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The Electronic Spectra of 1, 1′-Dianthrylpoly-ynes[1)]

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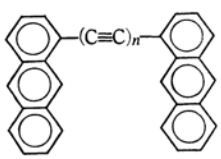
The electronic spectra of 1, 1′-dianthrylpoly-ynes have been studied by Hückel MO theory on the basis on various approximations for resonance integrals. A good agreement between theoretical and experimental values is obtained from a modified bond-alternation approximation. This result shows that the contribution of a cumulene-type ionic structure to the ground state of the molecule increases with an increase in the number of the triple bonds.

Recently, two of the present authors (S. A. and M. N.)[2)] found a peculiar spectral shift in the electronic absorption spectra of 1, 1′-dianthrylpoly-ynes (I). In this series, the maxima of the longest wave length absorptions increase linearly with the square of the number of the triple bonds. This fact forms a striking contrast to a well-known spectral shift in the series of linear polyenes or linear poly-ynes, in which the square of the absorption maxima, λ^2_{max}, varies linearly with the number of the conjugated multiple bonds.[3,4)] In order to elucidate this interesting spectral shift, we have carried out some MO calculations of the electronic structure of 1, 1′-dianthrylpoly-ynes.



(I)

Calculation

The calculations were carried out in the framework of the Hückel MO theory. All interpretations of the spectra of polyenes by the wave-mechanical method have hitherto required that there should be an alternation of double and single

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bonds along the polyene chain.[5-9] This requirement is most important for the interpretation of the spectra of poly-ynes. It is, however, desirable to carry out calculations on the basis on the following approximations: All conventional Coulomb integrals are assigned the same value, α. According to the study by Hinze and Jaffe,[10] the valence-state electronegativity of the carbon π-orbital is practically independent of its hybridization, so the constant Coulomb integral approximation is reasonable. The resonance integral associated with the aromatic carbon-carbon bond is assigned a constant value, β. On the other hand, there is at present no definite method for the estimation of the resonance integrals associated with a triple and a single bond of the polyacetylene system. In this paper, the following approximations will tentatively be used;

I Constant β approximation

$$\beta_{C\equiv C} = \beta_{C\text{-}C} = 1.0\,\beta$$

II Bond alternation 1

$$\beta_{C\equiv C} = 1.1\,\beta,\ \beta_{C\text{-}C} = 0.9\,\beta$$

III Bond alternation 2

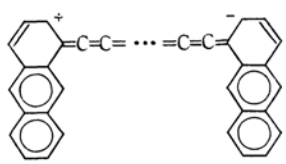
$$\beta_{C\equiv C} = 1.2\,\beta,\ \beta_{C\text{-}C} = 0.8\,\beta$$

IV Modified bond alternation

$$\beta_{C\equiv C} = (1 + 1/(n+4))\beta$$

$$\beta_{C\text{-}C} = (1 - 1/(n+4))\beta$$

Approximation I is most usual. Approximation II is suitable for polyenes.[11] The value of 1.2β in Approximation III was estimated for acetylene from an empirical relation.[12] Approximation IV is proposed with the following points in mind; for 1,1'-dianthrylpoly-yne, we can write down twenty-five cumulene-type ionic structures (II), in which the formal charges move in the anthracene nuclei:



(II)

In structure I, the bond alternation in poly-yne chain might be present. However, a rather uniform electron distribution may be expected in the cumulene chain in structure II. Therefore, the energy difference between the structure I and a given cumulene-type ionic structure may be given by;

$$\Delta E = I_C - A_C - n\Delta\gamma + C$$

where I_C and A_C are the ionization potential and the electron affinity of the carbon atom respectively. The core energy difference between the two structures is included in the correction term, C. $\Delta\gamma$ measures the energy difference between the electron repulsions in a classical triple bond, γ_t, and those in a cumulene-type bond, γ_c. It is natural that γ_t should be larger than γ_c, because in the classical triple bond the four electrons are packed in a small space. Therefore, the contributions of the cumulene-type ionic structures to the ground state of the molecule would increase with the number of the triple bonds, n, because the energy difference between the ionic and the non-ionic structures decreases with n. This situation might be characteristic of a poly-yne system. In order to take this situation into account, the values of $\beta_{C\equiv C}$ and $\beta_{C\text{-}C}$ are varied with n, The longest-wavelength absorption in anthracene is polarized in the direction of the molecular short axis (^1L_a species).[13] Similarly, the absorptions of poly-ynes are also polarized in this direction. It is, therefore, reasonable to assign the longest-wavelength absorption of 1,1'-dianthrylpoly-yne to the ^1L_a species. The absorption wavelengths of a conjugated system can be calculated by the Hückel MO theory, using very simple correlation equations.[12] The equation for the ^1L_a species is expressed by;

$$\lambda(^1L_a) = 474(\Delta m)^{-1/2} - 145\ m\mu$$

where $\lambda(^1L_a)$ is the absorption wavelength. Δm is the energy difference expressed in β between the highest-occupied and the lowest-vacant orbitals of the molecule. The calculated $\lambda(^1L_a)$'s for the various approximations are given in Table I and in Fig. 1, together with the experimental values.

Table I. Calculated and observed absorption wavelengths of 1,1'-dianthrylpoly-ynes

n	$\lambda(^1L_a)$ in mμ Approximation I	II	III	IV	Obs.[2]
1	490	468	430	430	—
2	531	466	427	437	428
3	573	476	424	449	437
4	616	486	421	465	450
5	658	495	419	483	466
6	699	503	418	503	487
7	—	—	416	525	—

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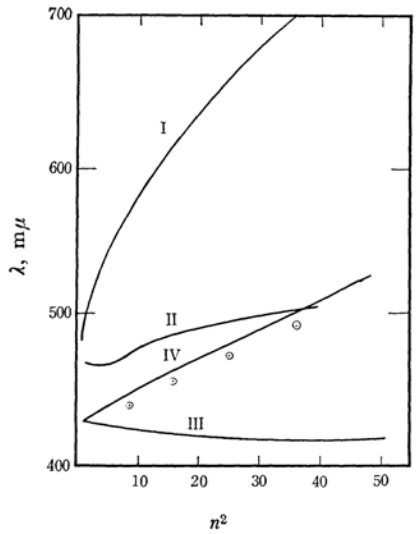

Fig. 1. The predicted and observed absorption wavelengths in the 1-1'-dianthrylpoly-ynes.

As Fig. 1 shows, the calculated results based on Approximation IV and the experimental data agree well. It should be noted that Approximation III leads to the very strange result that the $\lambda(^1L_a)$ value should decrease with n.

Conclusion

The present study has shown that the interpretation of the peculiar spectral shift in a series of 1, 1'-dianthrylpoly-ynes in the visible region requires a modified bond-alternation approximation which assumes that the contribution of cumulene-type ionic structures to the ground state of the molecule increases with an increase in the number of triple bonds. All other approximations give unsatisfactory results.

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