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SCF MO CALCULATIONS FOR THE THREE MONOBENZAZULENES (1)

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The two benzonaphthalenes, phenanthrene and anthracene, differ greatly in their properties, phenanthrene having a significantly larger resonance energy and being much less reactive. Since naphthalene and azulene are isomeric aromatic hydrocarbons, one might expect similar differences to exist between the three possible benzazulenes, a conclusion which seems at first sight to be supported by the failure of various attempts to obtain the 4,5-isomer.

Some time ago, however, one of us suggested (2) on the basis of a simple perturbational MO treatment that azulene is best regarded as a monocyclic aromatic system, the central bond contributing little to its resonance stabilization and serving mainly to enable the ring to exist in an unstrained planar configuration. This idea has since been supported by an x-ray structure determination which shows the central bond of azulene to be essentially single (3), and by more detailed calculations (4) using a more refined SCF MO procedure. If this conclusion is correct, then one might expect the three benzazulenes to be very similar in their properties; for if azulene is indeed essentially a monocyclic aromatic system, the point of annelation with the benzene ring should be relatively unimportant - and indeed crude calculations by the Hückel method suggested that this might be the case (5).

We have therefore calculated the properties of the three benzazulenes, using a modified Pople SCF MO method which has been described in detail elsewhere (4, 6). Two sets of values were used for the repulsion integrals; one (PPP) similar to those recommended by Pariser and Parr, the other (SPO) corresponding to a modified split p-orbital approach. The calculations were made self-consistent for variations in the one- and two-electron integrals with bond length for all pairs of neighboring atoms.

Table I shows π-binding energies calculated for the three hydrocarbons, together with derived (4) resonance energies; the values given by both methods agree closely, and the last column of Table I lists mean estimated values for the heats of formation at 25°. Possible strain energy has not been included.

TABLE I

Calculated π-binding energies, resonance energies and heats of formation at 25° (ΔH_f) for the three benzazulenes (in e.v.).

Compound	π-binding energy		resonance energy		ΔH_f
	PPP	SPO	PPP	SPO	
1,2-Benzazulene	18.24	16.87	2.32	2.35	123.68
4,5-Benzazulene	18.25	16.87	2.37	2.41	123.70
5,6-Benzazulene	18.25	16.90	2.37	2.37	123.69

It will be seen that the predicted resonance energies and heats of formation of the three benzazulenes are indeed virtually identical. The resonance energies are much less than the values calculated (4) for anthracene (PPP, 3.09; SPO, 3.08 e.v.) or phenanthrene (PPP, 3.46; SPO, 3.43 e.v.). They are somewhat smaller than a sum of the resonance energies calculated (4) for benzene and azulene (PPP, 2.54; SPO, 2.54 e.v.). The general picture seems entirely consistent with our formulation of the three compounds as bicyclic aromatic systems, formed by fusion of the C_6H_6 and $C_{10}H_{10}$ "Hückel" hydrocarbons but mildly perturbed by the presence of the additional transannular bond. This conclusion also seems consistent with the values calculated for the dipole moments (Table II) and bond lengths (Table III) in these three compounds. The calculated values indicate a marked alternation of bond lengths in the five- and seven-membered rings; it is to be hoped that the structures of these molecules will be determined experimentally, to test this prediction.

Since our SCF MO method has proved very satisfactory (4,6) for a wide range of conjugated hydrocarbons of varying type, both aromatic and non-aromatic, we feel that the calculations reported here are fairly reliable. If so, the failure to prepare 4,5-benzazulene cannot be attributed to any lack of aromaticity or resonance stabilization.

TABLE II

Calculated dipole moments (D) for the benzazulenes.

Compound	Dipole moment	
	PPP	SPO
1,2-Benzazulene	1.86	1.32
4,5-Benzazulene	1.96	1.41
5,6-Benzazulene	2.01	1.41

TABLE III

Calculated bond lengths (Å) for the benzazulenes.

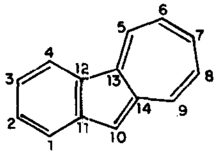
Compound	Bond	PPP	SPO
1,2-Benzazulene	1,11	1.417	1.419
	1,2	1.382	1.379
	2,3	1.412	1.416
	3,4	1.384	1.380
	4,12	1.415	1.418
	11,12	1.405	1.397
	10,11	1.441	1.450
	10,14	1.370	1.362
	12,13	1.447	1.455
	13,14	1.465	1.469
	5,13	1.375	1.366
	5,6	1.437	1.450
	6,7	1.369	1.360
	7,8	1.437	1.450
	8,9	1.366	1.357
	9,14	1.449	1.461

TABLE III (continued)

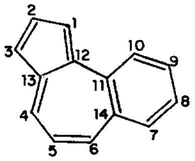
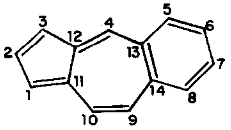
Compound	Bond	PPP	SPO
4,5-Benzazulene	1,12	1.373	1.366
	1,2	1.431	1.441
	2,3	1.370	1.363
	3,13	1.438	1.449
	12,13	1.464	1.468
	11,12	1.451	1.468
	4,13	1.377	1.367
	4,5	1.437	1.449
	5,6	1.366	1.358
	6,14	1.446	1.457
	11,14	1.405	1.397
	7,14	1.413	1.415
	7,8	1.384	1.382
	8,9	1.411	1.414
	9,10	1.394	1.381
	10,11	1.414	1.417
5,6-Benzazulene	1,11	1.374	1.365
	1,2	1.430	1.441
	2,3	1.370	1.362
	3,12	1.439	1.450
	11,12	1.448	1.461
	9,14	1.446	1.457
	9,10	1.362	1.355
	10,11	1.448	1.461
	4,12	1.374	1.365
	4,13	1.445	1.455

TABLE III (continued)

Compound	Bond	PPP	SPO
5,6-Benzazulene (continued)	13,14	1.405	1.396
	5,13	1.415	1.417
	5,6	1.383	1.380
	6,7	1.413	1.417
	7,8	1.382	1.379
	8,14	1.416	1.419

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