Tetrahedron Letters, Vol. 34, No. 5, pp. 835-838, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

STRUCTURAL AND CHEMICAL PROPERTIES OF 6-AZA- AND 6,7-DIAZAAZULENO[1,2-a]AZULENES[1]

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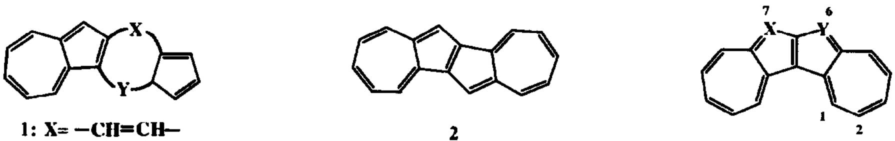
Summary: The NMR and electronic spectral studies including PPP-type MO calculation of the title compounds revealed that there are little contribution of peripheral 18-π electron conjugation, but those are rather composed of two azulene-type π-systems. The both compounds existing as cationic and dicationic species in acidic media were also studied.

Twelve isomers of cata-condenced azuleno-azulene have been reported to possess fairly large resonance energy per electron.[2] Among these compounds, two types of compounds, azuleno[1,2-f]azulene (1)[3] and azuleno[1,2-b]azulene (2)[4] were known in the form of their derivatives, and the parent azuleno[2,1-e]azulene (3)[5] has also been prepared. The molecular diagrams and singlet transitions of 2 and unknown azauleno-[1,2-a]azulene (4) have been calculated and the experimental data for 2 are in good accordance with the theoretical predictions.[4a,6] The chemistry of azaazulenes is also of interest for organic chemists, particularly in comparison with the chemistry of azulenes, and has played a major role in the advancement of our understanding of cyclic conjugation.[7] In the preceeding paper,[8] we have reported the synthesis of 6-aza- and 6,7-diazaazulenno[1,2-a]azulenes (5 and 6), both of which are the nitrogen containing analogues of hygrocarbon 4. In connection with the study, we report hereon the chemical and structural properties including PPP-type MO calculations of 5 and 6.



1: X= –CH=CH–
Y = –CH=
3: X=electron pair
Y = –CH=CH–CH=

2

Scheme 1.

4: X=Y=CH
5: X=CH ; Y=N
6: X=Y=N

The ^{1}H NMR, ^{13}C NMR and electronic spectral data of 5 and 6 are summarized.[9] The average chemical shift (δav=8.13 ppm) of azaazulene moiety of 5 is the same as that of seven-membered ring of 1-azaazulene (δav=8.13 ppm).[10] Similarly, the average chemical shift (δav=7.74 ppm) of azulene moiety is close to that of azulene (δav=7.47 ppm).[11] In addition, the observed coupling constants between neighboring protons (J_{1-2}, J_{4-5}=9.2, 10.3 Hz; J_{2-3}, J_{3-4}=10.3, 9.2 Hz; J_{8-9}, J_{11-12}=10.6, 8.8 Hz, J_{9-10}, J_{10-11}=8.8, 10.6 Hz) indicate the bond alternations at C_1-C_2-C_3-C_4-C_5 and C_8-C_9-C_{10}-C_{11}-C_{12} moieties.

The molecular diagram and singlet transitions of 5 calculated by PPP-type SCF MO method were shown in Figs. 1 and 2 and in Table 1. The molecular diagram indicates that 5 exhibits a bond-length alternation, which is in good accordance with the feature of the ^{1}H NMR spectrum. The degree of double-bond fixation in azaazulene moiety seems to be smaller than that in azulene moiety. This is probably due to the effect of electronegative nitrogen atom. Each absorption band of the electronic spectrum of 5 is also in good accordance with the theoretical predictions (Table 1 and Fig. 2).

Furthermore, the electronic spectra of 5 in acidic media are also shown in Fig. 2. A small hypsochromic shift was observed in 10% H_2SO_4. Accordingly, the protonation onto 5 occurred at the nitrogen atom to give 5-H (Scheme 2). In concentrated H_2SO_4, complete disappearance of the longest absorption band was observed. This fact implies the formation of dicationic species 5-2H, which is also supported by the ^{1}H NMR spectrum in concentrated H_2SO_4, exhibiting a signal of methylene protons on C-7 at δ 5.05.

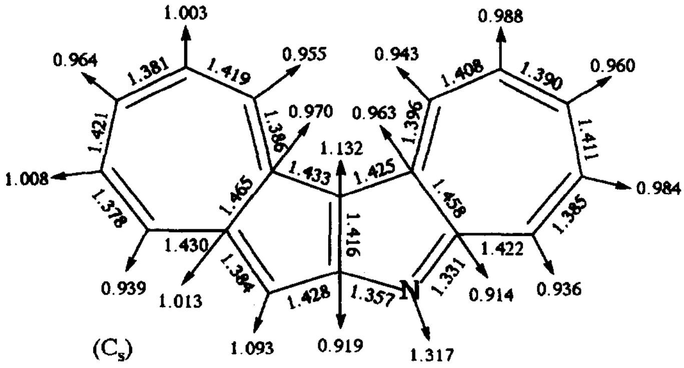
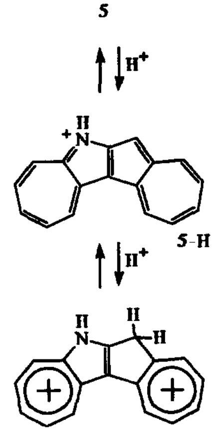


Fig. 1. Molecular diagram of 5: bond lengths (in Å) and electron densities



Scheme 2.

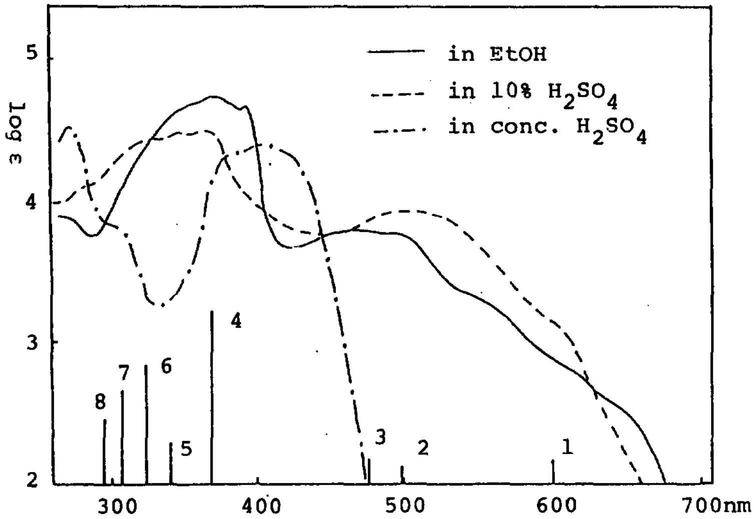


Fig. 2. Electronic spectra and calculated singlet transitions of 5

Table 1.
Singlet transition of 5

No	Symmetry	Energy eV (nm)
1	A'	2.07 (599)
2	A'	2.49 (498)
3	A'	2.60 (477)
4	A'	3.33 (372)
5	A'	3.69 (336)
6	A'	3.81 (325)
7	A'	4.06 (305)
8	A'	4.22 (294)
9	A'	4.69 (264)
10	A'	5.03 (246)
11	A'	5.17 (240)
12	A'	5.46 (227)

On the other hand, compound 6 exhibits a symmetric structure and the proton assignment was made by 2D ^{1}H-^{1}H NMR spectrum and by using Eu(fod)$_3$.[9] The average chemical shifts (δ_{av}=ca 8.35) of 6 is lower than that of 1-azaazulene (δ_{av}=8.13).[10] The observed coupling constant of neighbouring protons (J_{4-5}=J_{8-9}=10.3) is larger than the value (J_{1-2}=J_{11-12}=9.4), which was obtained through simulation of ^{1}H NMR spectrum by using LAOCOON III program, indicating a bond-length alternation at two azaazulene moieties. The comparison of the ^{13}C NMR spectrum with that of 1-azaazulene shows that the chemical shifts of two moieties (C_1-C_2-C_3-C_4-C_5 and C_8-C_9-C_{10}-C_{11}-C_{12}) are slightly different from that of 1-azaazulene.[12] Especially, the chemical shifts of C-5a, C-6a, and C-7a are very low as compared with those of C-1 and C-8a of 1-azaazulene.

The molecular diagram and singlet transitions of 6 calculated by PPP-type SCF MO method are shown in Figs. 3 and 4 and in Table 2. Each absorption band of the

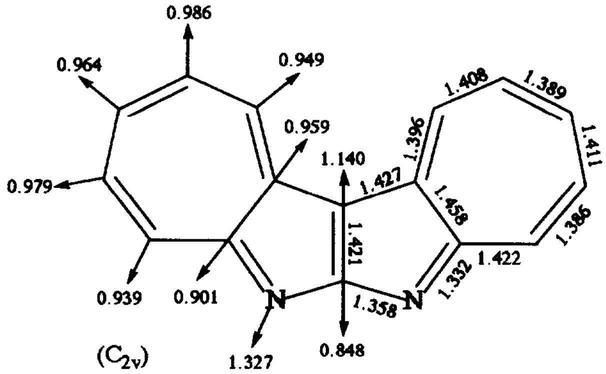
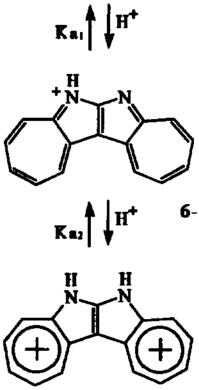


Fig. 3. Molecular diagram of 6: bond lengths (in Å) and electron densities

6



6-H

Scheme 3.

6-2H

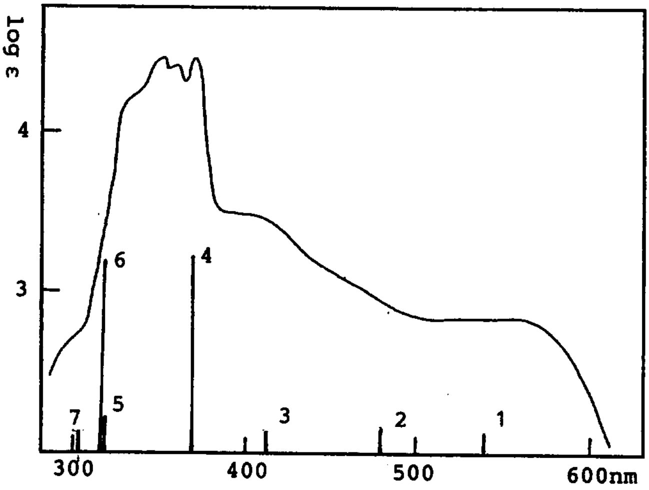


Fig. 4. Electronic spectrum and calculated singlet transitions of 6

Table 2.
Singlet transition of 6

No	Symmetry	Energy eV (nm)
1	B_2	2.30 (539)
2	A_1	2.59 (479)
3	A_1	3.01 (412)
4	B_2	3.34 (371)
5	A_1	3.79 (327)
6	B_2	3.84 (323)
7	B_2	4.08 (304)
8	A_1	4.51 (275)
9	B_2	4.79 (259)
10	A_1	5.04 (246)
11	B_2	5.24 (237)
12	A_1	5.44 (228)
13	B_2	5.75 (216)
14	B_2	5.98 (207)

electronic spectrum of 6 (Fig. 4) is in good accordance with the theoretical predictions. The molecular diagram (Fig. 3) indicates aslo that 6 exhibits a bond-length alternation, which is in good accordance with the features of ^{1}H NMR spectrum. The low electron densities at C-5a, C-6a, and C-7a are consistent with the chemical shifts of the ^{13}C NMR at the corresponding positions.

Just as the case of 5, the electronic spectrum of 6 is altered reversibly by the change of pH value of the solvent. The spectral change was monitered and it was clarified that the protonation of 6 giving cation 6-H occurs at the pH value ranging from 2.4 to 4.0, and double protonation giving dication 6-2H occurs at the pH value below 1.0 (Scheme 3). Thus, the dissociation constants, pKa$_1$ and pKa$_2$ in Scheme 3 were estimated to be 5.7 and 1.7, respectively.

In conclusion, spectral studies and PPP-type MO calculations of 5 and 6 revealed that there are little contribution of peripheral 18-π electron conjugation, but those are rather composed of two azulene-type π-systems.

Acknowledgement: This work was financially supported by a Grant-in-Aid for Science Research from Ministry of Education, Science and Culture, and by Waseda University Grant for Special Research Project.

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9. Spectral data of 5 and 6. 5: ^{1}H NMR (CDCl$_3$, 400 MHz) δ=7.23 (1H, dd, J=10.6, 8.8 Hz, H-9), 7.32 (1H, dd, J=10.6, 8.8 Hz, H-11), 7.36 (1H, s, H-7), 7.41 (1H, dd, J=10.6, 8.8 Hz, H-10), 7.70 (1H, dd, J=10.3, 9.2 Hz, H-3), 7.71 (1H, dd, J=10.3, 9.2 Hz, H-2), 7.82 (1H, dd, J=10.3, 9.2 Hz, H-4), 8.23 (1H, d, J=10.6 Hz, H-8), 8.51 (1H, d, J=8.8 Hz, H-12), 8.65 (1H, d, J=10.3 Hz, H-5), 8.79 (1H, d, J=9.2 Hz, H-1); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ=108.41 (C-7), 122.98 (C-12b), 126.42 (C-9), 136.75 (C-11), 128.27 (C-12), 128.46 (C-1), 130.08 (C-2), 131.43 (C-4), 132.83 (C-5), 132.93 (C-3), 133.01 (C-10), 134.65 (C-8), 135.55, 139.99, 150.78, 167.48, 174.88 (quarternary 4C); λ_{max} (log ε) in EtOH, 231 (4.52), 266 (3.91), 357 (4.70), 369 (4.75), 384 (4.69), 393 (4.69), 471 (3.82), 493 (3.79), 540 (3.36, sh), 600 (2.89, sh), 647 (2.53, sh). 6: ^{1}H NMR (CDCl$_3$) δ=7.92-7.98 (4H, m, H-2,3,10,11), 8.01-8.06 (2H, m, H-4,9), 8.91 (2H, d, J=10.3 Hz, H-5,8), 9.00-9.04 (2H, m, H-1,12); ^{13}C NMR (CDCl$_3$, 100.6 Hz) δ=117.4 (C-12b), 133.0-137.1 (C-1,2,3,4,5,6,9,10,11,12), 140.6 (C-12a,c), 168.9 (C-5a,7a), 183.7 (C-6a); λ_{max} (log ε) in EtOH, 357 (4.47), 364 (4.44), 374 (4.48), 410 (3.51, sh), 532 (2.82), 579 (2.83).
10. ^{1}H NMR (CDCl$_3$, 400 MHz) δ=8.27 (1H, d, J=0.97 Hz, H-2), 7.41 (1H, d, J=0.97 Hz, H-3), 8.59 (1H, d, J=9.76 Hz, H-4), 7.64 (1H, dd, J=9.76, 9.77 Hz, H-5), 7.89 (1H, dd, J=9.77, 9.76 Hz, H-6), 7.75 (1H, dd, J=9.76, 9.77 Hz, H-7), 8.77 (1H, d, J=9.77 Hz, H-8).
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(Received in Japan 13 June 1992)