

Calculations on the $\pi \rightarrow {}^1\pi^*$ Transitions in Large Conjugated Carbonyl Compounds Using the Molecules-in-Molecules Method

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Assignments of the $\pi \rightarrow {}^1\pi^*$ electronic transitions in large carbonyl compounds have been carried out using the molecules-in-molecules method.

Key words: $\pi \rightarrow {}^1\pi^*$ transitions – Conjugated carbonyl compounds – Molecules-in-molecules methods

Introduction

Sidman [1] observed that the electronic spectra of a large number of quinones [2] were similar, with three absorption regions in common – $\pi \rightarrow \pi^*$, weak $\pi \rightarrow {}^1\pi^*$ and strong $\pi \rightarrow {}^1\pi^*$. He also observed that these spectra were more similar than were those of the parent hydrocarbons. He concluded that this similarity was the result of a common structural feature – the quinone group, and that the molecules could be regarded as vinyl-substituted *p*-benzoquinones. Confirmation was given in the case of 9:10-anthraquinone by the single crystal studies of Sidman [1] who showed that as with *p*-benzoquinone [3] both $\pi \rightarrow {}^1\pi^*$ transitions were polarized perpendicularly to the C–O axis. As further evidence for a *p*-benzoquinone structure in the *p*-quinones he pointed out that unexcited resonance structures cannot be drawn in which the C–C bonds of the C–O carbon atom have double bond character, thus indicating a long bond as is known for *p*-benzoquinone [4]. An X-ray analysis of 9:10-anthraquinone by Sen [5] showed this bond-length to be 1.50 Å which is equal to that in *p*-benzoquinone. The model appeared to be well-founded and was used in interpreting the electronic spectrum of 9:10-anthraquinone [1]. However, in a later paper Sidman [6] drew attention to the X-ray work on *p*-benzoquinone of Brand and Goodwin [7] who had shown that the optical axes adopted by Sidman were *incorrect* and should be *reversed*. This gave an important difference between the spectra of *p*-benzoquinone and 9:10-anthraquinone (Sidman warned against his polarization analysis of 9:10-anthraquinone although there was no *a priori* reason why it should have been incorrect – it will be seen later that there was nothing at all wrong with it). The presence of the long C–C bonds in 9:10-anthraquinone cannot and need not be disputed. On examining the molecular dimensions of 9:10-anthraquinone more

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closely it is seen that the C–C bond-lengths in the two outer rings are in the range 1.38–1.40 Å, with the short C–C bond of the inner ring being 1.40 Å as compared to 1.31 Å in *p*-benzoquinone [4]. On the basis of geometry alone it is not only clear that Sidman's model of 9:10-anthraquinone was incorrect, but also that a more realistic model is that of a symmetric composition of two benzene rings and two carbonyl groups. It is concluded that similarity between the single crystal spectra of *p*-benzoquinone and 9:10-anthraquinone should not be anticipated, and that the observed similarity of the solution spectra is of no significance.

This model has previously been used in polarization excitation studies on 9:10-anthraquinone [8] and anthrone [8, 9], the interpretation of the spectra being carried out in terms of interaction between the benzene rings and with the aid of Platt's spectroscopic moment theory [10]. This is a very simple approach, but, if the assignment of the anthrone spectrum due to Drott and Dearman [9] (hereinafter D–D) is adopted, nonetheless a successful one. In the present work a more detailed theory has been used for the following compounds, where the validity of the model in each case is judged on the extent of agreement between the calculated and experimental $\pi \rightarrow {}^1\pi^*$ electronic transitions: 9:10-anthraquinone, methylene anthrone, 1:4-naphthoquinone, anthrone and fluorenone.

Theory

The method used was the molecules-in-molecules (MIM) method of Longuet-Higgins and Murrell [11] where the states are described in terms of local excitation (LE) and charge transfer (CT) configurations. This method has been used previously in calculations on simple carbonyl compounds [12]. Except for the electron affinity of benzene [13] all the integrals and integral-values necessary for the present work are contained in the latter paper. Ionization from the C–O group is not included. Further description is unwarranted.

Molecular Dimensions

9:10-anthraquinone. The dimensions used were essentially those determined by Sen [5], with the simplifications that all "benzene" C–C bond-lengths were taken as 1.39 Å and all bond-angles were assumed to be 120°. These changes are sure to have an insignificant effect on the results to be presented, and were made simply for easier calculation.

1:4-naphthoquinone. The dimensions used were taken from these used for 9:10-anthraquinone, with the short non-benzenoid C–C bond-length being taken from *p*-benzoquinone [4].

The dimensions for the above two molecules have been used in earlier calculations [14].

Anthrone and methylene anthrone. As with 1:4-naphthoquinone the dimensions were taken from those adopted for 9:10-anthraquinone, with the new C–C bond in the methode having the ethylene bond-distance [15].

Fluorenone. Iball [16] suggested that fluorene was non-planar, but in a later paper on an X-ray study Burns and Iball [17] concluded, "It is clear, therefore,

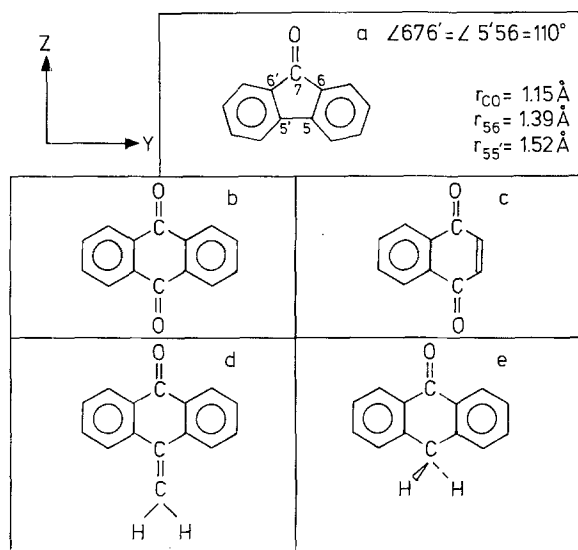


Fig. 1. Structures of investigated molecules: a fluorenone, b 9:10-anthraquinone, c 1:4-naphthoquinone, d methylene anthrone and e anthrone

that the molecule is planar ...". Commenting on this second paper Gray *et al.* [18] said, "... X-ray studies suggest that they (fluorene and fluorenone — the latter was *assumed* to have essentially the same structure as the former) are distorted". From the published data there is no doubt as to the planarity of fluorene. It is assumed that fluorenone too is planar.

The dimensions adopted for fluorenone are given in Fig. 1 together with the other molecules being investigated.

Results

In Tables 1 (i–v) the results of the MIM calculations are compared with experimental data. The configurations composing $> 10\%$ of each state are given. The positive combinations benzene states are symmetric to a 180° rotation about the C–O axis.

Discussion

Scott [23] and Singh *et al.* [24] used the CT and LE terminology in a qualitative interpretation of the electronic spectra of 1:4-naphthoquinone and 9:10-anthraquinone. It was hoped that their work would be complementary to that presented here, but, unfortunately, the impreciseness of the terms as used by these workers has made this impossible.

9:10-anthraquinone. Only the three lowest $\pi \rightarrow {}^1\pi^*$ transition energies can be measured from the polarization spectrum [8] — these agree moderately well with the values taken from the solution spectrum [19]. They also agree with the MIM results and those of previous *P*-method calculations. D–D reported that there

were indications of a Z-polarized transition at higher energy, but they could not be absolutely certain because of the poor resolution in this region. Such a band is predicted from the MIM results (and from the *P*-method results for that matter). However, there is considerable doubt as to the value of the experimental energy. Poquet [19] reported an intense fourth band at 4.9 eV, whereas Kuboyama and Wada [20] reported an intense fourth band at 6.1 eV. The latter agrees exceedingly well with the calculated energy, but the 4.9 eV band is clearly the fourth and is, therefore, included in Table 1 (i).

Using Platt's spectroscopic moment theory D-D deduced the following order of transitions: A Y-polarized transition consisting of benzene α states ($\alpha_1 - \alpha_2$); a Z-polarized transition consisting essentially of benzene *p* states ($p_1 + p_2$); a transition arising from the benzene β states – for Y-polarization this is

Table 1. Comparison of calculated and experimental $\pi \rightarrow {}^1\pi^*$ transition energies (eV), *s* solution, *r* rigid medium, *f* oscillator strength, ϵ_{\max} maximum of molar extinction coefficient, *M* transition dipole moment, *P* suffix results of previous *P*-method calculations (14), *b* benzene

1(i) 9:10-anthraquinone

Calculated				Experimental [19] <i>s</i>			Main configurations
E_{MIM}	<i>M</i>	E_p	f_p	<i>E</i>	ϵ_{\max}	Pol. [8] <i>r</i>	
4.26	0.18(Y)	4.06	0.51(Y)	3.8	5,000	Y	0.63 ($\alpha_1 - \alpha_2$), 0.39 (<i>b</i> → C–O)
4.27	0	3.99	0				0.64 ($\alpha_1 + \alpha_2$), 0.38 (<i>b</i> → C–O)
4.88 ₇	0	4.28	0				0.43 ($p_1 - p_2$), 0.62 (<i>b</i> → C–O), 0.36 (<i>b</i> → <i>b</i>)
4.88 ₄	0.39(Z)	4.68	0.37(Z)	4.5	16,000	Z	0.42 ($p_1 + p_2$), 0.66 (<i>b</i> → C–O), 0.38 (<i>b</i> → <i>b</i>)
5.38	0.92(Y)	5.66	1.76(Y)	4.7	20,000	Y	0.46 ($\beta_1 - \beta_2$), 0.61 (<i>b</i> → C–O), 0.35 (<i>b</i> → <i>b</i>)
5.82	0	5.62	0				0.40 ($\beta_1 + \beta_2$), 0.32 (<i>LEC</i> –O), 0.52 (<i>b</i> → C–O), 0.44 (<i>b</i> → <i>b</i>)
5.84	0	5.75	0				0.36 ($p_1 - p_2$), 0.42 ($\beta'_1 - \beta'_2$)
							0.54 (<i>b</i> → C–O), 0.32 (<i>b</i> → <i>b</i>)
5.92	0.70(Z)	5.92	0.71(Z)	4.9	50,000	Z	0.33 ($p_1 + p_2$), 0.37 ($\beta'_1 + \beta'_2$),
							0.58 (<i>b</i> → C–O), 0.41 (<i>b</i> → <i>b</i>)
6.55							

1(ii) Methylene anthrone

Calculated			Experimental [25] <i>r</i>		Main configurations
E_{MIM}	<i>M</i>	E_{MIM} (9:10-anthraquinone)	<i>E</i>	Pol.	
3.97	0.33(Z)	4.27			0.45 ($\alpha_1 + \alpha_2$), 0.33 (<i>b</i> → C–C), 0.32 (<i>b</i> → C–O), 0.39 (C–C → <i>b</i>)
4.22	0.10(Y)	4.26(Y)	3.6	Y	0.64 ($\alpha_1 - \alpha_2$)
4.88	0.09(Y)	4.88 ₇			0.47 ($p_1 - p_2$), 0.41 (<i>b</i> → C–C), 0.40 (<i>b</i> → C–C)
4.28	0.26(Z)	4.88 ₄ (Z)	4.4	Z	0.40 ($\alpha_1 + \alpha_2$), 0.22 ($p_1 + p_2$), 0.32 (<i>LEC</i> –C), 0.43 (<i>b</i> → C–C), 0.42 (C–C → <i>b</i>)
5.12	0.33(Z)	5.82			0.26 ($\beta_1 + \beta_2$), 0.48 (<i>b</i> → C–O), 0.38 (<i>b</i> → <i>b</i>), 0.39 (C–C → <i>b</i>)
5.24	0.93(Y)	5.38(Y)	5.2	Y	0.47 ($\beta_1 - \beta_2$), 0.41 (<i>b</i> → C–O), 0.42 (C–C → <i>b</i>)
5.50	0.15(Y)	6.55(Y)			0.44 (<i>b</i> → C–C), 0.62 (<i>b</i> → <i>b</i>), 0.57 (C–C → <i>b</i>)
5.61	0.39(Z)	5.92(Z)			0.37 ($p_1 + p_2$), 0.22 ($\beta'_1 + \beta'_2$), 0.42 (<i>b</i> → C–O), 0.34 (C–C → <i>b</i>)
5.81					

1(iii) 1:4-naphthoquinone

Calculated				Experimental <i>s</i>		Main configurations
E_{MIM}	$ M $	E_p	f_p	E [19]	ϵ_{max} [19]	
4.20	0.13(Y)	3.88	0.003(Z)	3.7	3,000	0.86 α , 0.23 ($b \rightarrow C-C$), 0.43 ($b \rightarrow C-O$)
4.62	0.28(Z)	3.97	0.25 (Y)	4.8	13,000	0.50 p , 0.26 β' , 0.47 ($b \rightarrow C-C$), 0.67 ($b \rightarrow C-O$)
4.70	0.37(Z)	4.76	0.89 (Z)	4.9	24,000	0.48 ($LE\ C-C$), 0.39 ($C-C \rightarrow b$), 0.76 ($C-C \rightarrow C-O$)
5.45	0.50(Y)	5.57	0.40 (Y)	5.0	22,000	0.40 α , 0.51 β , 0.44 ($b \rightarrow C-C$), 0.57 ($b \rightarrow C-O$)
5.90	0.45(Z)	5.69	0.49 (Z)			0.68 p , 0.48 β' , 0.29 ($b \rightarrow C-C$), 0.47 ($b \rightarrow C-O$)
6.46		6.43				

1(iv) Anthrone

Calculated		Experimental <i>r</i>				Main configurations
E_{MIM}	$ M $	E [9]	Pol. [9]	Benzophenone [21]		
				E	Pol. [9]	
4.47 ₆	0.09(Y)					0.66 ($\alpha_1 - \alpha_2$)
4.47 ₁	0.10(Z)	4.0	Z	4.2 [9]	Z	0.67 ($\alpha_1 + \alpha_2$)
5.16	0.47(Y)	4.5	Y	4.6 [9]	Y	0.43 ($p_1 - p_2$), 0.24 ($\beta_1 - \beta_2$), 0.55 ($b \rightarrow C-O$), 0.33 ($b \rightarrow b$)
5.42	0.21(Z)	4.7	Z	4.9 [9]	Z	0.48 ($p_1 + p_2$), 0.23 ($LE\ C-O$), 0.52 ($b \rightarrow C-O$), 0.32 ($b \rightarrow b$)
5.93	0.71(Y)			6.1		0.36 ($\beta_1 - \beta_2$), 0.35 ($\beta'_1 - \beta'_2$), 0.48 ($b \rightarrow C-O$) 0.38 ($b \rightarrow b$)
6.13	0.61(Z)					
6.18	0.63(Y)					
6.31	0.36(Z)			6.6		
6.69	0.73(Y)					
6.81	0.41(Y)					

1(v) Fluorenone

Calculated		Experimental <i>s</i>		Main configurations
E_{MIM}	$ M $	E [22]	ϵ_{max} [22]	
3.86	0.26 (Y)	4.2	3,700	0.48 ($\alpha_1 - \alpha_2$), 0.50 ($b \rightarrow C-O$), 0.42 ($b \rightarrow b$)
4.31	0.012(Z)	3.3	260	0.65 ($\alpha_1 + \alpha_2$)
4.56	0.21 (Y)	4.4	2,800	0.37 ($\alpha_1 - \alpha_2$), 0.36 ($p_1 - p_2$), 0.35 ($b \rightarrow C-O$), 0.50 ($b \rightarrow b$)
5.19	0.91 (Y)	4.8	91,000	0.51 ($\beta_1 - \beta_2$), 0.40 ($b \rightarrow C-O$), 0.57 ($b \rightarrow b$)
5.34	0.40 (Z)			0.41 ($p_1 + p_2$), 0.50 ($b \rightarrow C-O$), 0.49 ($b \rightarrow b$)
5.73				

the negative combination. This analysis is wholly substantiated by the results of the MIM calculations, although there is considerable $b \rightarrow C-O$ in the third state.

Methylene anthrone. In Table 1 (ii) the states of methylene anthrone have been correlated with the 9:10-anthraquinone states of the same symmetry. The calculated results for these two molecules are similar, as are the polarization and absorption spectra [25]. The three observed polarized bands are assigned to the states shown; the corresponding states in 9:10-anthraquinone are those to which its experimental bands are assigned. Adopting the exciton interaction

treatment previously used for diphenyl, diphenylmethane and dibenzyl by McClure [28], Smith and Dearman [25] predicted the following order of states: $(\alpha_1 - \alpha_2)$, $(\alpha_1 + \alpha_2) + (p_1 + p_2)$, $(p_1 - p_2)$. It is difficult to directly compare the results of this and the present method since the latter allows for a far greater interaction of configurations. However, the present results are essentially in accord with the assignments of Smith and Dearman, although it is felt that the third band will also contain a large proportion of the intense ground state to $(\beta_1 - \beta_2)$ transition.

1:4-naphthoquinone. Of the five calculated transitions reported in Table 1 (iii) the polarizations and energies for the last three agree with those calculated previously using the *P*-method [14]. In this previous work the two lowest transition energies (3.38 and 3.97 eV) were both assigned to the first observed band – partially because of their near degeneracy and partially because the former was virtually forbidden; the other three experimental bands were assigned to the calculated energies in order. Thus, the bands were predicted to arise from transitions polarized *Y* (predominately), *Z*, *Y*, and *Z*, in order of increasing energy. But the MIM results indicate that the first two transitions are both very much allowed and 0.42 eV apart. Moreover, the more intense band from the MIM results is the virtually forbidden band from the *P*-method results. From the MIM method results the order of polarization is *Y*, *Z*, *Z* and *Y*. The same sequence could be obtained for the *P*-method results by “unpairing” and reversing the first two transitions. Unfortunately, while agreement is thus improved in one way it is worsened in another – the second experimental band should then arise from a virtually forbidden transition, which it certainly does not. This is not a happy state of affairs. Certainly, the polarization spectrum of this compound would help to clear matters up, but because of the weakness of its phosphorescence it has not, as yet, been observed [25].

Platt's spectroscopic moment theory predicts that the first band would arise from a *Y*-polarized transition essentially of α character, with a second *Z*-polarized transition essentially of *p* character. This is in good agreement with the results of the calculation, although the amount of *p*-character is on the low side (25 %).

It is interesting to note the similarity of the MIM results for 1:4-naphthoquinone and benzaldehyde. The first band of benzaldehyde is generally considered to be essentially α with the second to arise from *p* and/or *b* \rightarrow C–O [26, 27]. The third band was of too high an energy to occur in the polarization spectrum [9], but Walsh [26] regarded it as essentially β . These conclusions are consistent with previous MIM calculations [12] where the second band arises from *p* + *b* \rightarrow C–O and the third arises from β (also with considerable *b* \rightarrow C–O). From Table 1(iii) it is clearly reasonable to compare the first three transitions of benzaldehyde with the first, second and fourth transitions, respectively, of 1:4-naphthoquinone. The third excited state of 1:4-naphthoquinone is composed almost entirely (95 %) of ethylene LE and CT from the ethylene group, and obviously has no place in the benzaldehyde spectrum.

Anthrone. The anthrone and benzophenone data taken from the spectra of Shimada and Goodman [9] are given in Table 1 (iv) and are in excellent agreement with the results of Smith and Dearman [25]. Shimada and Goodman attempted to correlate the two experimental bands of lowest energy with the ${}^1A_1(\alpha_1 + \alpha_2)$

and ${}^1B_1(\alpha_1 - \alpha_2)$ states which are Z- and Y-polarized, respectively. On estimating the energy separation using the exciton interaction treatment of McClure [28] they obtained a value of 700 cm^{-1} (0.09 eV) with the 1A_1 state at *higher* energy. The same ordering of states was obtained by these workers using the *P*-method, with the splitting being brought down from a high of 0.4 eV to a low of 0.025 eV by systematically increasing the complexity of the wavefunctions. The problem was left unsolved. From the present calculations it can be seen that the two lowest states are of 1A_1 and 1B_1 symmetry, with the former at a level only 0.005 eV higher than the latter. Since the states have different symmetries they could be made to interchange by judicious changes in the values of the semi-empirical parameters, but this is not a worthwhile exercise since no reasonable change in integral-values would give rise to the 0.5 eV splitting observed; this is also true of the *P*-method calculations of Shimada and Goodman. That the observed peak separation does *not* arise from the ${}^1A_1 - {}^1B_1$ splitting has been very convincingly argued by D-D. They calculated the -CHO group substituent contribution to the oscillator strengths for these two transitions using the spectroscopic moments derived by Petruska [29]. It was found that $f({}^1A_1)/f({}^1B_1) \sim 3$. The spectroscopic moment of a -CH₃ group is far smaller than that of a -CHO group, but giving the -CH₂ group in anthrone the value derived for -CH₃ in toluene results in a marked change in the *ratio* - $f({}^1A_1)/f({}^1B_1) \sim 8$. The very reasonable suggestion was then made that the two states are very close in energy with the ${}^1A_1 \leftarrow A_1$ transition masking the ${}^1B_1 \leftarrow A_1$ transition, thus giving the required polarization for the first band. This explanation is compatible with the results of the present calculation. It is true that the transition dipole moments are predicted to be of approximately the same magnitude, but in the calculation the -CH₂ group was neglected, and, as shown above, its effect is to increase the value of $f({}^1A_1)/f({}^1B_1)$. The calculated separation of 0.7 eV is somewhat greater than the experimental value, but it is comforting to note that the state has a good deal of ($p_1 - p_2$) character, in agreement with the assignments suggested by D-D.

In view of the similarity between the structures of benzophenone and anthrone and that between their spectra at long wavelengths (> 2500 Å) [9, 25, 30] similarity is expected between their spectra at shorter wavelengths. Certainly, the observed strong bands in the spectrum of benzophenone at 6.1 eV and 6.6 eV are consistent with the results calculated for anthrone.

Fluorenone. There is no doubt that the lowest energy band at 3.3 eV arises from a $\pi \rightarrow {}^1\pi^*$ transition [22, 31] and not from an $n \rightarrow {}^1\pi^*$ transition. The assignment suggested in Table 1 (v) is satisfactory as regards intensities, but this has caused the unhappy situation of having the 3.3 eV band assigned to a transition calculated to be 1.0 eV higher in energy. Kuboyama [22] has attempted the assignment using naïve Hückel theory. He deduced the polarizations to be Y, Y, Z and Z, which disagrees completely with the present results which are Z, Y, Y and Y. The polarization spectrum would be invaluable.

Conclusion

For 9:10-anthraquinone, methylene anthrone and anthrone the results of the calculations offer a reasonable interpretation of their electronic spectra, and,

consequently, justify the molecular model adopted. For 1 : 4-naphthoquinone and fluorenone insufficient experimental data has resulted in the assignments being hardly more than guesses: Knowledge of the polarizations is essential.

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