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SCC-EH MOLECULAR ORBITAL CALCULATIONS OF THE ELECTION DISTRIBUTION IN BENZOCYCLOPROPENE AND ITS CATION, ANION AND RADICAL

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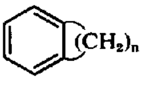
Abstract – The SCC-EH MO method is applied to benzocyclopropene and its as yet unknown cation, anion and radical. The π-electron distribution of the neutral molecule reflects the particular geometry assumed, but the total energy is relatively insensitive to small geometric changes. Significant stabilisation of the ions is predicted to occur by charge delocalisation with the free radical having a stability intermediate to the cation and anion.

The nature of the bonding in the benzocycloalkenes has been the subject of much debate.[1] Prior theoretical treatments have predicted that bond length and bond angle deformations result in partial localisation of the π-bonds in the more strained members of the series. The CNDO/2 molecular orbital method has led to the prediction that this bond fixation takes place in the direction indicated by the Kekulé structure 1[2] while the extended Hückel approach favoured 2.[3] For benzocyclopropene, the most highly strained member of the series, X-ray crystallographic data have only recently become available[4] and these show that, for the 1,4-diphenyl-7,7-dicarboxylate derivative examined, bond length and bond angle deformations result in a geometry depicted by 3. This compound has the C-1—C-6 bond shortened to the same length as the double bond in cyclopropene[5] with the C-1—C-2 and C-5—C-6 bonds also reduced in length. The C-2—C-3 and C-4—C-5 bonds were found to be longer than the corresponding bonds in the centre ring of *p*-terphenyl.[6] Thus the experimental geometry of 3 shows a shortening of the bonds around that half of the 6-membered ring which carries the fused cyclopropene and corresponds to a form of bond localisation depicted by neither 1 nor 2. We now wish to report the results of a theoretical examination of benzocyclopropene and the as yet unknown benzocyclopropenyl cation, anion and radical, based on the experimentally determined geometry of 3. For comparison purposes, calculations have also been performed using the calculated[2] geometry of the Kekulé structure 1 for benzocyclopropene.



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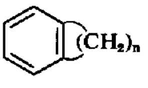

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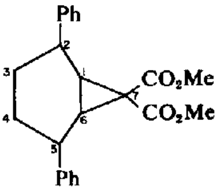

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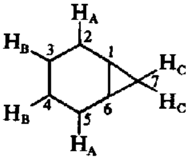
METHOD

SCC-EH-MO (Self Consistent Charge Extended Hückel Molecular Orbital) calculations were performed using the iterative procedures of Zerner and Gouterman.[7] Diagonal elements of the H-matrix were estimated from the valence state ionisation energies[8] and off-diagonal elements determined from the Wolfsberg-Helmholz relation[9] with a k value of 1·75. Slater atomic orbitals were used with exponents deduced from Slater's rules.[10] Iterations were continued until input and output orbital populations agreed to within 0·005 electron units, which was usually achieved within 15 cycles.

Two series of calculations were performed. In series A, the experimentally determined parameters of 3 were used for all C—C bond lengths and all bond angles of the parent molecule (4), but the geometry was idealised in that the ring system was assumed to be planar with a mirror plane passing through C-7 and bisecting the C-3—C-4 bond. This did not result in any deformation of bond lengths or angles beyond the experimentally determined limits. Aromatic C—H bond lengths were assumed to be 1·084 Å[11] and the methylene C—H bonds 1·087 Å[5] with a dihedral angle of 112·7°.[4] For the cation 5, anion 6 and radical 7 the same ring geometry was maintained while the H atom at C-7 was assumed to lie, in turn, out of the benzocyclopro-



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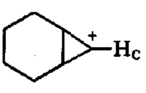

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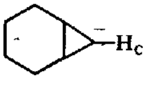

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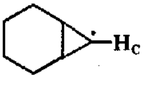

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pene plane with the C-1—C-7—H_C angle unaltered and in the plane of the ring system. These are referred to as non-planar and planar respectively. In series B, the geometry assumed for benzocyclopropene was that calculated by Manatt *et al.*[2] The derived species (**5**–**7**) were assumed to retain this calculated geometry with the C-7 H atom being treated as in series A.

Calculations were also performed on cyclopropene (**8**) and its cation (**9**), anion (**10**) and radical (**11**) using the known geometry.[5] Benzene and ethylene were examined to provide overlap populations based on the same theoretical model, for comparison.

RESULTS AND DISCUSSION

For each species studied a set of MO energy levels and coefficients was obtained together with the results of a Mulliken population analysis. However, only those results pertinent to the current discussion are presented here. Results obtained for benzene, ethylene and the cyclopropene species were comparable with those achieved by other workers[12] and therefore they are not reproduced here. Of particular interest are the π-overlap populations (OP) obtained for all the benzocyclopropene derivatives examined (Table 1) and the charge distribution in the cation **5** and anion **6** (Table 2). The former values provide a measure of π-electron density between each pair of atomic orbitals and consequently provide a prediction of π-bond localisation in the ring system. For benzocyclopropene (**4**), the OP values obtained from each calculation clearly reflect the particular geometry assumed. Thus in Series A (Table 1a) neither of the possible Kekulé structures are favoured for **4**, but π-electron density is greatest along the C-3—C-4 and the C-2—C-1, C-1—C-6 and C-6—C-5 bonds. However, the OP value between C-1 and C-6 (0·252) is not as great as the short bond length (1·333 Å)[4] might infer, and is far more comparable with the value calculated for benzene (0·241) than that for the corresponding bond in cyclopropene (0·463) or the olefinic bond in ethylene (0·429). The OP results for **4** in series B (Table 1b) are in marked contrast with those from series A. The calculated geometry adopted shows a clear preference for the Kekulé structure **1**, with increased OP values between C-1—C-2, C-3—C-4 and C-5—C-6. The Charge distributions obtained for **4** in both calculations (Table 2) is very similar to those obtained for benzene and cyclopropene, with a small negative charge on each carbon atom and a small positive charge on each H atom. It is interesting to note that both values of total energy of **4** are very similar (Table 1) and we take this insensitivity

Table 1. SCC-EH π-overlap populations and total energies for benzocyclopropene and its cation, anion and radical

Species	Bond[a]					Energy (eV)
	C-1—C-2 (C-5—C-6)	C-2—C-3 (C-4—C-5)	C-3—C-4	C-1—C-6	C-1—C-7 (C-6—C-7)	
(a) *Series A*						
(**4**)	0·262	0·213	0·263	0·252	−0·021	−577·21
(pl **5**)[b]	0·215	0·246	0·224	0·207	0·118	−552·71
(n-pl **5**)	0·212	0·249	0·200	0·153	0·133	−568·08
(pl **6**)	0·191	0·085	0·327	0·237	0·106	−506·08
(n-pl **6**)	0·254	0·154	0·297	0·225	0·040	−539·36
(pl **7**)	0·218	0·169	0·280	0·225	0·097	−531·33
(n-pl **7**)	0·242	0·209	0·253	0·205	0·065	−559·81
(b) *Series B*						
(**4**)	0·294	0·201	0·276	0·196	−0·020	−577·45
(pl **5**)	0·214	0·257	0·201	0·103	0·190	−568·49
(n-pl **5**)	0·229	0·247	0·207	0·109	0·148	−568·64
(pl **6**)	0·277	0·116	0·321	0·157	0·083	−540·28
(n-pl **6**)	0·282	0·141	0·308	0·171	0·048	−539·90
(pl **7**)	0·255	0·190	0·266	0·139	0·120	−562·56
(n-pl **7**)	0·265	0·198	0·262	0·151	0·080	−560·10

[a] Atoms are numbered as for **4**. [b] The abreviations used are: pl = planar and n-pl = non-planar

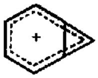
Table 2. SCC–EH net atomic charges for benzocyclopropene and its cation, anion and radical

Species	Atom[a] C-1 (C-6)	C-2 (C-5)	C-3 (C-4)	C-7	H_A	H_B	H_C
(a) *Series A*							
(4)	0·054−	0·062−	0·073−	0·068−	0·073+	0·072+	0·078+
(pl 5)[b]	0·047+	0·010+	0·003−	0·089−	0·090+	0·091+	0·619+
(n-pl 5)	0·099+	0·030+	0·035+	0·095+	0·189+	0·095+	0·099+
(pl 6)	0·135−	0·208−	0·164−	0·372−	0·003−	0·035−	0·461+
(n-pl 6)	0·143−	0·149−	0·130−	0·267−	0·026+	0·038+	0·016−
(pl 7)	0·045−	0·096−	0·085−	0·248−	0·036+	0·046+	0·536+
(n-pl 7)	0·031−	0·059−	0·061−	0·100−	0·073+	0·078+	0·089+
(b) *Series B*							
(4)	0·058−	0·070−	0·083−	0·029−	0·071+	0·072+	0·082+
(pl 5)	0·105+	0·032+	0·034+	0·132+	0·090+	0·095+	0·157+
(n-pl 5)	0·101+	0·035+	0·036+	0·100+	0·093+	0·095+	0·179+
(pl 6)	0·138−	0·170−	0·143−	0·212−	0·014+	0·031+	0·023+
(n-pl 6)	0·145−	0·155−	0·130−	0·252−	0·025+	0·038+	0·013−
(pl 7)	0·024−	0·077−	0·069−	0·052−	0·067+	0·075+	0·107+
(n-pl 7)	0·030−	0·063−	0·062−	0·090−	0·073+	0·077+	0·100+

[a] Atoms are numbered as for (4). [b] The abbreviations used are: pl = planar and n-pl = non-planar.

to geometry to infer that the actual geometry adopted by the parent molecule need not necessarily be the same as that for the derivative 3 whose structure has been accurately determined.

As with the data for the neutral molecule, the results obtained for the benzocyclopropenyl cation 5 predict comparable stabilities for three of the four calculations. The results are, however, somewhat unexpected in that both sets of calculations predict the non-planar ion to be more stable than its planar counterpart (Table 1). Furthermore, the positive charge is delocalised from the C-7—H_C moiety to a greater extent in the non-planar than the planar species considered (Table 2), particularly in series A. A feature of the calculations is the inherent assumption that the ring geometry of the neutral molecule is unaffected by the formal removal of a hydride ion. This is probably incorrect and indeed the results can be interpreted to infer a reorganisation of the cation geometry before stabilisation of the planar ion occurs. Both sets of calculations predict a more marked π-electron delocalisation in the cation than in the neutral molecule with a significant π-electron contribution to the C-1—C-7 and C-6—C-7 bonds. This is consistent with the data obtained for the cyclopropenyl cation 9 which is known to undergo stabilisation by charge and electron delocalisation to a 2π3C aromatic ion. We therefore take the π-overlap population and charge distribution data obtained for 5 to infer stabilisation by formation of a bridged 6π7C aromatic ion 5a. Furthermore, we would suggest that 5 should be capable of existence, since both 4 and 9 are known entities, and an active programme to obtain derivatives of 5 is underway in these laboratories.



5a

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The cyclopropenyl anion 10 is often cited as a classic example of an antiaromatic species, since delocalisation of the four π-electrons causes destabilisation. With the benzocyclopropenyl anion 6 however, the benzene ring prevents such complete destabilisation and, although 6 is predicted to be much less stable than 4 or 5 by both sets of calculations, it is possible that it could exist. The OP density is predicted to be greatest between C-3 and C-4 (Table 1) with the Kekulé structure corresponding to 1 being favoured. Delocalisation of π-electrons along the C-1—C-7 and C-6—C-7 bonds is predicted to be minimal, but 72% of the negative charge is delocalised from the C-7—H moiety into the 6-membered ring. Delocalisation for the radical 7 (Table 2) is calculated to be intermediate to 5 and 6, but, like 6, there is no appreciable π-contribution to the C-1—C-7 and C-6—C-7 bonds.

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