Theoret. Chim. Acta (Berl.) 36, 145—148 (1974)

Relationes

C.I. Calculations on the Lower Transitions in the Terphenyl and Quaterphenyl Di-Valent Ions

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Received May 22, 1974

Energies and transition dipole moments for the lower electronic transitions in the terphenyl and quaterphenyl di-valent ions have been calculated starting from the Pople SCF MO's for the ground state ions. The configuration interaction included about one-hundred singly and doubly excited configurations. The results of the calculations for the lower allowed electronic transitions are in very satisfactory agreement with the experimental spectra.

Key words: Terphenyl di-valent ion – Quaterphenyl di-valent ion

1. Introduction

In connection with a study of the photo-electron ejection of the negative ions of polyacenes and polyphenyls in ethers it was necessary to obtain some information about the locations of their lower excited states. As will be shown in a separate paper, for certain ions this may be achieved by unraveling the absorption spectra. In this way the lower excited states of the mono- and di-negative ions of naphthalene, antracene, tetracene and pentacene can be located with a high degree of certainty. In the polyphenyl series, however, this appears to be possible only for the mono-negative ion of biphenyl. The difficulty with ions in this series is that simple configuration interaction calculations predict a few weakly allowed or forbidden transitions leading to lower excited states which cannot all be traced from an analysis of the absorption spectra. This holds particularly for the dinegative ions of terphenyl and quaterphenyl. From experience in the past we know that in such cases a configuration interaction treatment of the Pariser-Parr type with the inclusion of doubly excited configurations gives a reliable qualitative picture for the lower excited states of the ions [1]. In the present paper such a treatment is presented for the dinegative ions of terphenyl and quaterphenyl.

2. Method and Results

As a basis set for the C.I. treatment we used the Pople SCF MO's for the ground state dinegative ions. In our calculations we used the following parameter values (in eV) [2]: $\omega = -9.574$; $\beta = -2.390$; $\gamma_{11} = 11.35$; $\gamma_{12} = 7.19$; $\gamma_{13} = 5.77$; $\gamma_{14} = 4.97$. For longer carbon-carbon distances the values of $\gamma_{i,j}$ were derived from the point charge model, $\gamma_{i,j} = e^2/r_{ij}$. As in previous calculations we also

Table 1. Results of PPP calculations for the lower allowed transitions in the terphenyl di-negative ion

	E eV	$cm^{-1} \times 10^{-3}$	M^2/e^2
$^1B_{3u}$	2.182	17.60	15.586
	2.721	21.95	0.052
	4.079	32.90	0.023
$^1B_{2u}$	1.130	9.11	0.106
	2.980	24.04	0.261
	3.038	24.51	0.078
	4.569	36.86	0.692

used other sets of parameters, but we found no significant change in the results of the calculations. The set given above, however, led to the best correlation with the experimental data.

In order to allow for as many configurations as possible the C.I. matrix was split into four blocks corresponding to the molecular symmetries A_{1g}, B_{1g}, B_{2u}, and B_{3u}. This, of course, implies the assumption of a planar nuclear configuration of the ions. The use of the IBM 1130 computer limited the number of singly and doubly excited configurations to about 25 for each of the four symmetry groups.

In the Tables 1 and 2 the energies of the lower lying singlet states with symmetry B_{2u} and B_{3u} are listed. Since transitions from the ground state $^1A_{1g}$ to these states are allowed we also give the squares of the corresponding transition dipole moments.

In the diagrams 1 and 2 all lower lying singlet and triplet states are illustrated as far as they are relevant for our further studies.

Since terphenyl and quaterphenyl are alternant molecules and differential overlap is neglected the calculated data also hold for the corresponding dipositive ions.

A similar treatment based on Hückel MO's instead of the SCF MO's of the ground state ions led to a very unsatisfactory correlation with the experimental spectra.

Table 2. Results of PPP calculations for the lower allowed transitions in the quaterphenyl di-negative ion

	E eV	$cm^{-1} \times 10^{-3}$	M^2/e^2
$^1B_{3u}$	1.717	13.85	23.281
	2.861	23.08	0.0001
	3.404	27.46	0.272
	4.260	34.36	0.0002
	4.538	36.60	0.194
$^1B_{2u}$	1.615	13.03	0.003
	1.672	13.49	0.030
	3.316	26.75	0.003
	3.411	27.51	0.008
	4.461	35.98	0.034

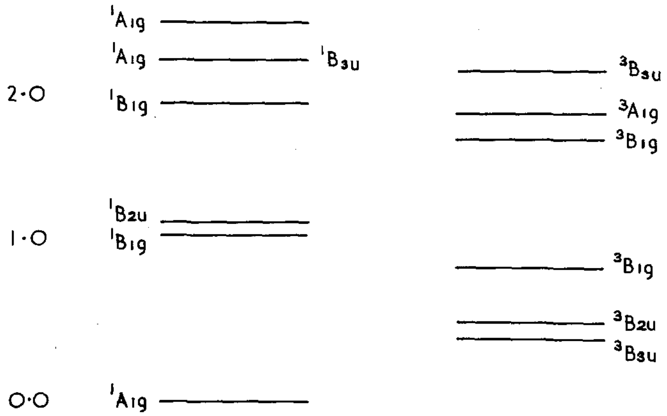

Fig. 1. Calculated lower energy levels of the terphenyl di-negative ion

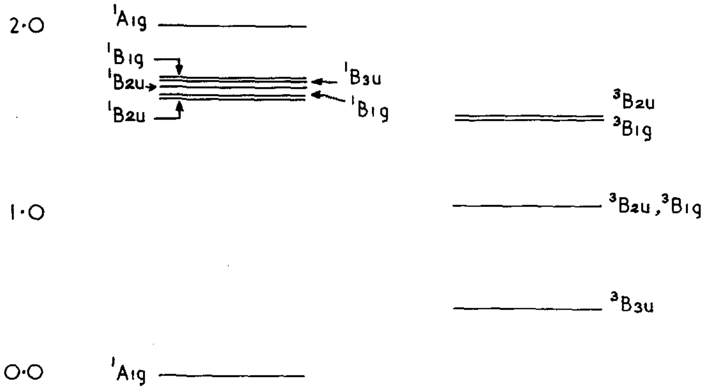

Fig. 2. Calculated lower energy levels of the quaterphenyl di-negative ion

3. Discussion

The results given in the Tables 1 and 2 are in very nice agreement with the experimental spectra. As is shown in the Figs. 3 and 4 the calculations indeed predict the appearance of a very strong absorption band at relatively low energy followed by very little absorption in the further visible and near ultraviolet. The very weak $^1A_{1g} \rightarrow {}^1B_{2u}$ transitions predicted by the calculations confirm the results of previous polarization measurements which gave no evidence for any measurable short axis polarized transitions [3]. This satisfactory agreement with the experimental spectra gives some confidence in the prediction of the lower forbidden and very weakly allowed transitions. As we see from the Figs. 1 and 2 there is a remarkable difference in location of the lower excited states for the terphenyl and quaterphenyl ion. For terphenyl the calculations predict a very weakly allowed and a forbidden transition in the near infrared, whereas for quaterphenyl we find no transitions in the near infrared at all. In the latter case the weakly allowed and forbidden transitions are all closely gathered around the

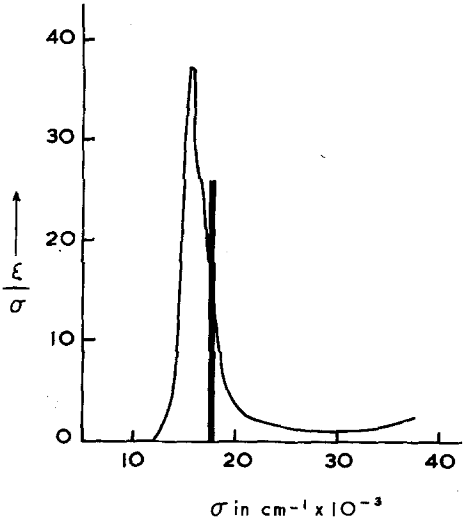

Fig. 3. Comparison between the experimental absorption spectrum and the calculated transition energy (solid line) for the strongly allowed $A_{1g} \rightarrow B_{3u}$ transition of the terphenyl di-negative ion. According to Table 1 all other transitions have very low or negligible intensities. Units on vertical axis: $10^2\ M^{-1}$

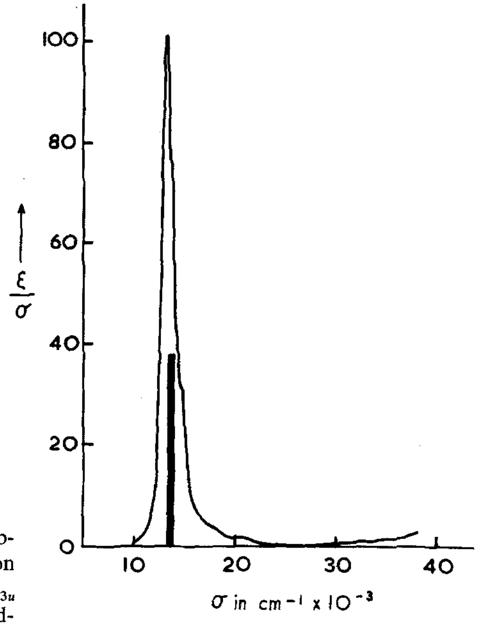

Fig. 4. As Fig. 3 for the quaterphenyl di-negative ion

strongly allowed ${}^1A_{1g} \rightarrow {}^1B_{3u}$ transition. Similar results were obtained for the mononegative ions of biphenyl, terphenyl and quaterphenyl where the calculations showed an increase in the frequencies of the lower lying weakly allowed and forbidden transitions with increasing number of phenyl groups [4].

Finally we should like to emphasize that, whereas for the mono-negative ions the inclusion of doubly excited configurations seems to have little effect on the locations of the lower excited states [5], for the di-negative ions the omission of doubly excited configurations would lead to completely false predictions. This is quite obvious since for the dinegative ions in the ground state configuration the lowest anti-bonding orbital is occupied by two electrons, so that the promotion of these two electrons leads to a large number of lower doubly excited configurations.

Acknowledgement. The authors are very grateful to Dr. D. B. Cook for his help with the computer calculations.

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