

Quantum Chemical Investigation of the Electron Structure, Physical Properties and the Reactivity of π -Electron Molecules in Excited Singlet and Triplet States

VI. Electron Structure and Dipole Moments in Excited States of Nonalternant Hydrocarbons

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Received March 27, 1970/September 29, 1970

Investigations by the method of limited configuration interaction (ASMO–CI) upon some classes of nonalternant hydrocarbons show that the excitation of the molecules to the fluorescent and to some higher singlet and triplet states is accompanied with considerable intramolecular charge transfer leading to recharge of the cycles with an odd number of carbon atoms. It is shown that the change of the dipole moments and of some values $|L|$ characterizing the electron structure in transition from ground to fluorescent state $|\Delta L^F|$, respectively from ground to phosphorescent state $|\Delta L^T|$, satisfy the inequalities:

$$|\Delta L^F| > |\Delta L^T|.$$

It follows that the fluorescent state differs more from the ground state in its electron structure and physical properties than does the phosphorescent state.

Die mit der Methode der begrenzten Konfigurationenwechselwirkung (ASMO–CI) für einige Klassen nichtalternierender Kohlenwasserstoffe durchgeführten Untersuchungen zeigen, daß die Anregung der Moleküle in den Fluoreszenz- sowie in einigen Singulett- und Triplettzuständen mit einer beträchtlichen intramolekularen Ladungsübertragung verbunden ist, die zur Umladung der Ringe mit ungerader Anzahl von Kohlenstoffatomen führt. Es wird gezeigt, daß die Veränderung der Dipolmomente und einiger die Elektronenstruktur kennzeichnenden Größen $|L|$ beim Übergang vom Grund- zum Fluoreszenzzustand $|\Delta L^F|$ bzw. vom Grund- zum Phosphoreszenzzustand $|\Delta L^T|$ folgende Ungleichungen erfüllen:

$$|\Delta L^F| > |\Delta L^T|.$$

Daraus folgt, daß der Fluoreszenzzustand seiner Elektronenstruktur und seinen physikalischen Eigenschaften nach sich vom Grundzustand mehr unterscheidet als dies beim Phosphoreszenzzustand der Fall ist.

Les calculs, effectués par la méthode de l'interaction de configuration limitée (ASMO–CI) pour quelques catégories d'hydrocarbures nonalternants ont montré que l'excitation des molécules jusqu'à l'état de fluorescence et certains états supérieurs singlets et triplets est liée à un transfert intramoléculaire de charges considérable, qui provoque un changement du signe de la charge des anneaux au nombre impair des atomes de carbone. On a montré que les variations des moments dipolaires et de quelques grandeurs $|L|$ caractérisant la structure électronique, accompagnant les transitions depuis l'état fondamental aux états respectivement de fluorescence $|\Delta L^F|$ et de phosphorescence $|\Delta L^T|$ doivent satisfaire à l'inégalité:

$$|\Delta L^F| > |\Delta L^T|.$$

Cela veut dire que la différence dans la structure électronique et les propriétés physiques entre l'état de fluorescence et l'état fondamental est plus grande que celle entre l'état de phosphorescence et l'état fondamental.

Introduction

The electron charge distribution in the nonalternant hydrocarbons is one of their basic structural characteristics. The theoretical study of its change in the excited molecules and the related change of the values characterizing the electron structure and the physical properties, for example, the dipole moments, is one of the ways to obtain the necessary information from which general rules can be drawn, characterizing the molecular structure in excited states. This is the main purpose of the present paper.

The monocyclic hydrocarbons with an odd number of carbon atoms are stable as ions, as all of them containing $3 + 4n$ atoms exist as cations (class *K*), while those containing $5 + 4n$ atoms (class *A*) exist as anions ($n = 0, 1, 2, \dots$). This ability of the cycles of both classes to exist as ions remains also in anelation or substitution, e.g. in the phenylcyclopropyl cation or the benzocyclopentadienyl anion.

In hydrocarbons with an even number of carbon atoms, containing cycles with an odd number of carbon atoms, the electron charge distributes so that the cycles of class *K* "charge" positively and the cycles of class *A* negatively (Fig. 1).

If the total electron charge of a given cycle containing p atoms is marked with

$$\xi_p = \sum_{v=1}^p q_v,$$

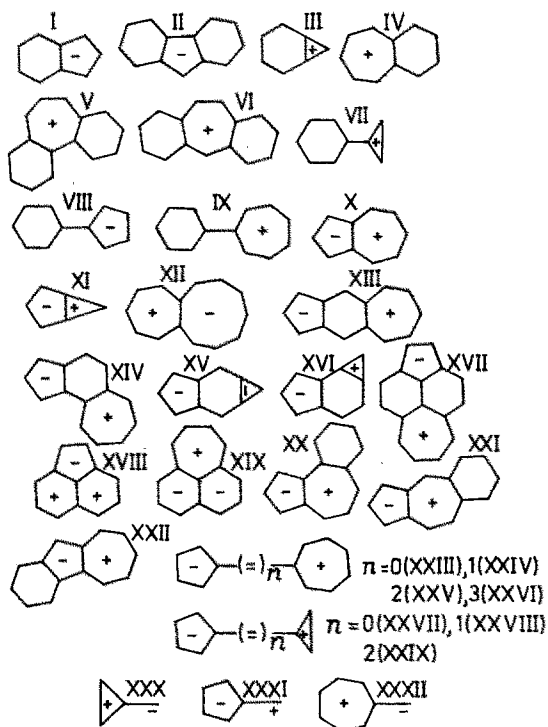


Fig. 1.

where q_v is the electron charge of the v atom, then in the cycles of class A

$$\xi_p > p$$

while in the cycles of class K (Tables 1, 2, 3)

$$\xi_p < p.$$

This property is a structural characteristic of the nonalternant hydrocarbons in the ground state.

The investigations in the present paper are carried out on the molecules given in Fig. 1 where the electron charge distribution in the cycles in the ground state is marked with (+) and (-).

Method

The investigations were carried out by the method of limited configuration interaction in the Pariser-Parr-Pople approximation [6]. For molecules containing up to 10 atoms the configuration interaction includes all monoexcited singlet-respectively triplet-configurations and for the rest of the compounds the first 25 configurations arranged by rising order of the values of the corresponding diagonal matrix elements of the energetic CI matrix. SCF-MO's as well as Hückel's MO's were used as basic function for all molecules.

For all compounds, except fulvene, heptafulvene, compounds VII-IX and the compounds from lines XXIII-XXIX, an ideal geometry is chosen-regular polygons with a side 1.397 Å. The angles of the five-atomic cycles in acenaphthilene and aceplayadilene (XVIII and XVII) are simply defined by the angles of regular benzene cycles while the angles of five-atomic cycles in compounds of the lines XXIII-XXVI are shown in Fig. 2. In compounds VIII and XXVII-XXIX the angle of the five-atomic cycles at the tertiary carbon atom is equal to 105° . The geometry of the seven-atomic cycles in playadylene (XIX) and aceplayadilene (XVII) as well as the seven-atomic cycles in the compounds XXIII-XXVI is determined by the angles shown in Fig. 2. Configuration "all trans" with valence angles \sphericalangle CCC equal to 120° is accepted for the polyene chain of compounds XXIII-XXIX. Geometry is accepted for fulvene (XXXI) and heptafulvene (XXXII) according to papers [10] and [1].

Since the geometry of compounds XXIII-XXIX as well as of compounds VII-IX is not known and the considerable alternation in the length of the chain strongly influenced on the results, the calculation in these compounds are carried out by the SC-procedure.

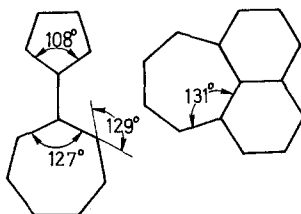


Fig. 2. Angles determining the geometry of the five- and seven-membered rings

SCF-MO as well as HMO-CI calculations are carried out in the first iteration step with an ideal geometry with a length of all bonds 1.397 Å. In every following iteration of the SC procedure, the bond lengths are calculated by the formula of Coulson Golebiewski [2] and the resonance integrals by the formula $\beta^{\text{core}} = \beta^0 \frac{S}{S_0}$ where S_0 is the overlap integral at $R = 1.397$ Å (calculated by effective charge of C atom $z_c = 3.18$). After the third iteration step the change in the lengths and in the bond orders is quite small ($|\Delta p| < 0.01$). All data for compounds given below are obtained after the third procedure.

The electron interaction integrals were calculated by the Mataga-Nishimoto approximation [4]: $\gamma = e^2 (1.328 + R)^{-1}$ eV as well as by the approximation [12]: $\gamma = e^2 (1.328 + 0.5 R)^{-1}$ eV by means of which more correct and closer to the experiment values are obtained for the energies of the triplet transition in the hydrocarbons.

In the Mataga-Nishimoto approximation the value of β^{core} at $R = 1.397$ Å is -2.318 eV [3] and -2.47 eV in approximation [12] (also at $R = 1.397$ Å).

All compounds were calculated by the four variations of the CI-method. All results and conclusions are qualitatively the same, i.e. they do not depend on the method and the approximation used for the γ -integrals. That is why, the tables contain only the results obtained with the SCF-CI methods and the Mataga-Nishimoto [4] approximation for the γ -integrals.

Spectra

The energies of the singlet transitions for the compounds studied by us for which experimental values are known, have been investigated by Koutecky and co-workers [3] (by the HMO-CI-method but with a strongly limited configuration

Table 1. Change of the quantities characterising the electron structure and of the dipole moments by excitation of nonalternant hydrocarbons, containing a cycle with an odd number of atoms

Molecule	ΔE^V	ΔE^T	μ^{0a}	μ^V	μ^T	Q^0	Q^V	Q^T	ξ^{0b}	ξ^V	ξ^T
I	3.389	2.157	0	6.95	1.94	0.500	0.686	0.500	5.705	5.136	5.520
II	2.889	1.910	0	2.46	1.71	0.500	0.319	0.460	5.483	4.931	5.287
III	3.942	2.118	1.49	7.57	2.16	0.500	0.680	0.500	2.357	2.845	2.378
IV	3.026	1.877	0	7.32	1.73	0.500	0.509	0.500	6.249	6.770	6.427
V	2.869	1.913	0	6.82	1.94	0.500	0.623	0.541	6.419	6.978	6.638
VI	2.746	1.600	0	1.65	2.20	0.500	0.604	0.455	6.446	6.830	6.665
VII	3.690	2.516	0	8.62	3.50	0.584	0.688	0.522	2.194	2.762	2.486
VIII	3.512	2.323	0	12.22	4.86	0.566	0.696	0.566	5.838	5.158	5.512
IX	3.250	2.257	0	10.11	5.44	0.557	0.668	0.588	6.132	6.649	6.471
XVIII	2.774	1.273	1.26	- 3.14	- 1.08	0.180	0.465	0.130	5.152	4.676	4.904
XIX	2.392	0.869	1.18	- 4.34	- 0.95	0.129	0.371	0.104	6.889	7.324	7.088
XXX	3.987	1.787	2.23	- 6.52	- 2.02	0.182	0.650	0.182	2.818	3.385	3.136
XXXI	3.255	1.259	1.28	- 5.17	- 1.22	0.104	0.504	0.115	5.097	4.645	4.890
XXXII	3.245	1.324	0.76	- 5.08	- 1.03	0.062	0.403	0.091	6.947	7.295	7.080

^a Since the dipole moment of the ions depends on the choice of the coordinate system, it is chosen so that in ground state the dipole moment is equal to zero.

^b The total charges ξ refer to the cycles with odd number atoms.

interaction). The results obtained by us for the energies of the singlet transitions differ but not insignificantly from the results of the work of Koutecky. Considerably better results are obtained for fulvene and heptafulvene which are calculated in this paper by real geometry while in the work of Koutecky an ideal geometry is used.

The phenyltropylium cation, investigated by Straub [11] and the sesquifulvalene (XXIII), investigated by Nakajima [5] by the SCF-MO-method, have not been investigated in the work of Koutecky [6]. The calculated energies for the singlet transitions in the phenyltropylium cation do not differ from these obtained in the work of Straub [11].

The first calculated intensive transition in sesquifulvalene is $\Delta E^V = 3.049$ eV with an oscillator strength 0.427. The experimental value is: $\Delta E_{\text{exp}}^V = 3.07$ eV [7].

Dipole Moments

The excitation of the molecule leads to a considerable change in the dipole moments in size and direction.

For the π -electron components of the dipole moments in the ground (μ^0), fluorescent (μ^V) and phosphorescent (μ^T) states in all compounds the following inequality is valid (see Tables 1, 2, 3)

$$|\mu^V - \mu^0| = |\Delta\mu^V| > |\Delta\mu^T| = |\mu^T - \mu^0|$$

i.e. the change of the dipole moment in the phosphorescent state is smaller than its change in the fluorescent state.

In almost all compounds the inequality

$$\mu^V > \mu^T$$

is fulfilled.

This dependence is less general than the one established in the heterocyclic compounds [13] and in the substituted hydrocarbons [14] where a still more general dependence is valid:

$$\mu^V > \mu^T > \mu^0.$$

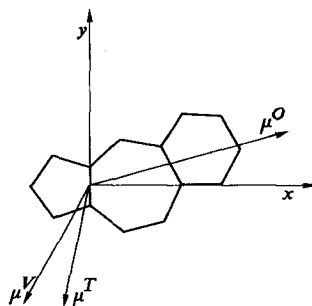


Fig. 3. Direction of π -components of dipole moments in 4,5-benzazulene in ground (μ^0), fluorescent (μ^V) and phosphorescent (μ^T) states

If we denote with α^T and α^V the angles between the dipole moments in the ground, the phosphorescent and the fluorescent state respectively, then in the asymmetric molecules

$$\alpha^V > \alpha^T$$

as α^V and α^T are read off in one and the same direction and for α^V is always being chosen as the angle smaller than π . It is shown as an example in Fig. 3 with the molecule of 4,5-benzazulene. In the case of molecules with C_{2v} symmetry the dipole moment changes its direction in the fluorescent state as a rule. In azulene this has been shown experimentally by Robertson, King, and Weigang [8].

Nonalternancy Index

A general characteristic expressing the degree of irregularity of the electron density distribution in the molecule, is the nonalternancy index:

$$Q = \frac{1}{2} \sum_v |1 - q_v|.$$

The molecular excitation is also connected with the change of the nonalternancy index and the indices of nonalternancy in the ground (Q^0), fluorescent (Q^V) and phosphorescent (Q^T) states satisfy the inequality:

$$|Q^V - Q^0| > |Q^T - Q^0|$$

or the inequality:

$$Q^V > Q^T > Q^0.$$

An exception from the above dependences are the molecules where cycles of an odd number of atoms (X, XI, XII) are condensed fast by and some molecules with a three-atomic condensed cycle (XV, XVI).

Intramolecular Charge Transfer

The molecular excitation is always accompanied by intramolecular charge transfer from one cycle to another. The charge migration can be expressed quantitatively by the total charges of the cycles $|\xi|$.

It is seen from Tables 1, 2, 3 where the total charges of the cycles with an odd number of atoms are given in ground (ξ^0), fluorescent (ξ^V) and phosphorescent (ξ^T) states, that the inequality.

$$|\xi^V - \xi^0| = |\Delta \xi^V| > |\Delta \xi^T| = |\xi^T - \xi^0|$$

is fulfilled in all cases, i.e. the charge of the total charge of a given cycle in transition from ground to fluorescent state is greater than in excitation to phosphorescent state.

In excitation of ions of hydrocarbons containing one cycle with an odd number of atoms, charge transfer takes place from the cycle with an odd number of atoms toward the cycles with an even number of atoms (benzene rings). In the

Table 2. Change of the quantities characterising the electron structure and of the dipole moments by excitation of nonalternant hydrocarbons, containing two cycles with odd number atoms with symmetry C_{2V}

Molecule	X	XI	XII	XIII	XV	XVII	XXIII	XXVII
ΔE^V	1.952	3.176	1.341	0.639	1.132	2.703	2.524	3.221
ΔE^T	1.485	2.488	1.024	0.333	0.582	1.631	1.181	1.541
μ^0	3.20	2.67	3.68	7.71	6.79	3.38	6.12	6.99
μ^V	-2.23	-2.78	-2.83	-2.82	-1.88	-1.65	-5.17	-2.15
μ^T	-0.30	-2.12	-2.10	-1.37	-0.10	0.09	2.22	2.23
Q^0	0.293	0.288	0.304	0.401	0.382	0.328	0.336	0.448
Q^V	0.445	0.470	0.457	0.329	0.416	0.193	0.552	0.548
Q^T	0.166	0.501	0.549	0.352	0.431	0.227	0.459	0.299
ξ_i^0 ^a	5.254	2.732	6.759	5.310	5.283	5.224	5.336	2.552
ξ_i^V	4.826	3.199	7.158	4.935	4.871	5.030	4.762	3.192
ξ_i^T	5.031	3.141	7.108	5.003	4.986	5.095	5.099	2.892
ξ_k^0 ^b	6.780	5.178	9.223	6.716	2.669	6.787	6.664	5.448
ξ_k^V	7.220	4.655	8.819	7.140	2.944	7.056	7.238	4.808
ξ_k^T	6.949	4.672	8.849	7.071	2.850	6.990	6.901	5.108

^a The index i notes the cycle with less number C atoms.^b The index k notes the cycle with bigger number C atoms.

Table 3. Change of the quantities characterising the electronic structure and of the dipole moments by excitation of nonalternant hydrocarbons containing two cycles with odd number atoms

Molecule	XIV	XVI	XX	XXI	XXII	XXIV	XXV	XXVI	XXVIII	XXIX
ΔE^V	1.784	2.538	1.789	1.910	1.770	2.456	2.433	2.241	2.738	2.583
ΔE^T	0.727	1.183	1.217	1.120	1.089	0.892	0.830	0.703	1.072	0.998
μ^0	6.28	5.39	3.40	3.32	3.39	6.65	7.30	8.97	8.70	9.92
μ^V	1.48	1.65	3.62	3.13	3.77	5.46	4.65	17.30	2.52	2.65
μ^T	0.73	0.52	3.00	2.07	2.07	4.40	6.17	8.08	5.31	8.43
Q^0	0.475	0.538	0.296	0.289	0.263	0.328	0.336	0.391	0.475	0.504
Q^V	0.193	0.302	0.456	0.456	0.463	0.583	0.604	0.436	0.674	0.732
Q^T	0.227	0.254	0.412	0.278	0.303	0.348	0.314	0.318	0.376	0.402
ξ_i^0	5.378	5.411	5.256	5.236	5.180	5.252	5.220	5.236	2.609	2.673
ξ_i^V	4.931	4.933	4.791	4.853	4.854	4.979	5.114	5.327	3.301	2.770
ξ_i^T	4.979	5.059	4.820	4.937	4.935	5.146	5.172	5.201	2.893	2.729
ξ_k^0	6.624	2.580	6.824	6.846	6.790	6.772	6.815	6.812	5.391	5.273
ξ_k^V	7.095	2.954	7.211	7.170	7.247	7.315	7.318	6.718	4.699	4.657
ξ_k^T	7.038	2.878	7.184	7.054	7.158	6.899	6.874	6.861	5.107	5.158
α^V	164°	100°	161°30'	176°	157°40'	178°54'	175°40'	9°24'	172°	176°
α^T	174°	30°	155°	172°	166°15'	6°40'	6°	5°30'	5°	9°
$ \Delta\mu^V $	7.71	5.91	6.93	6.45	7.02	11.94	11.93	9.09	11.20	12.56
$ \Delta\mu^T $	7.00	4.93	6.25	5.39	5.42	2.53	1.33	1.20	3.45	2.10

fluorescent state this transfer is so essential that for the ions the charge (positive or negative) localize in the benzene cycle.

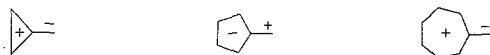
For example, in the benzocyclopentadienyl anion(I) the negative charge in the ground state is practically localized in the five-atomic ring and in the fluorescent state it is practically in the six-atomic cycle (Table 1).

In the ground state the five-atomic cycle in the acenaphthilene (XVIII) is negatively charged (class A) and the seven-atomic cycle in the playadilene (XIX)

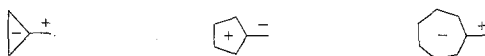
positively (class *K*). In the fluorescent state the five-atomic cycle of the acenaphthilene is positively charged and the seven-atomic cycle of the playadilene negatively (Table 1).

In the compounds containing two cycles with an odd number of atoms, the excitation of fluorescent state also leads to recharge of the cycles, e.g. in azulene or sesquifulvene (Tables 2, 3).

The methylenecyclopropene, fulvene and heptafulvene where the charge in ground state is distributed in the following way:



the excitation to fluorescent and phosphorescent states leads to recharge of the cycles:



The excitation of molecules and ions to the phosphorescent state is also accompanied with a considerable charge transfer taking place in all cases in the same direction as in the excitation to the fluorescent state but not always leading to recharge of the cycles.

The molecules' excitation to higher singlet and triplet states is also accompanied by intramolecular charge transfer, change of the dipole moments and the values Q and ξ but there exists no dependence between the extent of this transfer, the energy of the transitions and the oscillator strength.

Discussion

The ability of the monocyclic hydrocarbons with an odd number of atoms to exist as ions and to localize charge in the cycles with an odd number of atoms – positive in the cycles of class *K* and negative in the cycles of class *A* – is a structural characteristic of the nonalternant hydrocarbons in the ground state.

The charge localization in the benzene rings in excited states of the benzocondensed and of the aryl-substituted monocyclic ions and the change of the sign of the charges in the cycles with an odd number of atoms in the nonalternant hydrocarbons may be considered as a common structural characteristic of their excited fluorescent state. The phosphorescent state in which the tendency for the intramolecular charge transfer is the same as in the fluorescent but is quantitatively more weakly expressed $|\Delta\xi^V| > |\Delta\xi^T|$ and does not lead to a recharge in all cases. It lies in the intermediate position between the ground and the fluorescent state.

This qualitative conclusion is juxtaposed with the inequalities where quantitative values characterizing the electron structure are compared

$$\begin{aligned} |\Delta\mu^V| &> |\Delta\mu^T|, \\ |\Delta\xi^V| &> |\Delta\xi^T|, \\ |\Delta Q^V| &> |\Delta Q^T|; \quad Q^V > Q^T > Q^0, \\ \alpha^V &> \alpha^T \end{aligned}$$

and with the inequality

$$\Delta E^V > \Delta E^T,$$

which follows from the self-consistent field theory [9] as well as with the inequality:

$$\tau^0 > \tau^T > \tau^V,$$

where τ is the lifetime of the ground (τ^0), the phosphorescent (τ^T) and the fluorescent (τ^V) states. It contributes to formulate the rule: the electronic structure and physical properties of nonalternant hydrocarbons in the phosphorescent state are closer to the ground state than are the properties of the fluorescent state to the ground state.

A similar conclusion was made for some derivatives of hydrocarbons [14] and heterocyclic compounds [13].

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