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Structure and Energy Spectra of Non-Alternant Analogues of the Di- and Triphenylmethine Radicals and their Ions

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Dedicated to Professor Dr Jürgen Fabian on the occasion of his 60th birthday

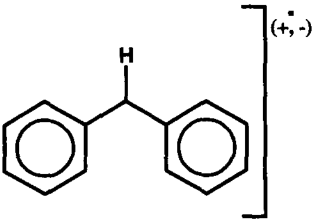
ABSTRACT

The results of a theoretical study of the structure and the energy spectra of iso-π-electronic non-alternant analogues (NA) of the di-and triphenylmethine radicals and their ions are presented. Based on the Sachs theorem, it is shown that the NA have also a non-bonding MO which is a characteristic feature of odd-alternant π-systems. The transition energies of the NA are similar to those of the corresponding di- and triphenylmethine species. The electron transitions of NA radicals are connected with a significant π-charge density redistribution and a change of the value and direction of the dipole moment. © 1997 Elsevier Science Ltd

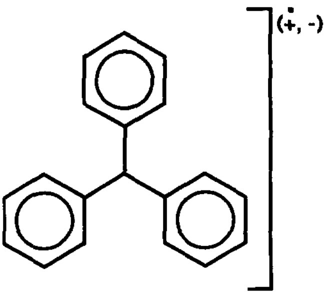
Keywords: non-alternant analogues of di- and triphenyl-methines, energy spectra, Sachs theorem, non-bonding MOs.

INTRODUCTION

The presence of a non-bonding MO (NBMO) in a molecular π-system is an important characteristic feature of its spectral properties (energy spectra). Typical examples are the diphenylmethine radicals (**Di**) and triphenylmethine radicals (**Tr**) and their ions, which are the basic chromophores of the large class of di- and triarylmethine dyes [1–3].



Di



Tr

The existence of an NBMO determines the general properties of the absorption spectra of the radicals, cations and anions of **Di** and **Tr**. The different charged ions $Ph_2CH^{+(-)}$ and also $Ph_3CH^{+(-)}$ absorb at similar wavelengths [1].

The **Di** and **Tr** are odd-alternant (non-Kekule) π-systems. The presence of NBMOs is caused by the topology of these systems, which follows from the Coulson–Rushbrooke Longuet-Higgins (CRLH) theorem [4–6].

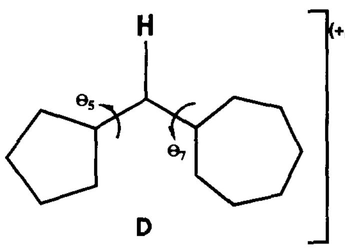
The CRLH theorem determines the structural principle of homonuclear odd-alternant Hückel π-systems which are characterized by NBMOs. This theorem provides a *sufficient* but not a *necessary* condition for the presence of NBMOs in homonuclear alternant systems. The CRLH theorem has been extended [7, 8] to some non-alternant and heteroatomic π-conjugated systems. This extended theorem formulates a more general, but again only a *sufficient* condition for the presence of NBMOs.

It does not predict all the possible π-systems having NBMOs. There exist many non-alternant and heteroatomic π-systems having NBMOs for which the conditions of the theorems [9] are not fulfilled.

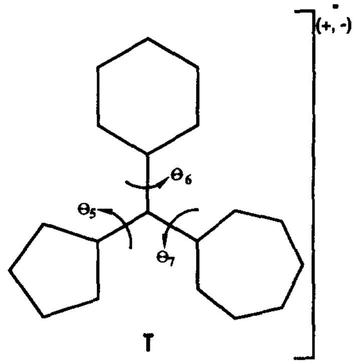
The aim of the present work is to extend the class of **Di** and **Tr** to a new family of iso-π-electronic non-alternant systems possessing NBMOs in the energy spectra, using the Sachs theorem [10]. These theoretical investigations may stimulate the synthesis of this type of organic colorants.

MODEL COMPOUNDS UNDER STUDY

The non-alternant hydrocarbon radicals **D** and **T** and their ions (iso-π-electronic with **Di** and **Tr** and their ions, respectively) have been investigated, (here and in the following structures only the σ-skeleton is given).

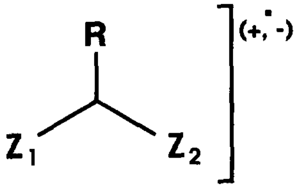


D



T

The general structure for which the Sachs theorem predicts the existence of a NBMO can be expressed by the graph (see Section 3)



where Z_1 and Z_2 are monocycles with an odd number of π-centers and $Z_1 + Z_2 = 4n$ (n = 2,3,...).

Most realistic species (systems) also with the chance of synthesis are the structures **D** and **T** which were investigated in this paper.

INVESTIGATION METHODS

Sachs theorem and its application

An alternative approach to solve the eigenvalue problem of a Hückel matrix **A** is the polynomial representation, which allows qualitative conclusions relating to the energy spectrum of a molecule to be derived. The characteristic polynomial of a conjugated π-system, in particular of a hydrocarbon with M π-centers is represented in eqn (1):

$$P_M(x) = \det |x\,\mathbf{I} - \mathbf{A}| = \sum_{m=0}^{M} a_m x^{M-m} \tag{1}$$

where **I** is the unity matrix. The MO energies e are coupled with the roots x by the relation: $x = (\alpha - e)/\beta$ (α and β are the Coulomb and resonance integrals, respectively; we choose the energy reference level $e_o = \alpha = 0$). If the free term in eqn (1) $a_M = 0$, then the molecule has at least one root $x = 0$ and $e(NBMO) = 0$. If a molecule has at least one NBMO, then $a_M = 0$. It follows that the necessary and sufficient condition for the existence of at least one NBMO is defined as in eqn (2):

$$a_M = 0 \tag{2}$$

According to the Sachs theorem [10], the value of $a_M = 0$ or $a_M \neq 0$ can be determined easily by means of eqn (3):

$$a_M = \sum_{s \in S_M} (-1)^{c(s)} \cdot 2^{r(s)} \tag{3}$$

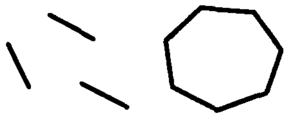
In eqn (3) S_M is the set of all Sachs subgraphs of **M** vertices, $c(s)$ is the number of components (connected parts) in the Sachs subgraphs, and $r(s)$ is the number of simple rings.

The components of a Sachs subgraph are either simple rings or two vertices connected by an edge (—).

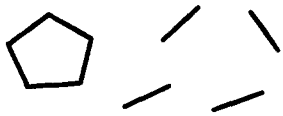
In accordance with eqn (3), the condition for the existence of a NBMO reads as in eqn (4):

$$a_M = \sum_{s \in S_M} (-1)^{c(s)} \cdot 2^{r(s)} = 0 \tag{4}$$

Let us consider the structure of **D**. There is a set of two subgraphs s_1 and s_2:



s_1, $c(s_1) = 4$



s_2, $c(s_2) = 5$

Because $c(s_1)$ and $c(s_2)$ are of different parity, it follows that:

$$a_M = (-1)^2.2 + (-1)^5.2 = 0$$

i.e. **D** has 1 NBMO. It is easy to show that **T** has also one NBMO.

Numerical methods

The molecular geometries were optimized in relation to their total energy by the semi-empirical all-valence electron method AM1 [11] using the program package Spartan [12]. Based on the optimized geometries, the excitation energies, oscillator strengths and the π-electron densities of the cationic and anionic forms were calculated by the Pariser Parr Pople (PPP) method in the π-electron approximation [13]. We used the CI expansion involving all single excited configurations of singlet (ionic species) and doublet (radicals) spin multiplicity. In the latter case, the method of Longuet-Higgins and Pople [14] and of Zahradnik and Carsky [15] was used.

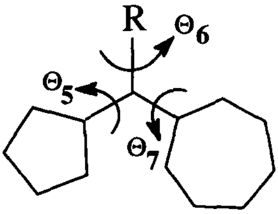
The dependence of the resonance integrals between neighbouring carbon atoms on the bond lengths R was calculated using Mulliken's formula [16] $\beta(R) = \beta_0 S(R)/S(R_0)$, where S is the overlap integral between 2pπ-2pπ AOs (calculated with $Z_c = 3.25$). For the two-center Coulomb repulsion integrals the Mataga–Nishimoto [17] potential was used.

NUMERICAL RESULTS AND DISCUSSION

Geometry

As in the case of **Di** and **Tr**, [18, 19] **D** and **T** and their ions have a propeller-shaped geometry; however the torsion angles of the five-, six- and seven-membered rings (given in Table 1) are different. The molecular geometry of the species **D** and **T** depends strongly on the total charge.

TABLE 1
Torsion Angles Θ_5, Θ_6 and Θ_7 (in degrees) of the Cations, Anions and Radicals of **D** and **T** Optimized Using the AM1 Method



Angle		D			T	
	Kation	Anion	Radical	Kation	Anion	Radical
Θ_5	4	13	8	3	20	11
Θ_7	41	9	24	49	11	38
Θ_6	—	—	—	57	77	43

The geometry of **D**, **T** and of the cationic forms $\mathbf{D}^+$, $\mathbf{T}^+$ is characterized by planar five-, six- and seven-membered rings and bond length alternation within the five-, and seven-membered rings. A fulvene-like structure within the five-membered ring is more marked than a heptafulvene-like structure in the seven-membered ring.

In the case of the cation $\mathbf{D}^+$, the bond lengths in the seven-membered ring are nearly equivalent, corresponding to an non-benzoid aromatic tropylium structure; the five-membered ring is characterized by a typical fulvenic structure with a marked bond length alternation. In all cases, the bond lengths within the phenyl residue are nearly equilised (between 1.39Å and 1.41Å).

In the case of the anions $\mathbf{D}^-$ and $\mathbf{T}^-$, the seven-membered ring is non-planar and has an envelope-like structure with a significant bond length alternation. A butadiene fragment is shifted out of the plane by about 20°. The bond alternation within the five-membered ring is significant, but strongly reduced in relation to those in the cations $\mathbf{D}^+$ and $\mathbf{T}^+$. A bond length equilization, typical for the non-benzoid aromatic cyclopentadienide anion, was not observed. Qualitatively, the same results have been obtained by means of the PM3 method [11, 12].

Excitation energies

In the simple Hückel approximation, the HOMO and LUMO are fourfold degenerate for $\mathbf{Tr}^{\cdot(+,-)}$ and triply degenerate for $\mathbf{Di}^{\cdot(+,-)}$ (see Fig. 1). If we

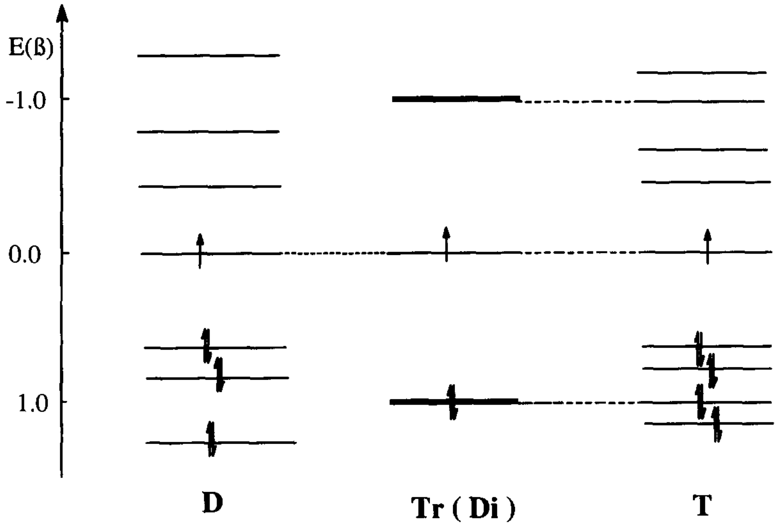


Fig. 1. Hückel frontier MOs of **Tr** and **Di** and of their non-alternant analogues **T** and **D**. The HOMO and LUMO are fourfold degenerate for **Tr** and triply degenerate for **D**.

assume C_3 symmetry for **Tr** and C_2 symmetry for **Di**, this picture is approximately true also in the PPP approach [20]. Because **T** and **D** and their ions belong to the symmetry group C_1, the degeneration of the frontier MOs is removed (Fig. 1). Therefore, in contrast to **Di** and **Tr**, the electron transitions of **D** and **T** are not degenerate.

In Tables 2 and 3 are collected the calculated values of the transition energies of the investigated π-systems.

The longest wavelength absorption maxima of di- and triphenylmethine cations are situated in the region between 400 nm and 440 nm [20, 22]. The calculated values of the 'color bands' (first intense absorption band) of the corresponding cations $\mathbf{D}^+$ and $\mathbf{T}^+$ lie in the same spectral region (see Tables 2 and 3).

The radical $\mathbf{Tr}^{\cdot}$ is characterized by a strong absorption band at 342 nm [23] (337 nm [24]) and a weaker absorption band at 511 nm [23] (514 nm [24]). The first intense transition of $\mathbf{Di}^{\cdot}$ lies at 336 nm [23]. The calculated values of the first intensive electron transitions are 440 nm for $\mathbf{D}^{\cdot}$ and 481 nm for $\mathbf{T}^{\cdot}$. The large difference in the geometry of the anionic forms $\mathbf{D}^-$ and $\mathbf{T}^-$ in comparison to the geometry of the corresponding cations $\mathbf{D}^+$ and $\mathbf{T}^+$ determines the substantial difference of the spectral features.

TABLE 2

Calculated Excitation Energies ΔE (in *nm*) and Oscillator Strengths *f* of the Radical **D** and the Ions $\mathbf{D}^+$ and $\mathbf{D}^-$; $|i \rightarrow j>$ is the Configuration with the Main Statistical Weight which Corresponds to the Excitation of an Electron from the i-th to the j-th MO and C is the Coefficient for the Configuration with Main Statistical Weight.

Kation			Anion			Radical		
ΔE	*f*	C |i→j>	ΔE	*f*	C |i→j>	ΔE	*f*	C |i→j>
591	0.002	0.92 |6→7>	903	0	0.97 |7→8>	1512	0	0.93 |7→8>
404	0.010	0.98 |6→8>	431	1.116	0.98 |7→9>	770	0	0.82 |6→7>
400	0.571	0.97 |5→7>	344	0.005	0.90 |6→8>	670	0.031	0.80 |7→9>
355	0.021	0.97 |5→8>	333	0.024	0.89 |6→9>	440	0.370	0.71 |5→7>
327	0.035	0.91 |6→9>	296	0.071	0.96 |5→8>	360	0.090	0.63 |7→10>

TABLE 3

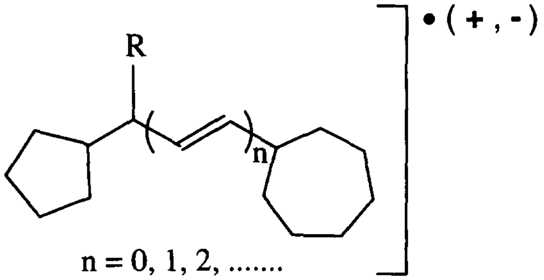
Calculated Excitation Energies ΔE (in *nm*) and Oscillator Strenghts *f* of the Radical **T** and the Ions $\mathbf{T}^+$ and $\mathbf{T}^-$

Kation			Anion			Radical		
ΔE	*f*	C |i→j>	ΔE	*f*	C |i→j>	ΔE	*f*	C |i→j>
574	0.002	0.92 |9→10>	880	0	0.97 |10→11>	2531	0	0.98 |10→11>
462	0.220	0.97 |8→10>	458	0.545	0.99 |10→12>	1000	0	0.85 |9→10>
424	0	0.95 |9→11>	421	0.003	0.99 |10→13>	756	0.075	0.86 |10→12>
414	0.005	0.93 |8→11>	417	0.45	0.98 |10→14>	481	0.353	0.74 |8→10>
395	0	0.99 |7→10>	357	0.009	0.79 |9→11>	411	0.032	0.86 |9→12>

Assuming planar five-, six- and seven-membered rings and all torsion angles $\Theta_5 = (\Theta_6) = \Theta_7$ equal to 30^0 for $\mathbf{D}^-$ and $\mathbf{T}^-$, nearly the same results were obtained for the excitation energies in comparison to $\mathbf{D}^+$ and $\mathbf{T}^+$, respectively.

Because $\mathbf{D}^{\cdot}$ and $\mathbf{T}^{\cdot}$ are non-alternant systems, the π-electron net charges q of the carbon atoms are different from zero. The electron transitions are connected with a significant charge density redistribution and a change of the value and direction of the dipole moment. The π-electron component of the dipole moment of $\mathbf{D}^{\cdot}$ in the ground state is 3.5 Debye (D) and in the first excited singlet state 2.1 D. The angle between the dipoles in the ground and excited state is $\phi = 16^\circ$. The π-electron component of the dipole moment of $\mathbf{T}^{\cdot}$ in the ground state is 4.6 D, and in the first excited singlet state 2.3 D, with $\phi = 41^\circ$.

In this paper, only the parent systems $\mathbf{D}^{\cdot(+\text{ or }-)}$ and $\mathbf{T}^{\cdot(+\text{ or }-)}$ have been considered. As in the case of di- and tri-arylmethine dyes, the subgroups **D** and **T** could be extended to the series **E**:



E

where **R** is H or an arbitrary alternant system with an even number of π-centers, e.g. 1(2)-naphtyl, 9-anthryl. It can easily be shown that the condition for the existence of an NBMO [eqn (4)] is satisfied for all π-systems **E**, i.e. they have one NBMO.

Substitution of a hydrogen atom in the participating aryl residue **R** (in the cationic form) by a heteroatomic group X (e.g. NMe_2 or OMe) or in the anionic form by oxygen leads to the substituted dyes. As in the case of substituted di- and tri-arylmethine dyes [1], a significant bathochromic shift can be expected for potentially synthesized non-alternant analogues of the arylmethine dyes.

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