Absorption Spectra of Dyes. IX.[1] Electronic Spectra of a 1 : 1 and a 1 : 2 Complex, and CT-Bands*

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Electronic absorption spectra are generally sensitive to the environment of the sample. In particular, the molecular complex formation brings about remarkable changes in the electronic absorption spectra of the component molecules. By applying the theory of charge transfer as developed by Mulliken[2] to electron donor and acceptor molecules, the authors have found that an intermolecular charge transfer spectrum is obtained from Chlorazol Sky Blue FF and Chrysophenine G in a complex state.[3] Moreover, by analogy with the known theoretical results, they have determined how the molecular orbitals of Chlorazol Sky Blue FF and Chrysophenine G are altered in the formation of a 1 : 1 and a 1 : 2 complex respectively. They have also assigned the actual electronic spectra of these dye complexes to empirical MO patterns, but they have not, however, discussed the relative configurations of the respective MO's in detail.

The purpose of the present investigation is to determine the absorption spectra of 1 : 1 and 1 : 2 complexes and, moreover, to explain the correlation between these electronic bands in terms of the more refined MO pattern derived from the complexes' spectra.

Experimental and Results

The samples were the same as those used in a previous investigation.[1] The procedure already described[1] was followed in carrying out the experiments. A Shimadzu recording spectrophotometer SV-50A and, when necessary, a Shimadzu QR-50 spectrophotometer were employed in the determination of the absorption spectra at room temperature (about 20°C). The absorption cells used were 10 mm. and 2 mm. long, and the wavelength region observed was 220—700 mμ. Mixed solutions of two different concentrations were prepared, one containing 1×10^{-5} mol./l. of a partner dye

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[1] Part VIII of this series: Y. Tanizaki, T. Hoshi and N. Ando, This Bulletin, **38**, 264 (1965).

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[2] R. S. Mulliken, *J. Am. Chem. Soc.*, **70**, 600 (1950); **74**, 811 (1952); *J. Phys. Chem.*, 56, 801 (1952).

[3] T. Kobayashi, Y. Tanizaki and N. Ando, This Bulletin, **33**, 661 (1960).

(abbreviated as P) with an equal concentration of G (Chrysophenine G), and the other with the same concentration of P, together with from two to nine times the concentration of G.

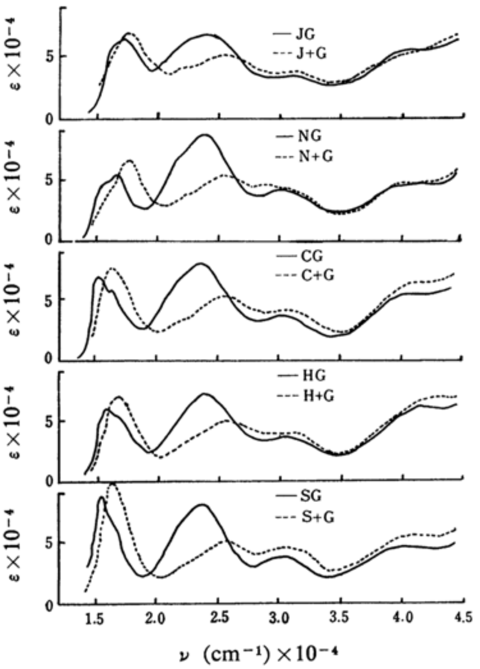

Fig. 1. Absorption spectra of a PG complex (solid lines) and the resultant ones of P and G (dotted lines).

The absorption spectra of the PG and the PG_2 species were determined by calculation, by applying, respectively, the equilibrium constants, K_1 and K_2 previously obtained[1] at 20°C, to the absorption spectra measured here. The results are illustrated in Figs. 1 and 2 respectively. In Fig. 1, the solid and the dotted lines indicate, respectively, the absorption curve of a 1 : 1 complex (PG) and the combined absorptions of P and G determined separately at an equimolar concentration. Similarly, the solid line in Fig. 2 indicates the absorption spectrum of a 1 : 2 complex (PG_2), while the dotted line represents the additive spectrum of the P curve and two times the height of the G curve.*

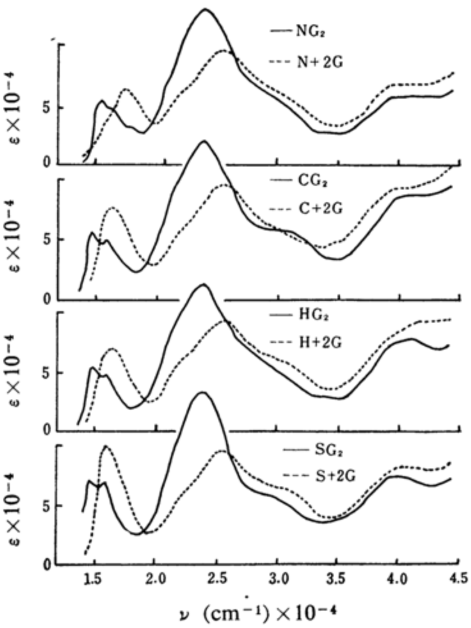

Fig. 2. Absorption spectra of a PG_2 complex (solid lines) and resultant ones of P and twice of G (dotted lines).

First of all, the following points may be noticed in Figs. 1 and 2. In the 16—18 kK ($kK = 1000 cm^{-1}$) region, the first band shifts progressively to the lower wave number, together with the decrease in intensity, with the formation of a 1 : 1 and a 1 : 2 complex, and, as the case may be, the main band is split into two bands. On the other hand, the second band (22.5 kK) is markedly intensifies by the formation of complexes. Moreover, the maximum point shift toward a much lower side with the 1 : 1 complex formation and then moves in the opposite direction to the higher side with the 1 : 2 complex formation (cf. Fig. 3). In the wave number-region higher than about 30 kK, the complex and the resultant spectrum are nearly the same in shape, but the intensities are somewhat smaller in the former than in the latter in most cases.

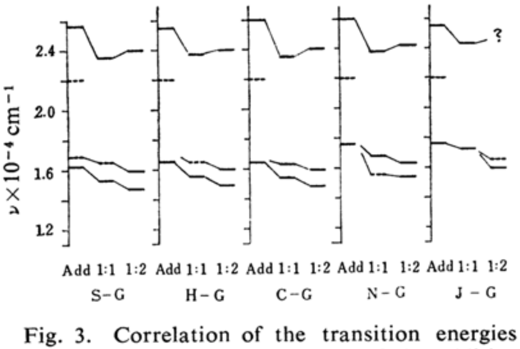

Fig. 3. Correlation of the transition energies (wave number) in the order of the additive (Add.), a PG (1 : 1) and a PG_2 complex (1 : 2) spectrum in the P-G system.

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* The absorption curves concerning JG_2 are not illustrated in Fig. 2. This is due to the fact that the quantity of a 1 : 2 complex (JG_2) could not be calculated with reliable presision at wave numbers higher than the second band on account of the smaller equilibrium constant (K_2).

The most important fact in the above results is that the first and the second band behave differently. The transition energies (wave numbers) of those parts are illustrated in Fig. 3 in the order of the results of P and G, the PG complex and the PG_2 complex spectrum. The figure makes it apparent that in every combination the absorptions at about 16 kK shift down progressively to the low-wave number side as a result of the formation of complexes, while the absorption at about 25 kK shifts up after once falling down. Since the absorption at about 16 kK of the additive spectrum is the first band of P itself and since the 25.5 kK absorption is that of G alone, it may be considered that the variety of complex formations revealed by Fig. 3 has been brought about by interaction between the orbital states of the components in a complex.

Discussion

The G molecule has two sulfonic groups at positions adjacent to the ethylene bond (see Fig. 4). The groups are so bulky that they may hinder the two monoazo dyes from the conjugation through the ethylene bond.[4] Therefore, the MO pattern which is responsible for the first band of G may be considered to be produced from the interaction (the weak coupling) between the MO's of the half structures (HS in Fig. 4) on the right side and on the left side of the ethylene bond. That is to say, the analogy with Platt's theory[5] leads to the relation shown in Fig. 4. Two pairs of HS levels in the same figure indicate the highest occupied (π) and the lowest unoccupied molecular orbitals (π^*). Applying the concept of the simple MO approximation, it can be said that the degenerate orbitals will split as a result of the interaction between two HS's, and that, in consequence the MO levels of FS (full structure) in Fig. 4 will be obtained; FS (i. e. the G molecule) can produce the electronic transitions $(\pi-\pi)\rightarrow(\pi^*+\pi^*)$ and $(\pi-\pi)\rightarrow(\pi^*-\pi^*)$. The actual first band of G is at 25.5 kK and is accompanied by a weak shoulder at about 22 kK.* Therefore, the main band of G may be assigned to the $(\pi-\pi)\rightarrow(\pi^*-\pi^*)$ transition and the shoulder to the $(\pi-\pi)\rightarrow(\pi^*+\pi^*)$. As most of the atoms constituting the conjugate system under consideration are carbon atoms, the location of the individual MO's may be determined without any large error by taking the Coulomb integral, Q, of the π electron on the carbon atom as a standardized zero level. In the approximation, the π^* and the π levels, and also the $(\pi^*+\pi^*)$ and the $(\pi-\pi)$ levels, are arranged at equal distances above and below the Q line, as Fig. 4 shows.

For the sake of convenience, let π_G and $\pi_G{}^*$ stand, respectively, for the $(\pi-\pi)$ and $(\pi^*-\pi^*)$ orbitals of G. The arrangement of π_G and $\pi_G{}^*$ can be determined with respect to the Q line by utilizing the absorption data of G alone, because Q lies at the middle point between π_G and $(\pi^*+\pi^*)$.

If the MO's of P could be determined for the Q level, the relative configuration of MO's of P and G could be decided. No such a situation as that in the case of G could, however, be found between the first band of P (disazo dye) and that of its half structure (monoazo dye). That is, for meta-Benzopurpurine, for example, the relation between the absorption specta of the half and the full structure is nearly the same as in the case of G, whereas in the case of ortho-Benzopurpurine, corresponding to P, the situation is quite different; here the first and the second band of the half structure change into an absorption delocalized over the full structure.[6] For that reason, let us suppose that the first

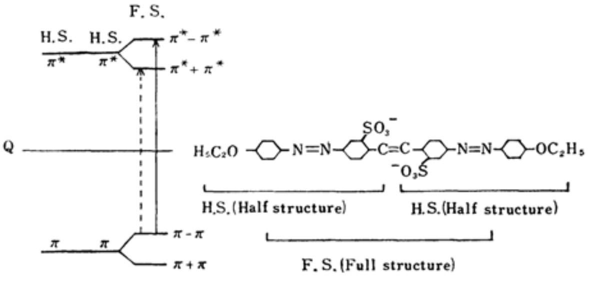

Fig. 4. Schematic MO pattern of the half (HS) and the full structure (FS) of Chrysophenine G.

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[4] Cf. T. Kobayashi, Y. Tanizaki and N. Ando, This Bulletin, 33, 913 (1960).

[5] J. R. Platt, *J. Chem. Phys.*, **19**, 101 (1951).

* This shoulder is indicated by the dotted line at 22kK in Fig. 3.

[6] H. A. Standing and M. Stein, *J. Textile Inst.*, **44**, T224 (1953).

band of P may be attributed to the transition between MO's which are uniformly delocalized, and let us further assume that the occupied and unoccupied MO's of P are arranged symmetrically about the same Q level as G, assuming that P has at least one symmetry species, as is seen in Fig. 1 of Part VIII.[1] Then the relative configuration of MO's concerning the first absorption bands of P and G can be decided by standardizing the Q level. Adopting S for P, the MO pattern labeled by G and S shown in the left part of Fig. 5 is obtained. Here, the Q line of S has been estimated from the maximum point of the first band corresponding to the $\pi_S \rightarrow \pi_S{}^*$ transition. As will be seen later, the first absorption of S (in general P) consists of two bands. One corresponds to the transition from the π-type orbital of the functional groups to the π^* orbital, while the other corresponds to the $\pi \rightarrow \pi^*$ transition in the usual sense. In Fig. 5 the two MO's responsible for these transitions are both indicated by π_S.

According to Fig. 3, the wave number of the $\pi_S \rightarrow \pi_S{}^*$ transition of S (Fig. 5) shifts downward with the formation of a 1 : 1 complex. This implies that the complex formation has induced some interactions between MO's of G and S. In this case, the interaction should be strongest between π_G and π_S because the locations of $\pi_G{}^*$ and $\pi_S{}^*$ are so far apart that they cannot interact with each other. The interaction between $(\pi^* + \pi^*)$ and $\pi_S{}^*$ will be also neglected, because it is difficult to suppose any strong interaction between the transition vectors of $\pi_G{}^* \rightarrow (\pi^* + \pi^*)$ and $\pi_S \rightarrow \pi_S{}^*$, for the transition intensity of the former is much weaker than that of the latter. Consequently, the main interaction must be considered to be between π_G and π_S, which are the nearest neighbors.

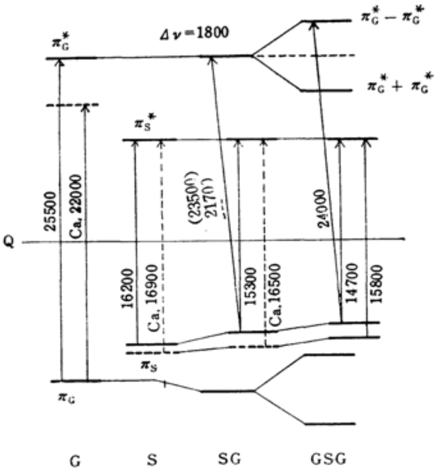

Fig. 5. Change in MO levels of S and G due to complex formations in the S-G system.

According to the assumption that the repulsive interaction is induced only between π_G and π_S, the SG pattern will be obtained as shown in Fig. 5, in which the upper level of π_S is adjusted so as to match the observed and the $\pi_S \rightarrow \pi_S{}^*$ distance. Figure 3 shows that the second band of the SG complex shifts also to the lower side in the same way as does the first band. However, we could not find any transition distance corresponding to the second band (23.5 kK) from the MO's of G in the SG pattern (Fig. 5). However, the distance between π_S and $\pi_G{}^*$ is 21.7 kK, which corresponds well to the observed one, with a difference of only 1.8 kK. This means that a intermolecular charge transfer occurs from S to G.*

Quite similar correlation diagrams have been obtained for all other P's. The relation of the wave numbers of the $\pi_P \rightarrow \pi_G{}^*$ transition, as estimated by the same procedure as above, to those of the experiment is summarized in Table I. In all cases, the experimental values are larger than the estimated ones. This may be due to the assumption that the repulsion acts only between π_G and π_S. If, for example, a small interaction between $\pi_G{}^*$ and $\pi_S{}^*$ is taken into account, the value to be estimated will become larger in some degree. At any rate, the results shown in Table I support the concept of the charge transfer.

TABLE I. COMPARISON OF OBSERVED AND ESTIMATED VALUE OF THE P→G CT-BAND

P	Charge transfer band		$\nu_{obs} - \nu_{est}$
	ν_{obs} kK	ν_{est} kK	
S	23.5	21.7	1.8
H	23.7	21.7	2.0
C	23.5	21.7	1.8
N	23.8	21.2	2.6
J	24.3	22.9	1.4

(kK = 1000 cm^{-1})

Electronic Spectra of the PG$_2$ Complex.—As may be seen in the explanation of Fig. 3, the first band of a PG$_2$ complex shifts further to the lower side than that of a PG complex, whereas the second band of the former moves in the opposite direction, to the higher wave number than that of the latter. A detailed interpretation of the behavior of the second band will be omitted at this time because the authors' previous explanation[3] can be applied here without any modification.

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* According to Ref. 3, the charge transfer takes place from S (electron donor) to G (acceptor).

There is, however, one more subject to be noticed. As has been described in a preceding paper,[1] it is considered that all the partner dyes (P) take a similar sterical configuration in the complex state. If this is true, the degree of interaction between the two G molecules in the GPG (1 : 2) complex state should be constant, regardless of P. That is to say, the distance between the levels of $(\pi_G-\pi_G^*)$ and $(\pi_G+\pi_G^*)$ in Fig. 5 must be equal in all cases. The estimation* provides 5.8 kK for the cases when P is S, H and C, and 6.2 kK when P is N. The expectation, therefore, may be said to be satisfied.

First Absorption Bands of Benzidine Disazo Dyes.—It has been well known as a general tendency that the first band of a benzidine disazo dye reveals one shoulder or other in the dyed state, even when it has a single band with a simple shape in an aqueous solution. A similar tendency appears for the variation in solvent polarity. The constitution of the first absorption band has been described in a preceding paragraph. One is the electronic transition between the molecular orbitals delocalized over the two terminal naphthalene rings, while the other appears on account of the transition of a π-type lone-paired electron.[7] This is a kind of $n\rightarrow\pi^*$ transition and is called the $l\rightarrow\pi^*$ transition.[8]

The electron which transfers from P to G is the lone-paired electron of the π-type on the functional groups.[3] Therefore, the transition probability of this electron within the P molecule in the complex state should be decreased, that is, the absorption intensity of the $l\rightarrow\pi_S^*$ transition should be decreased. Indeed, the $l\rightarrow\pi^*$ intensities of C, CG and CG_2, for example, decrease in this order (see Figs. 1 and 2). A similar tendency is found in all other cases but the N, NG and NG_2 series, which is considered at present to be an exceptional case. In this case, the locations of the two sub-bands to be split may be in a reverse order relative to the other cases. The fact just mentioned makes necessary a consideration of the charge transfer. Consequently, the low wave number band can be assigned to the $l\rightarrow\pi^*$ transition, and the high one, to the $\pi\rightarrow\pi^*$ transition.

Summary

1) The absorption spectra of binary mixtures of Chrysophenine G (notation: G) and disazo dyes (P), which were the same as those used in a preceding study,[1] have been measured at room temperature (ca. 20°C), and the characteristic spectra of the complexes have been determined by using the equilibrium constants, K_1 and K_2, previously obtained (at 20°C)[1] for the 1 : 1 (PG) and 1 : 2 (PG_2) complex formation.

2) The absorption spectra of the PG and PG_2 complex have been compared with the respective corresponding additive spectra (P+G and P+2G), and the correlations among these spectra have been discussed in detail.

3) The MO pattern of the G molecule has been decided empirically by applying Platt's theory; similarly, that of the P molecule has been decided by assuming that there is at least one symmetry species; then the spectral change caused by the complex formation could be explained in relation to the MO's of the component molecules.

4) It has been confirmed that there exists an intermolecular charge transfer from P as an electron donor to G as an acceptor. It has also been shown that the first band of a disazo dye (P) consists of two electronic transitions; one is a $\pi\rightarrow\pi^*$ (shorter wavelength) and the other an $l\rightarrow\pi^*$ transition (longer wavelength).

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* The estimation was done arithmetically as follows:

$$2\{\nu(CT)-[\nu(PG_2)-\nu(P)/2]-[25.5-22.0/2]\}\mathrm{kK}$$

where CT indicates the charge transfer band; $\nu(PG_2)$ and $\nu(P)$ the first band of the PG_2 complex and of the P dye respectively, and 25.5kK and 22.0kK, respectively, the first band and the shoulder of G in Fig. 5.

7) Y. Tanizaki, T. Kobayashi and N. Ando, This Bulletin, **32**, 119 (1959).

8) M. Kasha, "The Nature and Significance of $n\rightarrow\pi^*$ Transitions," presented at the Symposium on Light and Life, The McColum-Pratt Institute, The Johns Hopkins University, Baltimore, Maryland, March, 1960.