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pseudoAZULENES CONTAINING TWO FUSED FIVE-MEMBERED RINGS

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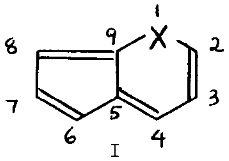
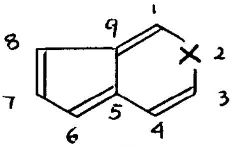
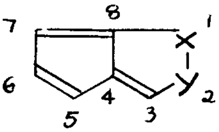
REPLACEMENT of a C=C unit in the seven-membered ring of azulene by an atom X, which can supply two π-electrons to the aromatic decet, gives rise to the *pseudo*azulenes(1) I and II. Representatives of all these heterocyclic systems, in which X = O, N, or S, are now known(2 - 7) and these compounds closely resemble azulenes. The introduction of a second hetero-atom Y = O, N, or S, results in the novel *pseudo*azulenes III and IV, the most noteworthy feature of which is that a classical structure can be written for III but not for IV. Theory suggests that such a molecule is best represented as an internal ylide IVa (see below).



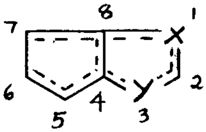
I



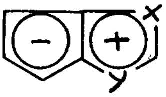
II



III

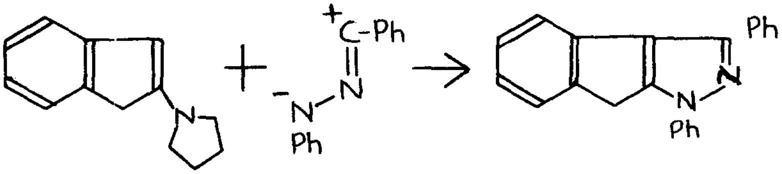


IV

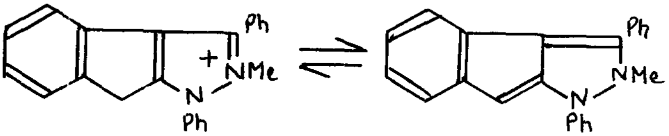


IVa

Examples of Type III and of Type IV have now been prepared.



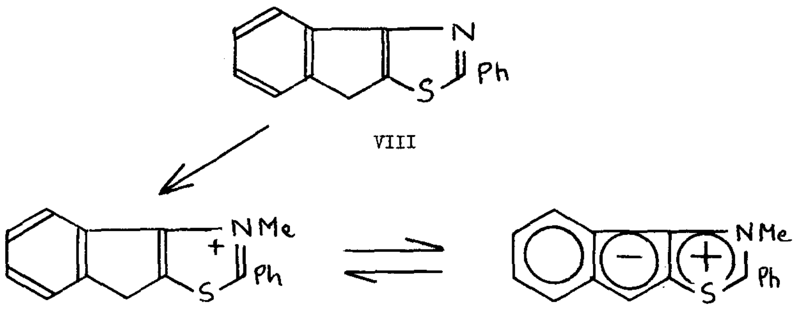
V



VI VII

1,3-Dipolar addition(8) of 1,3-diphenylnitrilimine to pyrrolidinoindene afforded the pyrazole V, m.p. 174° (Found: C,85.9; H,5.3; N,9.1. $C_{22}H_{16}N_2$ requires C,85.7; H,5.2; N,9.1%). Methylation to the pyrazolium cation VI, followed by treatment with alkali gave the indenopyrazole VII, dark red needles, m.p. 169 - 170° (Found: C,85.7; H,5.4; N,9.1. $C_{23}H_{18}N_2$ requires C,85.7; H,5.6; N,8.7%), λ_{max} 482 (ethanol), 490 mμ(cyclohexane). The new pseudoazulene is indefinitely stable in air, it resists the action of hot alkali, acids protonate it to the colourless cation VI. Preliminary experiments indicate that it can be acetylated and coupled with diazonium salts.

A representative of Type IV was obtained from 2-phenylindeno[1,2-d]-thiazole (VIII)(9) by methylation to form the nearly colourless thiazolium perchlorate IX, m.p. 244 - 245.5° (Found: C,56.1; H,3.8; N,3.7; S,8.6. $C_{17}H_{14}ClNO_4S$ requires C,56.1; H,3.9; N,3.85; S,8.8%), and subsequent treatment with alkali, which yielded the anhydro-base X as an unstable, light-sensitive dark purple solid which decomposes above 164°. (Found: N,4.9; S,11.9. $C_{17}H_{13}NS$ requires N,5.3; S,12.2%). Acids regenerate the cation IX.



VIII

IX

X

The position of the longest-wave absorption band in the spectrum of X is shifted to shorter wave-lengths with increasing polarity of the solvent: λ_{max} 550 (benzene), ca.540* (acetone), ca.490* (ethanol), ca.480* mμ (methanol), indicative of intramolecular charge-transfer, with a greater charge separation in the ground-state than in the first excited state. This is borne out by MO calculations on this molecule (but lacking the C-phenyl group): in the ground-state the total charge on the heterocyclic ring is +0.84, on the cyclopentadiene ring -0.54, on the benzene ring -0.30. In the first excited state the charges are reduced to +0.14, -0.11, and -0.03, respectively.

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* Inflexion.

TABLE 1

MO Calculations on pseudoAzulenes

	Type I	Type II	Type III	Type IV
CHARGES				
Atom 1	+ 0.315	+ 0.257	+ 0.190	+ 0.301
2	+ 0.221	+ 0.337	+ 0.285	+ 0.373
3	- 0.061	+ 0.044	+ 0.242	+ 0.301
4	+ 0.172	- 0.040	- 0.124	- 0.150
5	- 0.086	- 0.053	- 0.209	- 0.248
6	- 0.211	- 0.196	- 0.106	- 0.179
7	- 0.090	- 0.082	- 0.235	- 0.248
8	- 0.227	- 0.184	- 0.044	- 0.150
9	- 0.033	- 0.084	--	--
BOND ORDERS				
Bond 1,2	0.514	0.530	0.199	0.590
2,3	0.705	0.414	0.566	0.590
3,4	0.642	0.799	0.646	0.301
4,5	0.604	0.505	0.501	0.611
5,6	0.531	0.634	0.723	0.645
6,7	0.707	0.613	0.586	0.645
7,8	0.598	0.705	0.673	0.611
8,9	0.670	0.527	--	--
1,8	--	--	0.356	0.301
1,9	0.364	0.657	--	--
4,8	--	--	0.489	0.597
5,9	0.475	0.441	--	--
Delocalization energy (Azulene, 3.364β)	2.793β	2.768β	2.317β	2.343β
Charge separation between the rings (Azulene, 0.420)	0.588	0.530	0.634	0.825
Energy of $\pi \rightarrow \pi^*$ transition (Azulene, 0.878β)	0.901β	0.943β	0.993β	1.157β

The results of MO calculations by the standard Hückel method on the systems I - IV are summarised in the Table.* The parameters used were

$$\alpha_X - \alpha = \alpha_Y - \alpha = 1.5\beta$$

$$\beta_{CX} = \beta_{CY} = \beta_{XY} = 0.8\beta$$

and are appropriate for the cases X,Y = N or S.(10) For each molecule one obtains five bonding molecular orbitals which are filled with the ten π-electrons.

The results indicate a decrease in stability in the order azulene $>$ I $>$ II $>$ IV $>$ III, the extent of bond order variation shows that the aromatic character decreases in the same sequence. The unequal distribution of charges, while qualitatively similar to that calculated for azulene, is much accentuated in I and II and even more so in III and IV. Nucleophilic substitution on the heterocyclic ring and protonation and electrophilic substitution in the cyclopentadiene ring has been observed in all the pseudoazulenes investigated. The predicted sequence in the long-wave absorption: azulene $>$ I $>$ II $>$ III $>$ IV has been found in the series azulene $>$ I $>$ II. (X = N)(5,6) and (X = S).(6,7)

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* Similar calculations have been carried out on I and II (X = S)(11) and on I (X = O).(12)

REFERENCES

(1) R. Mayer, *Angew. Chem.*, **69**, 481 (1957).

(2) I (X = O): G. V. Boyd, *J. Chem. Soc.*, 1978 (1958).

(3) II(X = O): J. Harley-Mason and C. R. Harrison, *ibid.*, 4872 (1963).

(4) I (X = N): J. W. Armit and R. Robinson, *ibid.*, 827 (1922).

(5) I (X = N): C. B. Reese, *J. Am. Chem. Soc.*, **84**, 3979 (1962).

(6) II(X = N) and II(X = S): A. G. Anderson, W. F. Harrison, R. G. Anderson, and A. G. Osborne, *ibid.*, **81**, 1255 (1959).

(7) I (X = S): Ref. (1) and R. Mayer, J. Franke, V. Horák, I. Hanker, and R. Zahradnik, *Tetrahedron Letters*, 289 (1961).

(8) M. E. Kuehne, S. J. Weaver, and P. Franz, *J. Org. Chem.*, **29**, 1582 (1964).

(9) C. L. Arcus and G. C. Barrett, *J. Chem. Soc.*, 2740 (1958).

(10) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, 1961, Chapter 5.

(11) R. Zahradnik and J. Koutecký, *Coll. Czech. Comm.*, **28**, 1117 (1963).

(12) R. Borsdorf, *Z. Chem.*, **4**, 422 (1964).