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Environmental Intensity Increments of the $S_1(n\pi^*)\leftarrow S_0$ Absorption Spectra of Benzil in Fluid Solutions[1)]

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A remarkable solvent effect on intensity of molecular electronic transitions has been found in near UV absorption spectra of benzil. Great intensity enhancement is observed in alcohols and in chloromethanes as well as in nitriles. Parameters which are required to explain the origin of those environmental intensity enhancement are neither solvent refractive indexes nor polarities. A some rotationally flexible freedom around the -OC-CO- axis of benzil in the solvent seems important. Week complex formation between the solute and the solvent molecule is likely to play an important role. Similar solvent effects are found for absorption spectra of benzophenone and dicyclohexyl ketone, but with more complexity regarding their spectral shifts in contrast to the case of benzil.

There have been reported a lot of experimental data on the originally weak electronic transitions which become substantially enhanced through interactions with environmental solvent molecules. Roughly, two types of environmental intensification in the transitions have been reported. One is associated largely with solvent polarities (and partly to dielectric constants): e.g., $^1L_b\leftrightarrow S_0$ transition spectra of pyrene[2—4)] and coronene.[3)] The other is closely related to solvent dispersion forces or refractive indexes: e.g., $^1L_b\leftrightarrow S_0$ transition spectra of benzene[5—8)] and naphthalene[5,9)] and $^1U\leftarrow S_0$ absorption spectra of *p*-benzoquinone,[5)] aliphatic monoketones[10)] and benzaldehyde.[11)] Recently, Abe has proposed experimental and theoretical expressions for the molecular electronic oscillator strength of the latter type of molecules and successfully applied those equations to several ketones and benzenes.[12,13)]

In the present work we studied the $S_1(n\pi^*)\leftarrow S_0$ absorption spectra of benzil in various solvents and found that there was a remarkable solvent intensification on the electronic transition.

Experimental

Benzil (a Tokyo Kasei Co. zone-melting reagent) was used as received. Dicyclohexyl ketone, benzophenone, cyclobutanone, and cyclopentanone (all commercially pure grade reagents) were purified through repeated vacuum distillations. These ketones were stored in sealed-off glass tubings in vacuo. Almost all of the solvents employed (Dotite spectroscopically pure grade reagents) were deoxygenated by nitrogen gas bubbling before the measurements and used without further purification. Benzonitrile was purified by vacuum distillation. Carbon disulfide was purified in the same way as reported previously.[14)]

The oscillator strength of the $S_1(n\pi^*)\leftarrow S_0$ transition for each of the aromatic ketones in fluid solutions is difficult to estimate accurately from the observed spectrum because there is almost always its overlap with the $S_2(\pi\,\pi^*)\leftarrow S_0$ transition absorption. Integration over a certain part of the absorption system may in principle give relative oscillator strengths correctly as long as there are little changes in the Franck–Condon factors and as long as there is no strong intermolecular interaction. For benzil, in almost all cases we employed a band maximum around 27—28000 cm^{-1} as the upper wavenumber limit of the integration although small spectral pattern changes are found in benzene solution and the two nitriles (especially in benzonitrile solution) probably because of band overlappings (see Fig. 1). The exception is for CS_2 which has a substantial absorption originating from the onset around 430 nm; for this case the integration was taken up to the first band maximum and then the integration value was compared to another intensity integration value over the corresponding band region in a standard solution, hexane. For benzophenone, a treatment similar to that for benzaldehyde[10)] was employed. The other experimental details are similar to those described previously.[11)]

Results and Discussion

Benzil. Although the molecular structure of benzil in fluid solutions has been reported nowhere, we may suppose that it is close to the crystal[15—18)] or the vapor[19)] structure which has proven to belong to the C_2 point group with a CO/CO torsional angle of ca. 110° (for crystal)[15,16)] or 117°±3° (for vapor)[19)] and with the phenyl rings nearly coplanar with the carbonyl groups. Under this assumed molecular symmetry, the $S_1(n\pi^*)\leftarrow S_0$ absorption transition may formally be allowed. Further, if benzil is simply assumed to be an electronically composite compound of two equivalent aromatic monocarbonyls (e.g., benzaldehyde or acetophenone), the relevant $\pi^*\leftarrow n$ transitions involve both allowed and forbidden characters. Despite this drastic assumption and the formal geometrical discussion, however, the $S_1(n\pi^*)\leftarrow S_0$ transition of benzil still retains substantial forbidden character originating from $\pi^*\leftarrow n$ transition properties; the very small oscillator strength observed confirms that this is the case.

Near UV absorption spectra of benzil were studied in various solvents at room temperature. Several spectra were picked up and shown in Fig. 1. The spectra show a few broad vibronic bands irrespective of

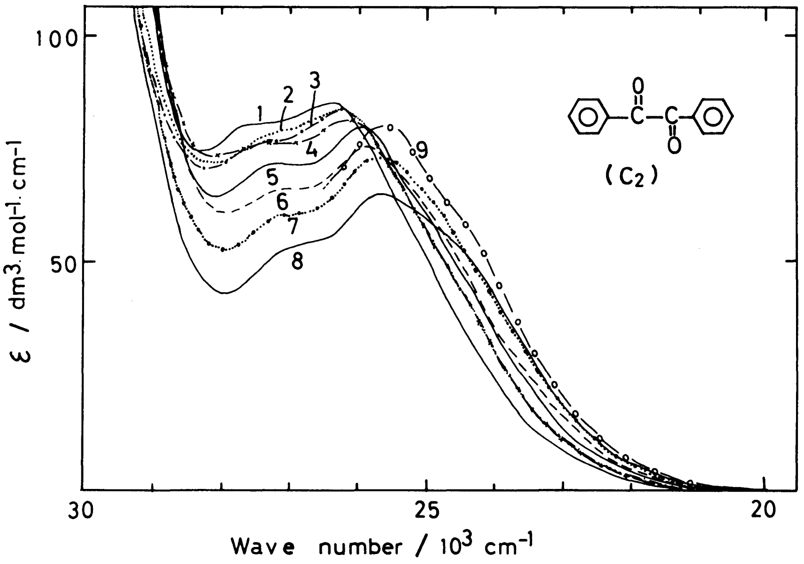

Fig. 1. $S_1(n\pi^*)\leftarrow S_0$ absorption spectra of benzil in various solvents at 20 °C. The solvents are: 1, acetonitrile; 2, 2-propanol; 3, chloroform; 4, benzonitrile; 5, benzene; 6, *p*-xylene; 7, carbon tetrachloride; 8, methylcyclohexane; and 9, carbon disulfide.

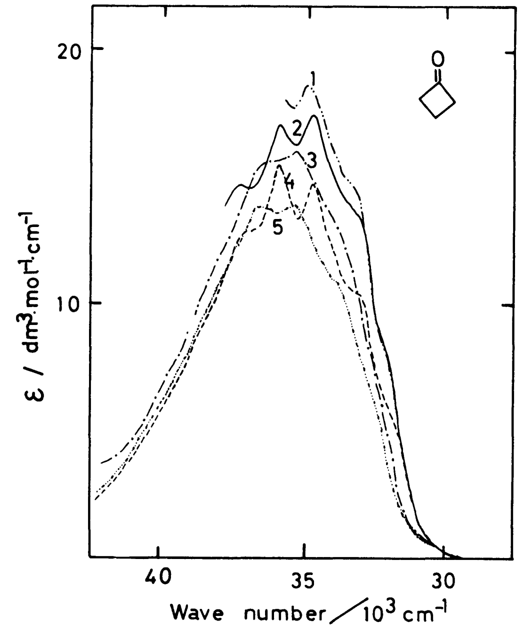

Fig. 2. $S_1(n\pi^*)\leftarrow S_0$ absorption spectra of cyclobutanone in some solvents at 20 °C. The solvents are: 1, benzene; 2, carbon tetrachloride; 3, chloroform; 4, cyclohexane; and 5, acetonitrile.

solvent polarity. Except for the spectrum in CS_2, it is generally found that toward the shorter the absorption wavelength of the peak maximum shifts, the greater the environmental intensity enhancement is. Solvents which effect such great intensity enhancement are alcohols, CH_2Cl_2, $CHCl_3$, and nitriles. With respect to the spectral increment in nonpolar and in several nearly nonpolar solvents such as hexane, methylcyclohexane, CCl_4, benzene, toluene, *p*-xylene, and CS_2, the usual refractive index or the dispersion force dependence[10–13] seems to hold qualitatively. The great intensity enhancement of the spectra in alcohols and chloromethanes differs from the case of pyrene.[2–4]

Cyclobutanone. Generally, cycloalkanones are chemically reactive and photochemically unstable.[20,21] Especially it has been known from the observation of the fluorescence excitation spectrum that cyclobutanone undergoes predissociation from its $S_1(n\pi^*)$ state.[22] As such, we were interested in observing near UV absorption spectra of cyclobutanone in fluid solutions. Similarly to the cases of acetone and cyclopentanone,[11] however, its $S_1(n\pi^*)\leftarrow S_0$ spectrum shows that the absorption transition is almost isolated from other absorption transitions lying at higher energies and gives a good example for a study on solvent intensification. The observed spectra are in part shown in Fig. 2. The deduced conclusion is in line with that reported previously for acetone and cyclopentanone[11]: The intensity enhancement observed is ascribed to the perturbation of dispersion forces between the solute and solvent molecules.

Benzophenone and Dicyclohexyl Ketone. Near UV absorption bands of benzophenone and dicyclohexyl ketone in polar solvents such as dichloromethane, chloroform, and acetonitrile become much broad and undergo intensity enhancement (see Fig. 3). This is a contrast to the results obtained for cyclobutanone, loc. cit. (cf. Fig. 2), for the other aliphatic monoketones,[11] and for benzaldehyde.[10] It has been known that these polar solvents form stoichiometric complexes with several aromatic carbonyl compounds such as benzophenone[23] and benzaldehyde[10] and with several aliphatic ketones.[24] Despite these facts of complex formation, however, it should be noted that the intensity enhancement of benzaldehyde (and also acetophenone) in dichloromethane and nitriles is not substantial; these solvents never belong to the most effective intensity perturbers, but are nearly in the dispersion force correlation line (for such a correlation diagram, see Fig. 3 of Ref. 10). For benzophenone, however, the great intensity enhancement in chloromethanes is quite remarkable.

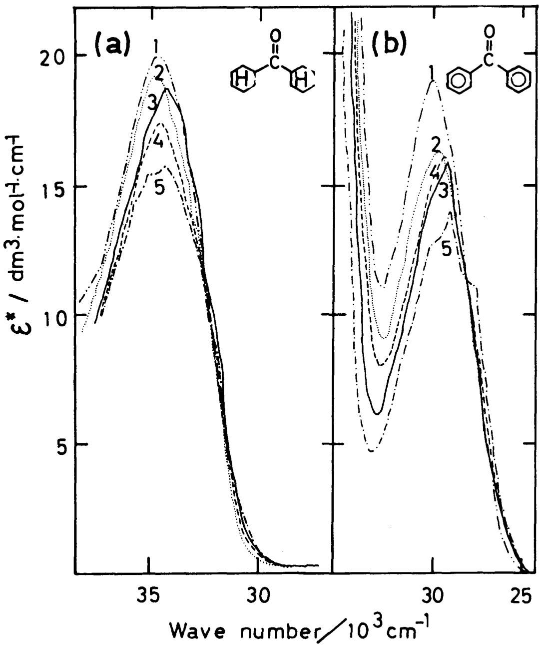

Fig. 3. $S_1(n\pi^*)\leftarrow S_0$ absorption spectra of (a) dicyclohexyl ketone and (b) benzophenone in some solvents at 20 °C. Note that the ordinate axis denotes ε^*, but not ε; where ε^* is a constricted molar extinction coefficient, i.e., $\varepsilon^*=c\cdot\varepsilon$ (c: constant). For case (a), $c=1/2$; and for case (b), $c=1/9$. The solvents are: 1, chloroform; 2, acetonitrile; 3, carbon tetrachloride; 4, benzene; and 5, cyclohexane.

Although no data on the ground state geometry of dicyclohexyl ketone has been reported, the molecule is thought to be considerably skewed as is supposed from photoselection experiments by Chandler and Goodman.[25] With the help of their experimental results, we investigated the near UV spectra of the molecule. The observed spectra are partially shown in Fig. 3a. Since this absorption system is almost isolated from other higher energy transitions like the other aliphatic monoketones, it is more clearly demonstrated that the absorption spectral intensity is certainly enhanced in acetonitrile and especially chloroform (and also in dichloromethane).

Complex Formation between Ketones and Polar Solvents. By measuring near UV and IR spectra in various fluid solutions, Becker has concluded that benzophenone forms 1 : 1 weak complexes with certain polar solvents such as nitriles, alcohols, and halomethanes.[23] We also confirmed that benzaldehyde belongs to the case.[10] These facts necessitated a simlar investigation for benzil, acetone, dicyclohexyl ketone, and the cyclic ketones. In almost all of the cases, we measured several isosbestic points which are manifestations of such 1 : 1 complex formation. As an

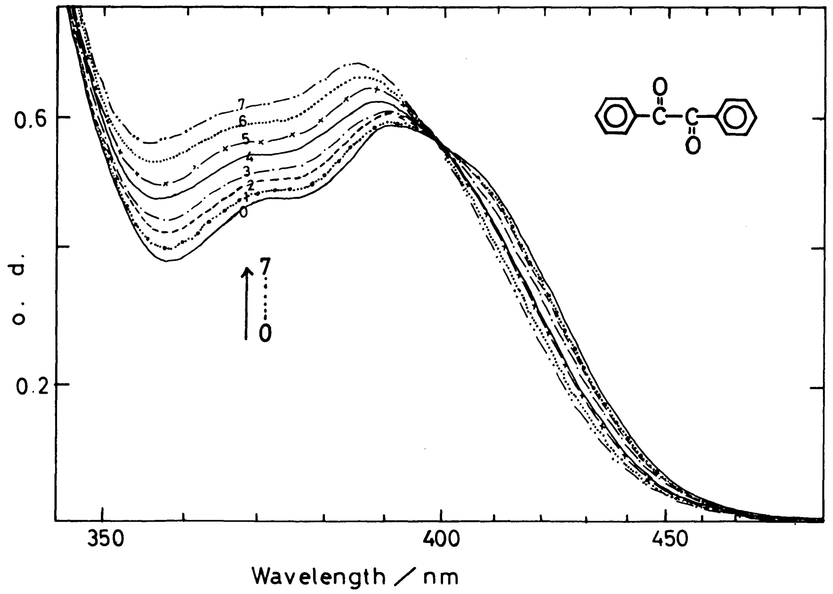

Fig. 4. Absorption spectral change of benzil with an increase in propionitrile concentraton. [Benzil]= 9×10^{-3} M in propionitrile-methylcyclohexane mixed solvents at 20 °C. Propionitrile concentrations in 10^{-1} M units are: (0), 0; (1), 1.41; (2), 2.83; (3), 5.66; (4), 11.3; (5), 14.2; (6), 28.3; and (7), 42.5.

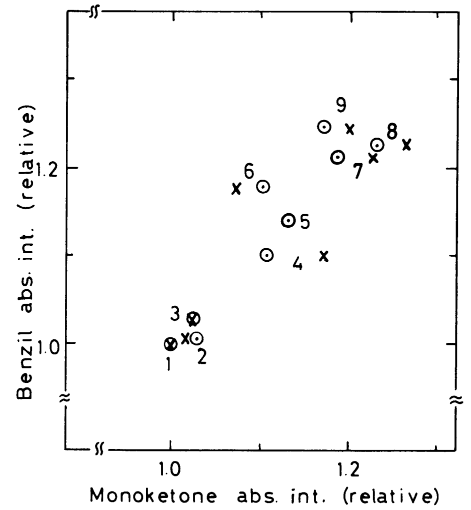

Fig. 5. Correlation between the environmental absorption intensity increment of benzil and that of each flexible monoketone: X, for benzophenone; and O, for dicyclohexyl ketone. The solvents are: 1, hexane; 2, cyclohexane; 3, methylcyclohexane; 4, carbon tetrachloride 5, *p*-xylene; 6, benzene; 7, dichloromethane; 8, chloroform; and 9, acetonitrile.

example, the absorption spectra of benzil in propionitrile–methylcyclohexane binary solvent solutions are shown in Fig. 4 although those are not so stoichiometric as the other monoketones' spectra (vide infra).

The absorption spectra of the ketones investigated are characterized and classified as follows:

(1) Almost all the spectra give several isosbestic (or nearly isosbestic) points when changing concentration of an active solvent in binary mixed solvent solutions. Such active solvents are: CH_3CN, C_2H_5CN, CH_2Cl_2, $CHCl_3$, ethanol, and 2-propanol. Appearance of these isosbestic points is a manifestation of 1:1 complex formation between the ketone and the solvent molecule. The equilibrium constants obtained are lying in the range of 10^0—10^{-2} M^{-1} (mostly at ca. 10^{-1} M^{-1}; 1 M=1 mol dm^{-3}).

(2) From their environmental intensity enhancement behaviors, the ketones observed are classified into two groups: (i) acetone and the cyclic ketones[26] and (ii) benzophenone, dicyclohexyl ketone, and benzil (see also Fig. 5).

(3) Despite of the existence of two carbonyl groups in benzil, nearly isosbestic points in binary mixed solvent solutions are observed even at a high concentration of such a polar solvent. This suggests that the kinetic reaction of 1:1 complex formation occurs dominantly. (An example for the benzil in propionitrile–methylcyclohexane mixed solvent system is shown in Fig. 4.)

(4) Among the group (ii) molecules, benzil seems to show a nearly linear relation between intensity enhancements and spectral shifts. This means that predominant environmental perturbing forces are, to a certain extent, restricted in the case of benzil. As such, benzil may be considered as a representative of the group (ii) molecules.

Table 1. Intensities of $S_1(n\pi^*) \leftarrow S_0$ Absorptions for Some Ketones[a)]

Ketone	$f^{b)}/10^{-4}$	$\varepsilon_{max}/M^{-1}\cdot cm^{-1}$
Group(i)		
Cyclobutanone	4.7	18
Cyclopentanone	4.8	18
Acetone	4.1	14
Benzaldehyde	(5.6)	24
Group(ii)		
Benzophenone	(22)	115
Dicyclohexyl ketone	7.8	33
Benzil	(12)	54

a) In cyclohexane solution at 20 °C. b) Evaluated oscillator strengths within ±5% errors. However, parentheses indicate some roughly evaluated values with larger errors (±15%) because of band overlaps.

The environmental intensity enhancement for the group (i) ketones is interpreted in terms of the dispersion force (or the solvent refractive index) scheme[10,11] while that for the group (ii) is neither in terms of the solvent polarity nor in terms of the refractive index.

Although we can not proceed further without speculations, a comparison among the absorption oscillator strengths (or absorption molar extinction coefficients) of those ketones is very interesting (see Table 1). The intensity of dicyclohexyl ketone in a hydrocarbon is about 1.6 times as great as that of cyclobutanone or cyclopentanone (or acetone) in the same solvent while the intensity of benzophenone is about four times greater than that of benzaldehyde (or acetophenone). Similarly, the intensity of benzil is about twice as great as that of benzaldehyde (or acetophenone) and also that of 2,3-butanedione (i. e., biacetyl).[27,28] A common factor in the group (ii) ketones is a rotationally flexible freedom about the adjacent bond(s) to the carbonyl group(s). A hydrogen bond[29] or a charge transfer type complex formation may deform the ground state geometry a little bit along the relevant torsional coordinate(s). This may bring forth further intensity increment by borrowing from $^1n\sigma^* \leftarrow S_0$ (and also $^1\pi\pi^* \leftarrow S_0$ for the aromatic ketones) transitions. In order to discuss further on benzil somewhat quantitatively, we feel a need to seek a much more suitable complex system in which the spectral intensity change may surpass ordinary solvent effects.

Concluding Remarks

In this paper we used the term "solvent effects" in a broad sense. On the occasion of comparison between the theoretical and the experimental data many authors have rather kept away from solvents with a special local interaction with guests as best as possible. As for clear-cut complex forming systems, there is no problem in selecting out such solvents. However, a problem arises when the solvent forms a very weak complex with a certain solute with its low stabilization energy which is comparable to or somewhat higher than the usual Boltzmann energy, i.e.,~kT: Even an "inert" solvent may generally form complexes (or clusters) at low temperature. Pyrene is one typical example of such cases.30) The present case for benzil may be another one: Intensity increment observed in the present work seems to occur in most all hydrogen donating solvents.29) This is in part supported by a preliminary work, that is in progress, on benzil in many binary solvent solutions into which 10^{-2}—10^{-3} mol dm^{-3} of trifluoroacetic acid or trichloroacetic acid added.

We are now being inclined to accept an assumption that a big deviation of an experimental data from the theory, if it is not easily explainable, is due to these weak local interactions.

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