On the Question of a Planar Tetravalent Carbon Centre in the Ethylene- and Acetylene-benzenium Ion - a Semiempirical SCF–LCAO-Study

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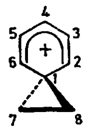
Summary Optimized equilibrium geometries of the acetylene- and ethylene-benzenium ion are computed by the semiempirical MINDO/2 method for a tetrahedral [(**1**) and (**2**)] and planar arrangement [(**4**) and (**5**)] of the spiro atom; comparison of the tetrahedral conformations with their planar counterparts reveals an energy difference of 22·3 kcal mol^{-1} for (**1**) *vs.* (**4**) and 15·5 kcal mol^{-1} for (**2**) *vs.* (**5**).

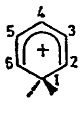
The ethylenebenzenium ion (**1**) has been the subject of detailed experimental and theoretical investigations.[1] Lately a study of the acetylenebenzenium ion (**2**) has been reported.[2]

The question of how close in energy the corresponding structures (**4**) and (**5**) are in view of the fact that (**1**) and (**2**) have a tetrahedral spiro-atom, whereas (**4**) and (**5**) have a tetravalent planar carbon centre has been raised on the basis of qualitative calculations by Hoffmann and co-workers.[3] This qualitative prediction on the basis of EH and CNDO/2 calculations nevertheless does not render possible a quantitative prediction because the validity of the Hückel approximation in charged species is questionable and also the geometries and energies of non-classical carbonium ions cannot be derived from ground state geometries.



(1)


(2)



(3)


(4)


(5)

In the following we report optimized MINDO/2 calculations[4] on the problem of a planar tetravalent carbon centre in (**1**) and (**2**). The equilibrium bond lengths and heats of formation for the cations (**1**) to (**4**) and (**5**)[1] are given in the Table. The charge densities (not published) indicate decreasing delocalization of the positive charge in the six-membered ring in the order (**3**) > (**1**) > (**2**) > (**4**) > (**5**). Our results, as given in the Table, reveal an energy difference of 22·3 kcal mol^{-1} between the tetrahedral (**1**) and the planar (**4**) and of 15·5 kcal mol^{-1} between (**2**) and (**5**),[5]† Although semiempirical SCF methods tend to overestimate the stability of strained-ring systems, accurate energy differences result for close related structures as has been shown recently for the Cope-rearrangement.[6]

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Table. Equilibrium geometries and heats of formation of (**1**)—(**5**).

	Bond lengths/Å					Bond angles/°		Heats of formation
Compound	$C_1C_2=C_1C_6$	$C_2C_3=C_5C_6$	$C_3C_4=C_4C_5$	$C_1C_7=C_1C_8$	C_7C_8	$C_2C_1C_6$	$C_3C_4C_5$	/kcal mol^{-1}
(**1**)	1·444	1·358	1·391	1·534	1·459	115·1	121·9	193·23
(**2**)	1·418	1·376	1·390	1·570	1·252	118·1	120·5	231·68
(**3**)	1·443	1·361	1·403	—	—	116·8	123·1	197·29
(**4**)	1·415	1·382	1·379	1·607	1·383	114·6	118·2	215·57
(**5**)	1·405	1·383	1·380	1·606	1·231	115·8	118·2	247·19

† For methane itself the energy required to convert from a tetrahedral to a planar structure has been estimated to 10·8 eV (approximate *ab initio*),[7] to 5·5 eV (EH)[3] and to 7·8 eV (open shell SCF minimum basis).[8] In contrast the MINDO/2 method results in an energy difference of only 3·3 eV between the two structures in their singlet ground states. The energy differences between the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals for the planar structures (in their singlet ground states) are: for methane 9·1 eV, for (**4**) 8·7 eV, and for (**5**) 8·9 eV. This makes a triplet ground state for the planar structures unlikely. However the triplet state[9] of square-planar methane is only 0·4 eV higher in energy than its corresponding singlet state, suggesting both states being close in energy [no convergence was achieved in the computation of the triplet states of (**4**) and (**5**)].

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[5] For the energy difference between (**1**) and (**4**) see also M. Shanshal, *J.C.S. Perkin II*, 1972, **335**.

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