Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Tatsuya Tachikawa, Kimihiro Hiruta, Sumio Tokita & Kichisuke Nishimoto (2000): PPP Molecular Orbital Calculations of Polyenyl Cations and their Analogs using New-γ and Pseudo Atom Modeling, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 345:1, 63-68

To link to this article: http://dx.doi.org/10.1080/10587250008023896

Mol. Cryst. and Liq. Cryst., 2000, Vol. 345, pp. 63-68
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PPP Molecular Orbital Calculations of Polyenyl Cations and their Analogs using New-γ and Pseudo Atom Modeling

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The first absorption bands of the tetramethyl polyenyl cations were calculated by the Pariser-Parr-Pople molecular orbital method. By considering the extraordinary hyperconjugation effect of methyl substituents and using the new-γ, the calculated absorption wavelengths reproduce well the observed ones.

Keywords: PPP MO Calculations; New-γ; Polyenyl Cation; First Absorption band; Hyperconjugation

INTRODUCTION

Semi-empirical Pariser-Parr-Pople molecular orbital (PPP MO) calculations are often useful for the prediction of the color of the organic compounds [1,2]. However, the calculated wavelengths of the absorption maxima are often shorter than the observed ones for the large π-conjugated systems. Cyanine dyes indicated the tendency and we have called such compounds to be spectrochemically soft compounds [2,3]. The compounds such as simple polyenes showed the calculated wavelengths to be longer than the observed ones. We have called them to be spectrochemically hard compounds [2]. In order

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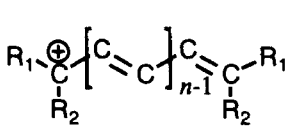
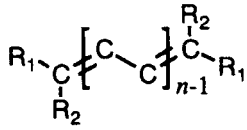
to improve these tendencies, a novel two center electron repulsion integral new-γ was proposed. New-γ takes into account the spectrochemical softness (SCS) of the π-conjugated system as a parameter [2]. The usefulness of the new-γ was confirmed by the calculations of the excitation energies of the *p*-band of the polycyclic aromatic hydrocarbons[4] and those of the first absorption band of linear *para*-acenoquinones [5]. We introduced the new- γ to the calculation of polyenyl cations.

In the conventional PPP MO calculations, only π-conjugated planar systems are taken into considerations. For example, methyl substituents are ignored for the calculation of the tetramethyl derivatives of polyenyl cations (**1c**). **1c** are considered to be **1a**, which have no methyl substituents. The observed wavelengths are not reproduced by such conventional calculations. The methyl substituents gave large bathochromic shifts in the absorption spectra for **1c**, which are larger than those of neutral systems, as mentioned in the latter section. The pseudo atom model was proposed especially for the elucidation of hyperconjugation effects by Mulliken [6], and are often considered for the HMO [7] or semi-empirical MO [8] calculations of compounds possessing methyl substituents.



1a) $R_1=R_2=H$
1b) $R_1=Me$, $R_2=H$
1c) $R_1=R_2=Me$



2a) $R_1=R_2=H$
2b) $R_1=Me$, $R_2=H$
2c) $R_1=R_2=Me$

In this paper, practical PPP MO calculations of the tetramethyl polyenyl cations (**1c**) are performed with the consideration of the hyperconjugation effects of methyl substituents as the pseudo atom model and using the new-γ. We investigate their reproduction of the

energies of the first absorption bands comparing with the calculations of simple polyenes (**2a**), which are typical members of liner π-conjugated compounds.

MO CALCULATIONS

PPP MO calculations were performed with a computer software PPP-PC [9], in which variable β approximation [10] was used. Bond length of 1.40 Å and the bond angle of 120° were used for the input molecular geometry, respectively, because the molecular geometry is modified with the progress of the SCF calculations. Methyl substituents were treated as pseudo atoms. Atomic parameters used for calculations are shown in TABLE 1 [9]. Valence state ionization potential (VSIP) I_r of methyl substituents was determined to be 23.88 eV, which is the second ionization potential, because core charge of methyl substituents is considered to be 2 in the pseudo atom modeling. Twenty five lower singly excited configurations in the CI calculations were considered.

Atom	I_r	γ_{rr}	Core Charge
C	11.16	11.13	1
Me	23.88	11.13	2

TABLE 1 Ionization potential (I_r /eV), one-center electron repulsion integral (γ_{rr} /eV), and core charge values.

For the two-center electron repulsion integral γ_{rs} in the variable γ method [11], the following new-γ was used [2]:

$$\gamma_{rs} = e^2/(R_{rs}+ka_{rs}) \quad (1)$$

where R_{rs} is the interatomic distance (in Å) between the r-th and s-th atoms in a π-conjugated system; a_{rs} is given by

$$a_{rs} = 2e^2/(I_r-A_s+I_s-A_r) \quad (2)$$

where e^2 is 14.397 eV·Å, I_r [I_s] and A_r [A_s] are VSIP and the valence state electron affinity, respectively. Parameter k is a relative magnitude of dynamical π-electron polarizability at the region between r-th and s-th atoms. Namely, k shows the SCS of π-electrons. When the value of k is 1.0, the new-γ is equivalent to the conventional Nishimoto·Mataga-γ (N·M-γ) function [11]. In other words, the N·M-γ is contained as the special case in the new-γ. Large k values are suitable for spectrochemically soft compounds, and small k values are suitable for spectrochemically hard ones [2].

The observed wavelengths are referred as it is, because the solvent effects to the compounds treated in this paper are certainly small.

RESULTS AND DISCUSSION

The wavelengths of the first absorption band of polyenes (**2a**) were calculated using the new-γ with some k values of 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0, respectively. The calculated wavelengths using k=0.6 reproduce well the observed ones (measured in isooctane [12]). The result is supported by the statistical parameters such as correlation coefficients and standard deviations. This result shows **2a** are relatively spectrochemically hard compounds. The calculated wavelengths of the first absorption band of dimethyl polyenes (**2b**) using the new-γ (k=0.6) also reproduced well the observed ones (measured in methanol, ethanol or chloroform [13]). The wavelengths of bathochromic shift by the substitution of a hydrogen atom with a methyl substituent are about 5nm, which coincided with Fieser's rule.

On the other hand, k=1.0 in the new-γ was suitable for the calculations of the wavelengths of the first absorption band (measured in 96 % or 80 % H_2SO_4 [14]) of tetramethyl polyenyl cations (**1c**) as shown in FIGURE 2. **1c** are considered to be spectrochemically softer compounds than polyenes (**2a**) by comparison of k value. **1c** have a charge resonance π-conjugated system and the π-electrons can move

almost freely in the molecular framework.

The wavelengths of the first absorption band of non-substituted polyenyl cations (**1a**) were calculated. Their absorption spectra have not been reported. The wavelengths of bathochromic shift per one methyl substituent are thought to be larger than 5nm in the case of **1c**. The hyperconjugation effect of methyl groups in **1c** considered to be extraordinary stronger than polyene.

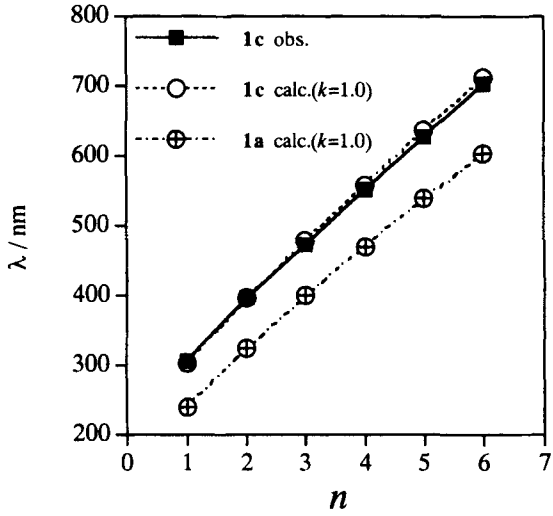


FIGURE 2 The observed and calculated wavelengths of the tetramethyl polyenyl cations (**1c**) and non-substituted polyenyl cations (**1a**).

The calculated bond lengths in the ground state of **1c** (n=3) showed the polyenic C-C bond lengths are 1.39, 1.40 or 1.41 Å, which indicate the bond alternations in **1c** are very little. This result supports the π-conjugated systems of **1c** are spectrochemically soft systems.

CONCLUSION

The new-γ and pseudo atom modeling of the methyl substituents were

utilized to the PPP MO calculations of the polyenyl cations (**1a-c**) and polyenes (**2a-c**). The calculated wavelengths of the absorption maxima of polyenyl cations well reproduce the experimental values when k = 1.0 was used. On the other hands, calculated wavelengths of the absorption maxima of polyenes well reproduced the observed values when k = 0.6 was used. The results coincide with the prediction that the polyenyl cations are spectrochemically softer than the polyenes. The application of the pseudo atom modeling to the methyl substituted compounds revealed to reproduce well the observed wavelengths for the polyenyl cations.

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