration[2], is observed in both isomers. The correct interpretation should thus be the vertical displacement[6] of H_4 (H_8) from the facing azulene ring in the barrel-shaped azulenophane as is disclosed by the preliminary X-ray analysis[7,8].

In CMR spectra of **1** and **2**, only carbons having a hydrogen attached were recognized[5] because of their poor solubilities. Chemical shifts of azulenic carbons are listed in Table together with those of **3**.

Table. CMR chemical shifts of **1**, **2** and **3** (ppm from TMS in $CDCl_3$)

compds / positions	**1**	**2**	**3**	$\Delta\delta_{1-3}$	$\Delta\delta_{2-3}$
1, 3	123.3	123.1	118.3	5.0	4.8
4, 8	132.7	132.8	133.4	-0.7	-0.6
5, 7	127.2	128.0	124.6	2.6	3.4

It is clear from the Table that, C1(C3) and C5(C7) move down-field and C4(C8) slightly up-field both for **1** and **2** in comparison with the respective corresponding carbons in **3**, and further the shifts are comparable between two compounds. This is unexpected from the dipolar resonance contribution of azulene which may be accentuated in **1** but retarded in **2**. The best explanation appears to be the steric compression which causes the redistribution of π-electron density of azulene when incorporated in the phane systems[9]. Thus, the shift (Δδ) is larger at the severly compressed positions (C1, C3, C5, C7) more than the others (C4, C8), and the shift at C1(C3), which has the largest π-electron density[10], is larger than that at C5(C7), which is equally compressed[7] but has smaller π-electron density, regardless of the orientation of the facing azulene ring.

The electronic spectra of **1** and **2** are again similar with each other (Fig. 2a, b), both exhibiting the broadening of all bands (more extensive in **2**) and appreciable bathochromic shift (62 nm for **1** and 58 nm for **2** compared with that of **3**)[2] of the structureless bands in the 600 nm region (corresponding 'Lb band of **3**). However, no clear band due to charge-transfer (CT) interaction is observed[11]. On the other hand, such a band is clearly observed in the spectra in acidic media (Fig. 2a-d): Thus, on addition of trifluoroacetic acid (TFA), new band appears at ~460 nm for both compounds, in addition to general increase in intensities for all bands except the 276-280 nm band. The former bands reach the maximum intensities at 0.268-0.536 M TFA in both cases. The spectra at this stage of acid concentration should be those of monoprotonated species and the bands are assigned as intramolecular CT bands between protonated and nonprotonated azulene rings, because no such an absorption is observed for **3**2). At higher concentration, the CT bands as well as 'Lb bands continuously decrease their intensities (other changes see the Fig. 2), to reach diprotonated species with no CT band. The fact that the acid concentration to produce monoprotonated species is much weaker for **1** and **2** than for **3** (~2 M TFA2)) indicated that the formers are much stronger base due to the CT interaction. Judging from the acid concentration to reach the maximum intensity of the CT-band, **2** is slightly stronger base than **1** for monoprotonation, in agreement with the chromatographic behavior, and its monoprotonated conjugate acid is weaker base than that of **1** for diprotonation, as can be seen in Fig. 2c, d. Although the reason for this is not clear, the general feature shown in PMR, CMR and UV spectra of **1** and **2** culminates in the peripheral 10π-structure as a principal resonance contributor to azulene in its ground state.

References and Notes

1) N. Kato, Y. Fukazawa and S. Itô, Tetrahedron Letters, 2045 (1976).

2) R. Luhowy and P.M. Keehn, ibid., 1043 (1976); J. Am. Chem. Soc., 99, 3797 (1977).

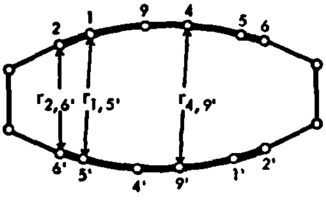
3) We have improved the yield of pyrolysis to 56% by decreasing the amount of toluene and gentle heating until all water was distilled off. Cf. T. Otsubo, H. Horita and S. Misumi, Synth. Commun., 591 (1976).

4) Chromatography at room temperature causes a considerable loss of **2**.

5) These signals were assigned comparing with the spectra of 1,1',3,3'-tetradeuterio compound synthesized1) from 1,3-dideuterio-6-dimethylaminomethyl-2-methylazulene and 4,4',8,8'-tetradeuterio compound from 3,7-dideuterio-5-methyltropolone. [Cf. S. Itô, J. Tsunetsugu, T. Kanno, H. Sugiyama and H. Takeshita, Tetrahedron Letters, 3659 (1965)].

6) T. Umemoto, S. Satani, Y. Sakata and S. Misumi, Tetrahedron Letters, 3159 (1975).

7) Crystals of **1** and **2**, as well as the mixture, were found to be disordered ($P4_2/mnm$, Z=2). Structure solved for the mixture using 280 unique reflections and assuming anti orientation clearly shows the barrel shape with $r_{4,9'}$ 3.7 Å, $r_{1,5'}$ 3.2 Å, $r_{2,6'}$ 2.8 Å.



8) The barrel shape is quite common in [2.2]phanes: e.g. [2.2]paracyclophane; H. Hope, J. Bernstein and K.N. Trueblood, Acta Cryst., B28, 1733 (1972), [2.2](2,7)pyrenophane; H. Irngartinger, R.G.H. Kirrstetter, C. Krieger, H. Rodewald and H.A. Staab, Tetrahedron Letters, 1425 (1977).

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10) P.C. Lauterbur, J. Am. Chem. Soc., 83, 1838 (1961).

11) However, some of the bands may be due to transitions to CT state as was found in [2.2]paracyclophane. S. Iwata, K. Fuke, M. Sasaki, S. Nagakura, T. Otsubo and S. Misumi, J. Mol. Spect., 46, 1 (1973), K. Fuke and S. Nagakura, Bull. Chem. Soc. Japan, 48, 46 (1975).

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