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Homoconjugation in Radical Cations

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Recent studies of nuclear spin polarization effects in cyclo-propane derivatives have provided considerable information on the structure as well as the spin and charge density distributions in this class of radical cations. In the present work we report an extension of the frontier MO/perturbation MO theory of homo-conjugation to include such species in an attempt to rationalize further the experimental results mentioned above, and to provide guidelines for understanding the structures of radical cations derived from other types of cyclopropane derivatives.

The structures observed for the radical cations of diphenyl-cyclopropane, trimethylcyclopropane, and benzonorcaradiene are rationalized, and the structures of the radical cations of spiro-cyclopropanefluorene and vicinally cyclopolyene-substituted cyclo-propanes are predicted.

INTRODUCTION

Recent studies of nuclear spin polarization effects in cyclopropane deri-vatives have provided considerable information on the structure as well as the spin and charge density distributions in this class of radical cations.[1-7] In the present work we report an extension of the frontier (F) MO/perturbation (P) MO theory of homoconjugation[8-10] to include such species in an attempt to rationalize further the experimental results mentioned above and to provide guidelines for understanding the structures of radical cations derived from other types of cyclopropane derivatives.

Following previous practice,[8-10] we utilize molecular fragments and consider the interactions of the component FMOs from the standpoint of the PMO theory. As before we assign the charge (and in this case spin) density to one of the fragments, and build up the composite molecule in a heuristic sense by union with the missing (neutral) fragment. The assignment of the principal cationic site is made on the basis of the ionization potentials (IPs) of the fragment components, whereas the nuclear spin polarization experiments are conducted in the solution phase. However, this should not introduce major inconsistencies, since a strong correlation has been shown between electro-chemical half-cell potentials and IPs.[11-19] Given the fact that each fragment is in reality a component of the same molecule, differential medium effects should be held to a minimum. The model structures for the fragments and their IPs are given in Table I, and the FMOs are presented in Table II.

In assessing the fragment perturbations, we make use of the standard FMO/PMO approach[24] in which the strength of interaction is approximately

Model Structures and Ionization Potential of Fragments

1

(10.6 eV, C-C)[20]

CH$_4$

2

(13.6 eV, C-H)[20]

3

(10.51 eV, π)[20]

4

(9.03 eV, π)[20]

5

(8.29 eV, π)[20]

6

(9.25 eV, π)[20]

7

(8.50 eV, π)[21]

OMe

OMe

8

(7.90 eV, π)[22]

9

(8.15 eV, π)[23]

10

(8.34, 9.04 eV, π)[21]

11

(7.91, 8.77 eV, π)[21]

TABLE II

Frontier Molecular Orbitals of Model Structures

CYCLOPROPANE, 1

S   A
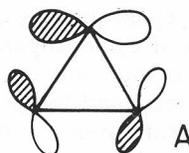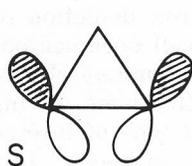
ETHYLENE, 3   BUTADIENE, 4   HEXATRIENE, 5
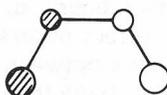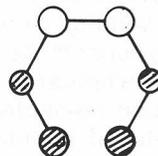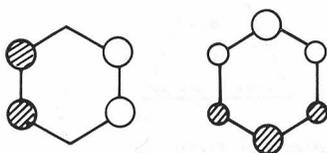
BENZENE, 6   STYRENE, 7
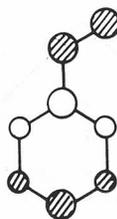
1,4-DIMETHOXYBENZENE, 8
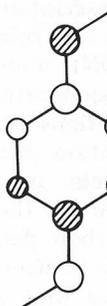
NAPHTHALENE, 9
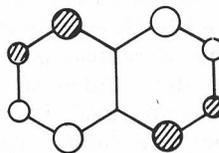
BIPHENYL, 10
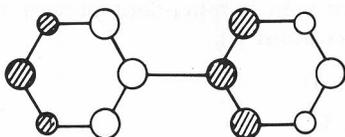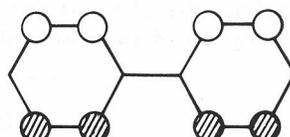
HOMO, A   2nd HOMO S

proportional to $S^2/\Delta E$, where S is the overlap integral between components and ΔE is the FMO orbital energy difference. In the first term, three factors will be of primary importance: the FMO orbital symmetry (where present); the magnitude of the coefficients at the point(s) of union; and the orientation of the fragments.

The structural consequences of electron depletion of the pair of highest occupied (HO) MOs of cyclopropane are well documented. Removal of electron density from the S orbital involves loss of bonding electrons from between the 2,3 carbons, weakening and lengthening this bond, giving rise in essence to a »trimethylene« radical cation — it is this type of interaction which underlies homoconjugation and homoaromaticity in cations.[8,10] Loss of electron density from the A orbital exerts a more complex effect on the cyclopropane, for this orbital is bonding between the 1,2 and 1,3 carbons and antibonding between the 2,3 carbons.[8,10] As a result two bonds in the molecule are weakened and lengthened whereas the opposite effect occurs for the third bond. This type of radical cation resembles a pi complex between ethylene and a methylene radical cation. Detailed calculations of the trimethyelene cation ($^2A_1$) and the π complex cation ($^2B_2$) have been reported.[25,26]

(ionization from S)   (ionization from A)
»trimethylene cation«   »π complex«
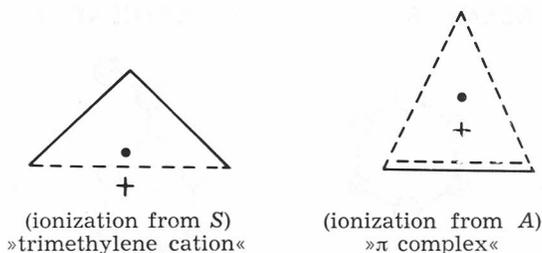
THE CIDNP METHOD

Since we will compare the predictions of the FMO/PMO method with CIDNP results, it appears useful to include a brief description of the CIDNP technique and to detail the way in which the results are related to the spin densities of the radical cation intermediates. The CIDNP method is based on transient enhanced NMR signals in absorption or emission which may be exhibited by products of radical pair reactions. The directions and intensities of these effects are determined by reaction and relaxation parameters of the radical pair, the individual radicals, and the products. In all experiments referred to below, the radical cations were generated by the same reaction type, electron transfer from a strained-ring hydrocarbon donor to a photo-excited (triple) quinone. These reactions are moderately to strongly exothermic. The resulting radical ions have limited lifetimes since they readily undergo intersystem crossing and recombination. Nevertheless, a small fraction of the ions also separate by diffusion. The competition between the electron spin dependent reaction (Eq. (3)) and the electron spin independent process (Eq. (4)) causes the generation of nuclear spin polarization (†).

$$^3A^* + D \rightarrow \overline{^3A^-\ D^+} \tag{1}$$

$$\overline{^3A^-\ D^+} \rightleftarrows \overline{^1A^-\ D^+} \tag{2}$$

$$\overline{^1A^-\ D^+} \rightarrow A + D\dagger \tag{3}$$

$$\overline{^{1,3}A^-\ D^+} \rightarrow {}^2A^- + {}^2D^+ \tag{4}$$

Because of the similarity of these reactions, the parameters governing the polarization are the same, except for the hyperfine coupling constants (hfc) of the individual nuclei. Accordingly, the signal directions observed for a product reflect the signs of the hfc's in the intermediate and the signal intensities reflect the magnitudes of the hfc's. For CIDNP effects generated by the above reaction scheme in a hydrocarbon-quinone system, emission signals generally indicate positive hfc's whereas enhanced absorption signals suggest negative hfc's.

The ^1H hfc's are related to carbon spin densities by different mechanisms of interaction. For π radicals, there are two principal coupling mechanisms involving either an exchange interaction or hyperconjugation. Protons attached directly to carbon atoms bearing positive spin density have negative hfc's because of the preferred exchange interaction between the unpaired π spin density and the carbon σ electron (Figure 1a). Positive hfc's on the other hand, are usually observed for protons which are one C—C bond removed from a carbon bearing positive spin density. The positive sign is due to a hyperconjugative interaction which delocalizes the π spin density on carbon into an H_n »group orbital« (cf. Figure 1b).
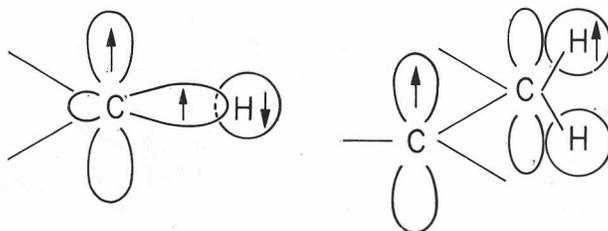
Figure 1.a. Preferred configuration of electron spins in the σ orbital connecting a hydrogen atom to an sp^2 hybridized carbon atom bearing unpaired π spin density. b. »Molecular π orbital« consisting of two carbon pz orbitals and an H_2 »group orbital« generated by hyperconjugative interaction of an sp^2 hybridized C atom bearing unpaired spin with a CH_2—R group.

In summary, CIDNP signal directions and intensities observed for diamagnetic products can be related to signs and magnitudes of ^1H hfc's of paramagnetic intermediates. The hfc's, in turn, can be interpreted in terms of carbon spin densities and these reveal important structural features of the intermediates.

RADICAL CATIONS OF SEVERAL CYCLOPROPANE DERIVATIVES

For most simple cyclopropane derivatives experimental results indicate the involvement of the symmetrical HOMO. In contrast, the results obtained for several cyclopropane derivatives with appropriate molecular fragments, arranged either vicinally or geminally, support an interaction of the antisymmetrical HOMO with the radical cation derived from the primary donor fragment.

Alkylsubstituted Cyclopropanes

The IP of cyclopropane falls below that of the alkanes, so the primary ionization is expected to occur from the cyclopropane ring. As a result of the coefficients in the degenerate pair of HOMOs in cyclopropane, methyl sub-

stitution(s) at a single carbon will most effectively stabilize the A orbital, whereas methyl substitution(s) at two carbons will best stabilize the S orbital.

Experimental results are available for 1,1,2-trimethyl- and for 1,1,2,2--tetramethylcyclopropane. The CIDNP results observed for the tetramethyl derivative do not permit a rigorous distinction between the two structures but the effect observed for the trimethyl derivative are unambiguous. These spectra indicate positive spin density in the 1- and 2- positions and, thus, support a trimethylene structure (12) for the intermediate radical cation (ionization from the S orbital of 1) and, at the same time, are incompatible with the structure (13) resembling a π complex (cf. Table III).[5,6]

<div align="center">

TABLE III

Hyperfine Coupling Pattern of Trimethylcyclopropane Radical Cations and CIDNP Results

</div>

	gem CH_3	CH_3	H_A	H_B	H_C
trimethylene cation, 12	+	+	—	+	+
π complex, 13	+		+	+	+
CIDNP	E	E	A	E	E

12

13
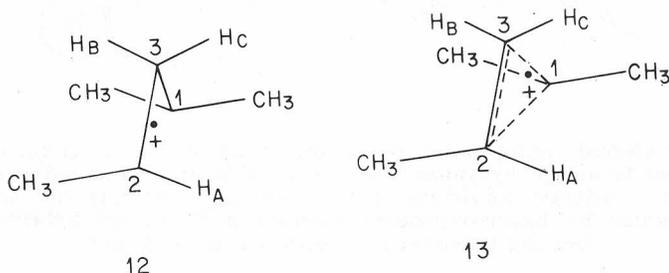
Phenylcyclopropanes

As the IP of cyclopropane lies above that of benzene, the primary ionization is not expected to occur from the cyclopropyl group, but from the substituent. Nevertheless the similarity in the IPs of the two fragments should lead to a strong interaction, and the charge and spin densities should be highly delocalized with conjugation through the S orbital in the 1,2-diphenylcyclopropanes. The utilization of this orbital maximizes the coefficients at the points of substitution in vicinal cyclopropane derivatives.

Experimental results obtained for cis- and trans-1,2-diphenylcyclopropane suggest that the intermediate radical cations have positive spin density (and negative hfcc's) in the benzylic cyclopropane positions as well as in the benzene rings. This result is compatible with the involvement of the S orbital of 1.

Bicyclic and Tricyclic Cyclopropane Derivates

Benzonorcaradiene. — In this molecule, a styrene fragment is linked with the cyclopropane moiety. The IP of styrene falls well below that of cyclopropane, and the ionization will occur from this fragment of the norcaradiene

molecule. Although symmetry does not totally preclude an interaction between the styrene FMO and the S orbital of cyclopropane, it is clear that it is the A orbital which will play the major role. As a result, the 2,3 cyclopropane bond is strengthened at the expense of the 1,2 and 1,3 bonds.

Two experimental facts can be adduced in support of this assignment. First, the CIDNP effects observed for benzonorcaradiene during its photoreaction with chloranil match the pattern expected for an intermediate with an appreciable contribution from structure 16 (Table IV). Second, 1- and 2-methyl-naphthalene are observed as products from this reaction, indicating that both of the tertiary-secondary cyclopropane bonds are readily cleaved, as would be expected for a structure derived from an involvement of the A orbital.[5]

TABLE IV

Nuclear Spin Polarization Observed for Benzonorcaradiene and Hyperfine Coupling Patterns of Related Radical Ions

	14	15	14 ↔ 16	CIDNP
H_{arom}	—	—	—	A
H_{olef}	—	—	—	A
H_D	+	—	+	E
H_C	+	—	+	E
H_B		+	—	A
H_A		+	—	A
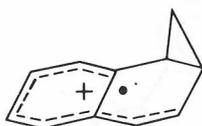
14

15
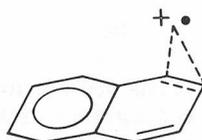
16

Methanoacenaphthene. — As in the case of benzonorcaradiene, this molecule contains an aromatic moiety which is joined to the cyclopropane ring. The ionization will occur primarily from the naphthalene fragment, and its HOMO symmetry dictates that it is the A orbital of cyclopropane which is involved in the interaction. As the orbital energy difference is quite large, the degree of involvement of the cyclopropane will be diminished with respect to the previous cases.

The CIDNP results observed for this system indicate that most of the spin density is located in the naphthalene fragment of the molecule suggesting an intermediate of structure **17**. A significant involvement of the cyclopropane *A* orbital is ruled out, but a marginal contribution from structure **18** cannot be eliminated.

17   **18**
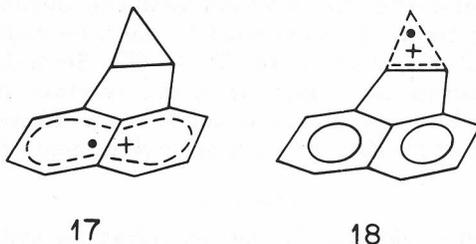
The [2.3]-Benzo-[5.6]-cyclopropanorbornene System. — The bichromophoric system, **19**, contains a fluorene fragment and a dimethoxybenzene moiety in addition to the cyclopropane ring. Of the two π systems, the dimethoxybenzene fragment appears to be the primarily involved in the ionization because of its lower IP. The FMO symmetry of this fragment (A) dictates that the *A* orbital of the cyclopropane ring should be involved in the interaction, although the overlap of the two fragments is not ideal. Since the difference in orbital energy is quite large, the involvement of the cyclopropane ring will be limited. The experimental results[5] confirm that the spin density is principally located in the dimethoxybenzene moiety, and that the participation of the cyclopropane ring is small. No involvement of the fluorene unit is indicated.

19
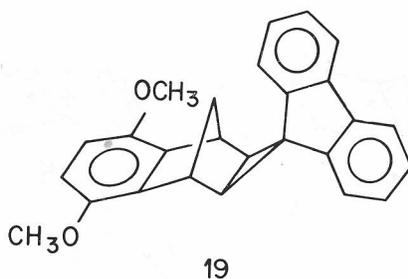
However, the experimental results are not unambiguous, since they do not rule out the possible homohyperconjugation of the dimethoxybenzene radical cation with the (tertiary) cyclopropane protons. In order to resolve this ambiguity, a somewhat simpler substrate could be studied. The hydrocarbon [2.3]-benzo-[5.6]-cyclopropanorbornene (**20**) contains two different types of cyclopropane protons and, thus, should permit a more definitive assignment of the cation structure (*cf.* Table V). This molecule also has the advantage that the IPs of the benzene moiety and the cyclopropane fragment lie closer together allowing a stronger interaction. On the other hand, the absence of the methoxy groups in **20** (and the presence of the vicinal alkyl substituents) may favor the involvement of the symmetrical HOMO of benzene and, therefore, may change the nature of the interaction.

TABLE V

Hyperfine Coupling Patterns of Radical Cations Derived from [2:3]Benzo[5:6]-cyclopropanobornene, 20

	21	22	23
2° H	+	negl.	—
3° H	—	+	+
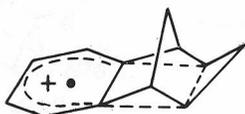
21
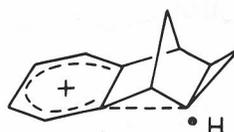
22

23

Spiro(cyclopropane-1,9'-fluorene). — The potential interaction of the cyclo-propane ring with the (slightly distorted) biphenyl moiety perpendicular to it can be evaluated in adducts of fluorenylidene to olefins (24). Unlike the previous substrates in which the aromatic moiety and the cyclopropane ring were joined vicinally, this system contains a geminal union of the two interacting groups (spiro conjugation) which rules out the involvement of the S orbital.[10] The gap between the IPs of the two components is not large so that an interaction can be expected. Only the second highest MO of unperturbed biphenyl allows a nonzero interaction with the A orbital of cyclopropane. Several derivatives of 24 have been studied;[19] in most cases the spin (and charge) density is primarily located in the biphenyl unit, and the involvement of the cyclopropane ring is limited.

The interaction with the cyclopropane moiety is strong only in two cases. When one of the substituents is a phenyl group (24, $R_1 = C_6H_5$, $R_2 = CH_3$), the involvement of the S orbital of cyclopropane is suggested. It is apparent that the biphenyl unit is not the exclusive site of ionization.
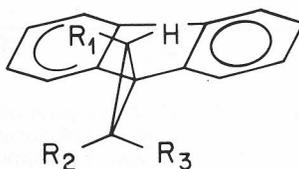
24
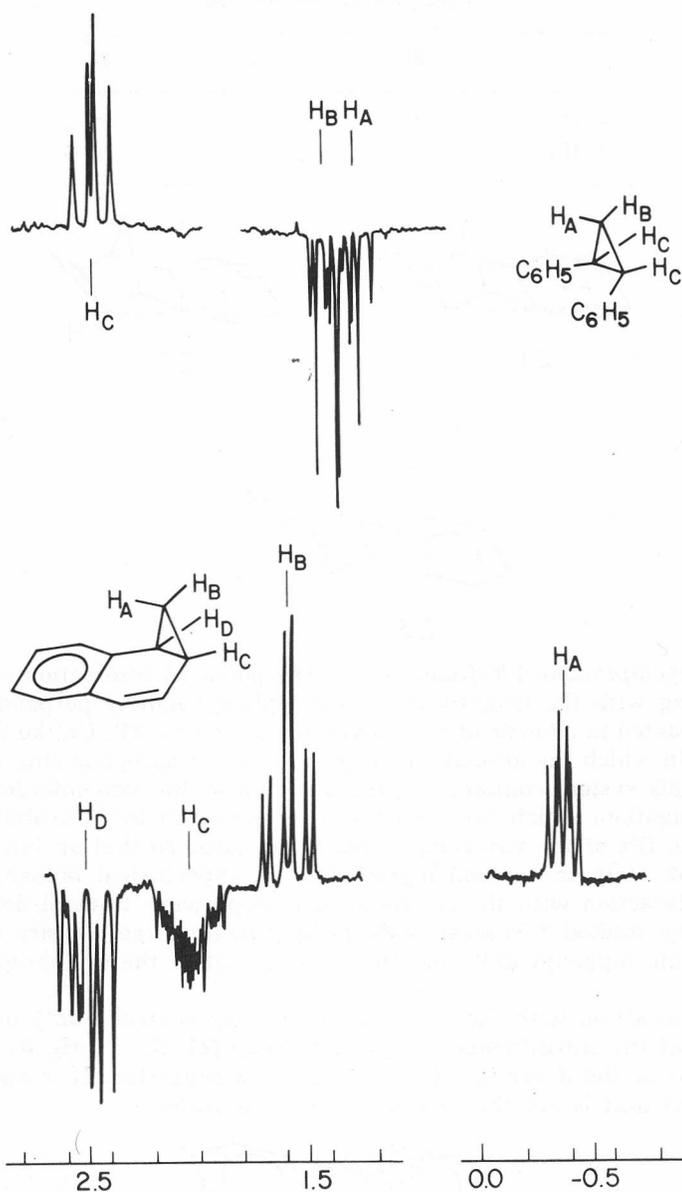
Figure 2. ¹H CIDNP spectra observed during the photoreaction of chloranil with cis-
-1,2-diphenylcyclopropane (top) and with benzonorcaradiene (bottom). Only the re-
sonances of the cyclopropane protons are shown. The opposite signal directions observ-
ed for analogous protons in the two compounds constitute evidence that the two
radical cations belong to two different structure types.

The second case of a strong interaction between the biphenyl fragment and the cyclopropane ring involves the parent molecule, which shows strong emission for the cyclopropane protons. This observation is compatible with the presence of positive spin density on the quaternary carbon. The biphenyl fragment is the primary seat of ionization but charge and spin are delocalized through the involvement of the *A* orbital of cyclopropane.

Vicinally Substituted Cyclopolyene Derivatives of Cyclopropane

As a result of the symmetries of the FMOs of ethylene (*S*), butadiene (*A*), hexatriene (*S*), *etc.*, an alternation between trimethylene and π complex structure types is predicted for the radical cations in this series. This behavior parallels that of the closed-shell homoaromatic systems.[8–10]

25   26   27
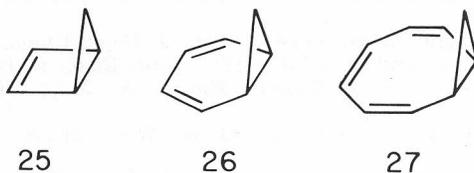
Of the potential substrates in this series, bicyclo[2.1.0]pentene (25) and several derivatives have been prepared, but they do not appear to be sufficiently stable for the photo-induced electron transfer experiments. Most derivatives of bicyclo[4.1.0]heptadiene (norcaradiene, 26) exist as the monocyclic valence isomers (cycloheptatrienes). Of the few derivatives of the bicyclic structure, at least one radical cation has been observed, in which the *A* orbital of cyclopropane interacts with the butadiene moiety.[5] Several bicyclo[6.1.0]nonatrienes 27 have also been investigated[27] and the radical cation of the parent species has spin density in the 1- and 8-positions suggesting the involvement of the *S* orbital of cyclopropane, in agreement with the present theoretical analysis.

CONCLUSION

It is clear from the foregoing analysis that cyclopropane radical cations are susceptible to treatment by the FMO/PMO theory of homoconjugation, which previously had been applied mainly to closed shell species.[8–10,28–31] By analysis of the cyclopropane FMO involved in the delocalization of spin and charge density — which usually follows from the symmetry of a fragment HOMO — it is possible to draw specific conclusions regarding the distribution of the spin density in the composite molecule. The CIDNP results provide an unusually direct evaluation of the analysis — in almost all cases it is possible to distinguish between the involvement of the *A* or *S* FMOs of cyclopropane. The only limitation to the use of the technique in this connection stems from the requirement that the difference between the orbital energies of the molecular fragments cannot be so large that the cyclopropane remains unpertubed. In view of the success of the FMO/PMO method in explaining the structures of radical cations, the extension of this method to radical anions[32] should be straightforward.

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SAŽETAK

Homokonjugacija kod radikal-kationskih sustava

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Nedavna eksperimentalna istraživanja efekata spinske polarizacije jezgri kod ciklopropanskih derivata dali su značajne informacije o strukturi i raspodjeli kako spinske tako i ukupne elektronske gustoće za tu skupinu kationskih radikala. U radu se razmatra proširenje perturbacijske MO-teorije homokonjugacije na spomenute sustave. Svrha rada je dvojaka: prije svega žele se interpretirati spomenuti eksperimentalni rezultati, a zatim se analizom rezultata teorijskog modela nastoje izvesti općenitiji zaključci s pomoću kojih bi se mogla predvidjeti struktura ostalih tipova ciklopropanskih derivata.

Struktura opaženih radikal-kationa difenilciklopropana, trimetilciklopropana i benzonorkaradiena racionalizirane su s pomoću upotrijebljenoga teorijskog modela, a strukture spirociklopropanfluorena i vicinalno supstituiranih ciklopolien-ciklopropanskih radikal-kationa teorijski su predviđene.