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structural formulas I–VIII

Figure 1: structural formulas I–VIII

Abstract

Full Text

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MOLECULAR ORBITALS OF RADICALS WITH NONALTERNANT RINGS

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In work ([1]) we calculated the molecular orbitals of certain systems with three fused rings—analogs of perinaphthenyl with five- and seven-membered rings. We found that systems of this type with an odd number of electrons differ from the perinaphthenyl radical in that the nonbonding level of the latter, when one of the six-membered rings is replaced by a five-membered one, passes into a bonding level (so that the molecule should readily add an electron with formation of an anion), while when it is replaced by a seven-membered ring it passes into an antibonding level (which favors loss of an electron and conversion into a positive ion). For the system of three five-membered rings (I) with 10 π-electrons it turned out that there are six bonding and four antibonding orbitals, while for the system of three seven-membered rings (II) with 16 π-electrons there are only seven bonding levels and nine antibonding ones. Thus, in the case of systems I and II we encounter an anomaly in the distribution of molecular orbitals, first discovered in the work of Bergmann and co-workers ([2]) for fulvalene (III), fulvadiene (IV), fulvatriene (V), heptafulvalene (VI), heptafulvadiene (VII), and heptafulvatriene (VIII), which distinguishes compounds I–VIII from alternant hydrocarbons. In all alternant hydrocarbons with an even number of π-electrons the number of bonding levels is equal to half the number of π-electrons, so that in the ground states of the molecules the π-electrons pairwise occupy all bonding levels, while the antibonding levels are vacant. In contrast, in I and III–V the number of bonding levels is greater by one than the number of pairs of π-electrons. From this one may conclude that such compounds

should possess a tendency to add an extra electron with formation of a singly charged anion (paramagnetic, in contrast to the anions corresponding to the cyclopentadienyl radical and its analogs) or even

two electrons with formation of a doubly charged diamagnetic anion. On the other hand, in II, VI, VII, and VIII the number of bonding levels is smaller by one than the number of pairs of π-electrons. In this case one should expect

easy loss of an electron with formation of a singly charged cation-radical, or even loss of two electrons with the appearance of a doubly charged cation.* The difference between systems I–VIII and alternant hydrocarbons is manifested also in the discrepancy between the number of bonding molecular orbitals and the number of double bonds that can be drawn in the structural formulas of these compounds. In alternant hydrocarbons the number of bonding orbitals is always equal to the number of double bonds. By contrast, in case I one can write a structural formula with five double bonds, whereas the bonding levels number six. The number of bonding levels exceeds the number of double bonds also in molecules III–V. In compounds with seven-membered rings the number of bonding levels is smaller than the number of double bonds. Thus, the eight double bonds in II correspond to only seven bonding orbitals.

Systems III–VIII were investigated in connection with the problem of thermochromy. The possibility of thermochromy is determined by the ease of transition of the molecule into the triplet state. In this connection it is interesting to note that the systems I and II studied by us are characterized by the fact that, for the corresponding neutral molecules, the highest occupied level (the last bonding level in I and the first antibonding level in II) is doubly degenerate. This means that for the last two electrons there are two levels of the same energy, so that, along with a singlet state, when both of these electrons occupy one of the degenerate levels, a triplet state is possible, when one electron is located on each of the degenerate levels. Within the framework of the simplified molecular-orbital method the energies of the corresponding singlet and triplet states are identical. Taking electron interaction into account will probably lead to a difference in the energies of these states, but nevertheless one may suppose that the energy difference will be small, so that for systems I and II in the form of neutral molecules one may expect either that the triplet state will be the ground state or that the energy of transition to the triplet state will be small, so that thermochromic properties may appear.

The described features of systems with nonalternant rings prompted us to consider other compounds with five- and seven-membered rings, namely radicals—analogs of diphenylmethyl and dinaphthylmethyl with cyclopentadienyl, cycloheptatrienyl, and azulenyl residues. The calculations were carried out by the simplified molecular-orbital method under the usual assumptions of this method. The systems considered are given in Table 1, where the numbers of bonding, nonbonding, and antibonding levels in these molecules are indicated. As is seen from the table, in the first four of the systems considered, in contrast to diphenylmethyl, there are no nonbonding levels, and the diphenylmethyl level with zero exchange energy becomes, in the system with five-membered rings (IX), a bonding level, and in the system with seven-membered rings (XI), an antibonding one. Therefore one may expect that IX, like the cyclopentadienyl radical, should be stable in the form of a singly charged anion, while XI should be stable in the form of a singly charged cation, like tropylium. The systems in which, besides the nonalternant ring, there is also a fused six-membered ring (X and XII) should behave analogously. The radical with heptalinyl residues (XIII)

has a nonbonding level, but in this case there are only 11 bonding orbitals, on which

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* This does not mean the impossibility of the existence of the compounds considered in the form of neutral molecules, since the ease of addition or loss of electrons is determined not only by the fact of the presence of an extra bonding or antibonding level, but also by the energy of this level. Thus, in case VI, although the highest occupied level is antibonding, its exchange energy is small ($-0.20\ \beta$), and therefore VI can exist in the form of a neutral molecule that is not very stable, owing to destabilization caused by the presence of electrons on an antibonding level.

Table 1

Molecule	Number of π-electrons	Number of levels: bonding	Number of levels: nonbonding	Number of levels: antibonding	Predicted stable state
(IX) structural formula shown	11	6	–	5	A–
(X) structural formula shown	19	10	–	9	A–
(XI) structural formula shown	15	7	–	8	A+
(XII) structural formula shown	23	11	–	12	A+
(XIII) structural formula shown	25	11	1	13	A+

Molecule	Number of π-electrons	Number of levels: bonding	Number of levels: nonbonding	Number of levels: antibonding	Predicted stable state
(XIV) structural formula shown	21	10	1	10	A
(XV) structural formula shown	21	10	1	10	A
(XVI) structural formula shown	21	10	1	10	A
(XVII) structural formula shown	21	11	–	10	A–
(XVIII) structural formula shown	21	10	–	11	A+

can accommodate only 22 π-electrons, so that the nonbonding level is occupied not by an unpaired electron, but by a pair, while the unpaired electron must pass to an antibonding level. In this case one naturally expects not only an easy conversion into a positive monovalent ion, as in tropylium and XI, but also the possibility of further removal of electrons from the nonbonding level. Systems XIV–XVIII are isomeric diazulenylmethyls, differing in the position of the methine group in the azulenyl residue. As is seen, in cases XIV–XVI we have radicals with equal numbers of bonding and antibonding levels and one level with zero exchange energy. In these systems, as in alternant hydrocarbon radicals, the π-electrons occupy all the bonding levels in pairs, while one unpaired electron is located on the nonbonding level. As is seen from the formulas, such a situation always occurs when the methine group is connected with a ring atom separated by at least two bonds from the atoms common to the five- and seven-membered rings, irrespective of whether the methine group is in the five- or seven-membered ring. If, however, the methine group is con-

nected with a carbon atom situated next to the carbon atom common to the five- and seven-membered rings, the situation is different. If the methine group is bonded to the seven-membered ring, as in XVII, there are 11 bonding levels and 10 antibonding levels. Since the radical has only 21 π-electrons, it follows from the calculation that such a radical should add an extra electron, becoming a negative ion. On the other hand, in XVIII, in which the methine group is bonded to the five-membered ring, the bonding levels are alto-

10, and 11 antibonding levels, so that on the bonding levels there is room for only 20 electrons, while the last electron must occupy an antibonding orbit; hence this system should be stable in the form of a positive ion. This result of the calculation is confirmed by the experimental data of F. N. Stepanov and N. A. Aldanova ([3]), who obtained diazophenylmethyl of structure XVIII in the form of a cation.

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CITED LITERATURE

[1] M. E. Dyatkina, E. M. Shustorovich, DAN, **117**, 1021 (1957). [2] E. Bergmann, J. Hirschberg et al., Bull. Soc. Chim. France, **18**, 697 (1951). [3] F. N. Stepanov, N. A. Aldanova, in press.

Note: Figure translations are in progress. See original paper for figures.