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The $n \rightarrow \pi^*$ Bands of Phenyl Carbonyl Compounds, α-Diketones, and Quinones at Low Temperatures

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The positions and intensities of the $n \rightarrow \pi^*$ absorption bands in solutions at 77°K (in the rigid glass state) and at 201°K (in the liquid state) have been studied in comparison with those at room temperature. At 201°K the positions and intensities are similar to those at room temperature. At 77°K some distinct facts have been found in EP (ether-isopentane (1:1) mixture) which are different from those which hold in the liquid state: 1) In desoxybenzoin the absorption is remarkably weak in intensity. 2) In some α-diketones and β-naphthoquinone, the $n \rightarrow \pi^*$ bands shift greatly to the blue. 3) In β-naphthoquinone the absorption is remarkably strong in intensity. Discussions of the obtained results have been presented.

Heretofore, the electronic spectra of organic compounds at low temperatures have not been very extensively studied. It is expected that, in some cases, low-temperature electronic spectra may show valuable information about the structural and analytical chemistry because of their sharp vibrational structures and strong solvent effects.

The positions and intensities of $n \rightarrow \pi^*$ absorption bands are, in general, structure- and solvent-sensitive. The $n \rightarrow \pi^*$ bands of phenyl carbonyl compounds, α-diketones, and quinones in solutions at room temperature have been studied by many authors. In this work, the positions and intensities of these $n \rightarrow \pi^*$ bands in solutions at low temperatures have been studied in comparison with those at room temperature.

Experimental

Measurements. The electronic spectra were measured with a Cary recording spectrophotometer, 14 M. The partly-silvered quartz vacuum-flasks and quartz cells used in this work are shown in Fig. 1. A cylindrical cell had a long tube through which a sample solution was introduced into the cell. The cell was immersed in a cooling medium except for a part of the tube. The shaded portions in Fig. 1 were flanges which were attached to the inner windows of the vacuum flask and used in order to support the cell and make bubbles deviate from the optical path. The distance between a window of the cell and an inner window of the vacuum flask was *ca.* 1 mm. Vacuum flasks with cells 1 and 5 cm in optical path were made. The solvents used in this work have shown no absorption in the wave-region studied at 201°K and 77°K, using those at room temperature as references. Therefore, usual cylindrical quartz cells with the same path length as those of the sample cells were used as references in this work. With this apparatus measurements at low temperatures were made easily and precisely. The solvents used in the measurements were an ethyl ether-isopentane (1 : 1) mixture (EP), an methanol-ethanol (1 : 4) mixture (ME), an ethyl ether - isopentane - ethanol (5 : 5 : 2) mixture (EPA), and methylcyclohexane (MCH). The measurements were carried out at the temperature of liquid nitrogen (77°K), at the temperature of dry ice - ethanol (201°K), and at room temperature. At 77°K all the solutions used were transparent in the rigid glass state, while at 201°K they were transparent in the liquid state.

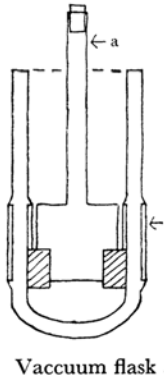

Fig. 1. Vaccuum flask and cell.
a cell b window

Materials. The reagents used in this work were all of the purest grade commercially available except for the β-naphthoquinone and the *N*-acetylisatin. The acetophenone, isobutyrophenone, and diacetyl of the G. R. grade of the Tokyo Kasei Kogyo Co., and the 1-phenyl-1,2-propanedione of the Eastman grade of

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Distillation Products Ind. were used without further purification. The benzophenone, desoxybenzoin, and benzil were purified by recrystallization. The *p*-benzoquinone was purified by sublimation. The 2-methylanthraquinone and camphorquinone were purified by vacuum sublimation. The α-naphthoquinone was purified according to Fieser's method.[1] The β-naphthoquinone was prepared and purified according to Fieser's method.[1] The *N*-acetylisatin was prepared by the *N*-acetylation of isatin and was purified by recrystallization. The *n*-heptane, ethyl ether, and isopentane were purified according to the methods described in our previous papers.[2,3] The methylcyclohexane, methanol, and ethanol were of the same quality as those described in a previous paper.[3]

Results

In order to compare the absorption intensities of the $n\rightarrow\pi^*$ bands at low temperatures with that at room temperature, a ratio of the integrated absorption intensity was obtained. The shift in the wave number of the positions of the $n\rightarrow\pi^*$ bands, ($\Delta\bar{\nu}$), and the ratio of the integrated absorption intensity of the $n\rightarrow\pi^*$ bands, (R.I.), between a low temperature and room temperature, are shown in Tables 1—3. In Tables 1—3, I—XIII are acetophenone, isobutyrophenone, desoxybenzoin, benzophenone, diacetyl, camphorquinone, 1-phenyl-1,2-propanedione, benzil, *N*-acetylisatin, *p*-benzoquinone, α-naphthoquinone, 2-methylanthraquinone, and β-naphthoquinone respectively. As for the $\Delta\bar{\nu}$ and R.I. in these tables, for example, if $\Delta\bar{\nu}$ is positive, the $n\rightarrow\pi^*$ band at a low temperature shifts to the blue relative to that at room temperature, and, for example, if R.I. is larger than one, the integrated absorption intensity of the $n\rightarrow\pi^*$ band at a low temperature is larger than that at room temperature. In order to correct for the volume contraction at a low temperature, the measured absorption intensities at low temperatures were multiplied by factors (0.9 for 201°K and 0.8 for 77°K) chosen in view of the reported data.[4] The results obtained at 77°K for α-naphthoquinone in EPA and desoxybenzoin in EP with 1 cm and 5 cm path cells were the same.

The $n\rightarrow\pi^*$ bands, obtained mainly in EP, are shown in Figs. 2—14. In these figures all the spectra have been corrected for the volume contraction at low temperatures. In quinones there are uncertainties in the R.I. values due to a large overlapping of $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ bands, as may be seen in Figs. 12—14.

Discussion

As is shown in Tables 1—3 and in Figs. 4, 6, and 14, the positions and absorption intensities at 201°K

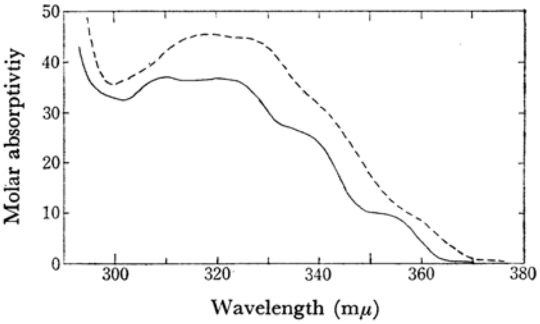

Fig. 2. Acetophenone, solvent EP.
------ Room temperature, —— 77°K

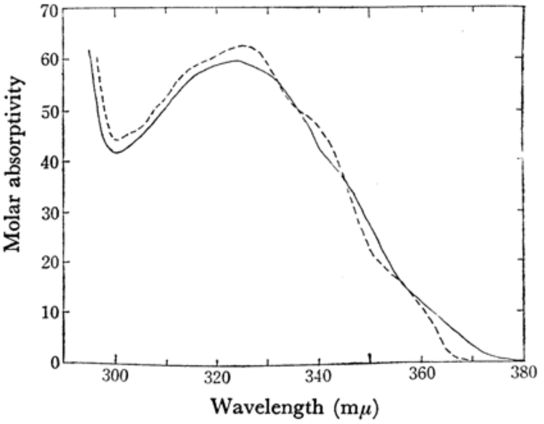

Fig. 3. Isobutyrophenone, solvent EP.
------ Room temperature, —— 77°K

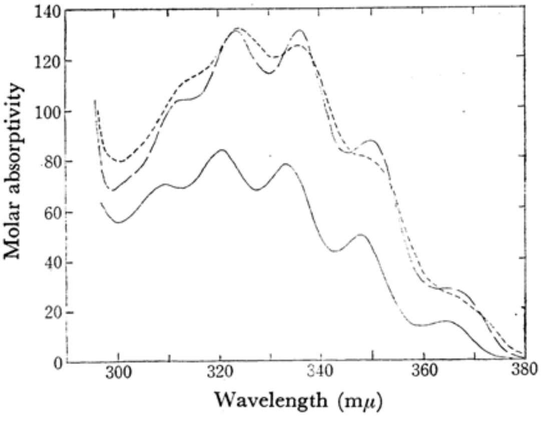

Fig. 4. Desoxybenzoin, solvent EP.
------ Room temperature, —— 201°K, —— 77°K

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[1] L. F. Fieser, "Experiment in Organic Chemistry," D. C. Heath and Co., Boston (1941), pp. 230, 232 and 233.

[2] A. Kuboyama, This Bulletin, **33**, 1027 (1960).

[3] A. Kuboyama and S. Yabe, *ibid.*, **40**, 2475 (1967).

[4] KJ. Rosengren, *Acta Chem. Scand.*, **16**, 1421 (1962); R. Passerini and I. G. Ross, *J. Sci. Instr.*, **30**, 276 (1953).

are in all cases similar to those at room temperature. This fact is thought to be mainly due to the fact that solutions at 201°K are in the liquid state the same as it is at room temperature.

As for the phenyl carbonyl compounds in Table 1, the $n \rightarrow \pi^*$ bands at 77°K shift to the blue relative to those in the liquid state except for that of isobutyrophenone, the shift of which at 77°K relative to that at room temperature is not clear. This blue-shift in EP may be mainly due to a charge transfer (CT) interaction of the n–π type,[5] to be mentioned later, between an oxygen atom in ethyl ether and phenyl carbonyl compounds, while the blue-shift in EPA may be due to hydrogen-bond formation between carbonyl groups and alcohols, both probably stronger than those in the liquid state.

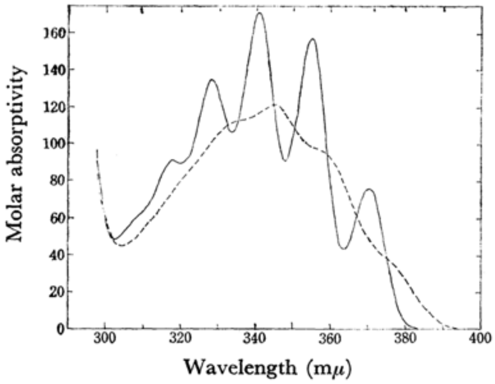

Fig. 5. Benzophenone, solvent EP.
------ Room temperature, —— 77°K

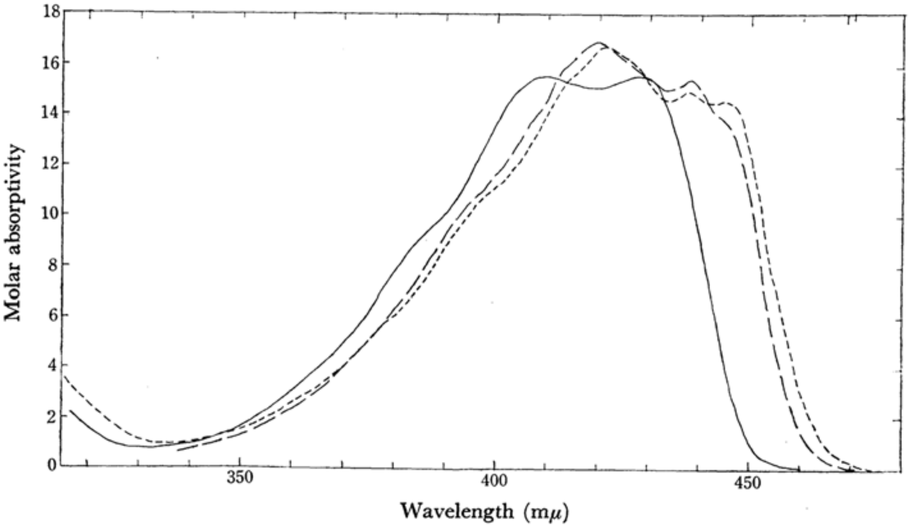

Fig. 6. Diacetyl, solvent EP.
------ Room temperature, — — 201°K, —— 77°K

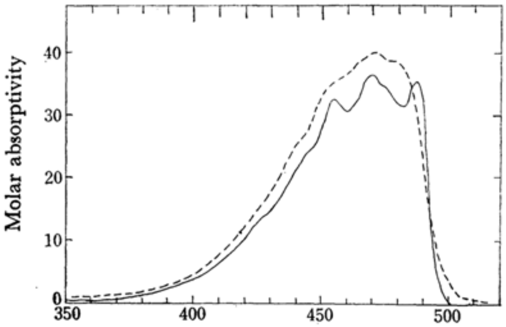

Fig. 7. Camphorquinone, solvent EP.
------ Room temperature, —— 77°K

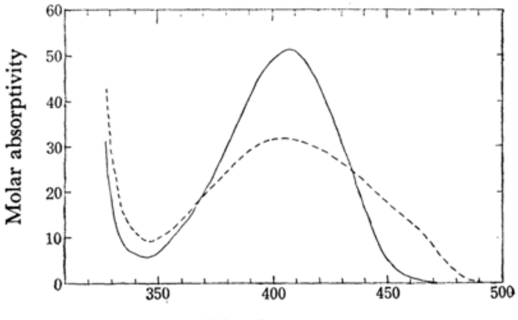

Fig. 8. 1-Phenyl-1,2-propanedione, solvent EP.
------ Room temperature, —— 77°K

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[5] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

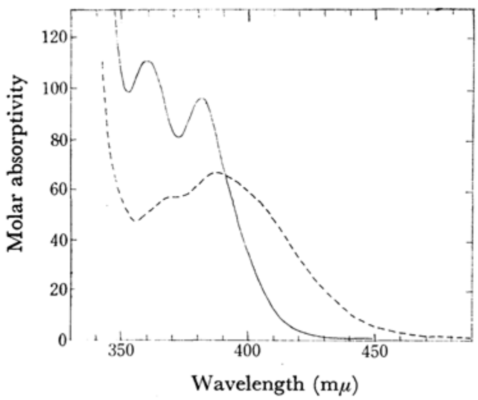


Fig. 9. Benzil, solvent EP.
------ Room temperature, —— 77°K

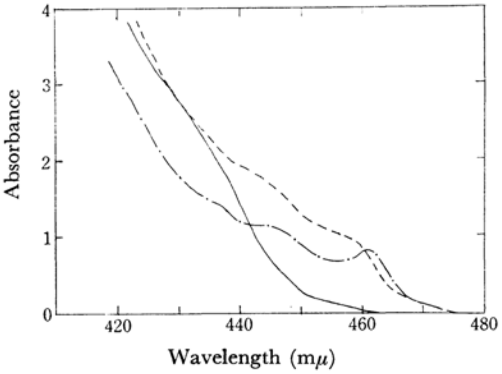


Fig. 10. *N*-Acetylisatin.
—·— *n*-Heptane (Room temperature),
------ EP (Room temperature),
—— EP (77°K),
(The scale of the ordinate is arbitrary.)

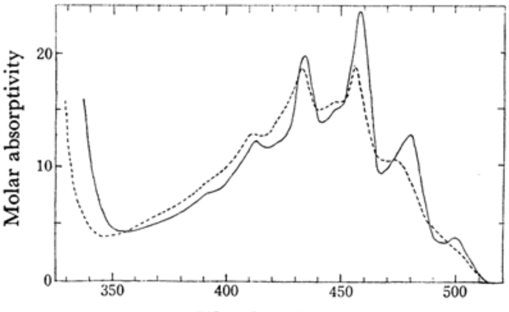


Fig. 11. *p*-Benzoquinone, solvent EP.
------ Room temperature, —— 77°K

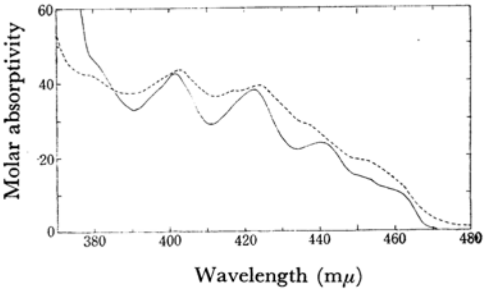


Fig. 12. α-Naphthoquinone, solvent EP.
------ Room temperature, —— 77°K

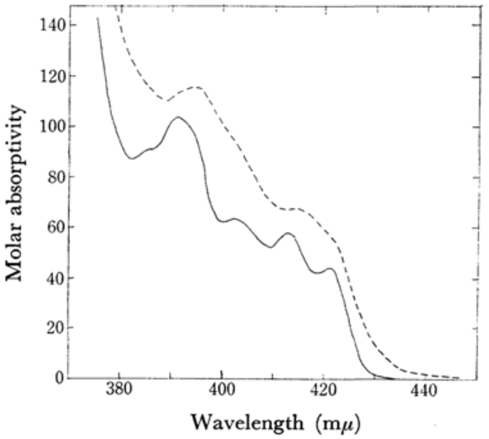


Fig. 13. 2-Methyl-anthraquinone, solvent EP.
------ Room temperature, —— 77°K

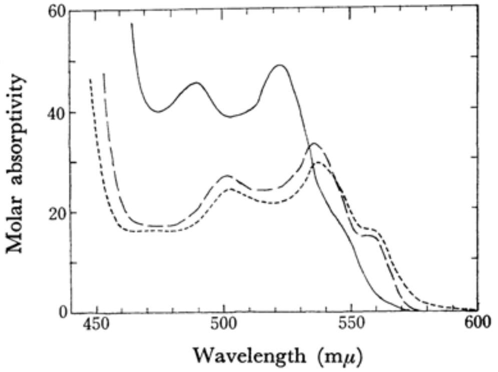


Fig. 14. β-Naphthoquinone, solvent EP.
------ Room temperature, —·— 201°K,
—— 77°K

As for the R.I. values in Table 1, a remarkable decrease in the absorption intensity of desoxybenzoin is found in EP and EPA at 77°K, especially in the former, relative to those in the liquid state, as may also be seen in Fig. 4. The strong intensity of the $n \rightarrow \pi^*$ band of benzophenone may be attributed to the mixing of the (n, π^*) state with (π, π^*) states due to the overlapping of the n-orbital of a carbonyl oxygen atom and the π-orbitals of two phenyl groups, because of the non-coplanarity of the benzophenone molecule resulting from steric hindrance between the two phenyl groups. On the other hand, the strong intensity of the $n \rightarrow \pi^*$ band of desoxybenzoin in the liquid state may

TABLE 1. PHENYL CARBONYL COMPOUNDS

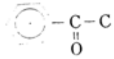
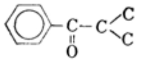
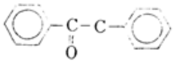
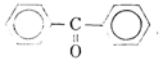
		Solvent	$\Delta\bar{\nu}$ (cm^{-1})	IR	Temp. (°K)
(I)		EP	~350	0.80	77
(II)		EP	~ 0	1.00	77
(III)		MCH	0	0.98	201
		EP	0	0.95	201
		EP	300	0.59	77
		EPA	320	0.70	77
		ME	~480	~0.85	77
(IV)		MCH	80	1.10	201
		EP	320	1.13	77
		ME	~240	~0.9	77

TABLE 2. α-DIKETONES

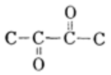
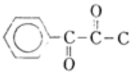
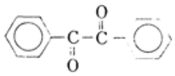
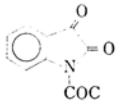
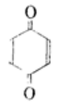
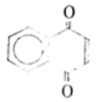
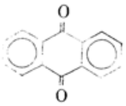
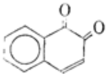
		Solvent	$\Delta\bar{\nu}$ (cm^{-1})	IR	Temp. (°K)
(V)		MCH	0	1.02	201
		EP	0	1.00	201
		EP	890	0.89	77
(VI)		EP	− 50		77
		EPA	−100	0.9	77
		ME	−200		77
(VII)		EP	−180	1.11	77
(VIII)		EP	~500	~1.0	77
(IX)		EP	~800		77

TABLE 3. QUINONES

		Solvent	$\Delta\bar{\nu}$ (cm^{-1})	IR	Temp. (°K)
(X)		EP	− 50	1.00	201
		EP	− 90	1.0	77
(XI)		EP	110	0.8	77
		EPA	40	0.8	77
(XII)		EPA	~120	0.8	77
(XIII)		EP	50	1.05	201
		EP	550	~1.5	77

be assumed to be mainly attributable to the mixing of the (n, π^*) state with (π, π^*) states of the non-conjugated phenyl group, due to the overlapping of the *n*-orbital of the carbonyl oxygen atom and the π-orbitals of the non-conjugated phenyl group; this assumption is based on the facts about α-phenylcarbonyl compounds presented by Kumler *et al.*[6] Therfore, the above-mentioned fact about desoxybenzoin at 77°K may be attributed to the decrease in the overlapping of the oxygen *n*-orbital and the π-orbitals of the non-conjugated phenyl group in the rigid glass state relative to those in the liquid state.

As for the α-diketones in Table 2, it is noticeable that the $n \rightarrow \pi^*$ bands of diacetyl and *N*-acetylisatin in EP at 77°K shift greatly to the blue relative to those in the liquid state, while the $n \rightarrow \pi^*$ bands of camphorquinone and 1-phenyl-1,2-propanedione shift a little to the red, as may also be seen in Figs. 6, 7, 8, and 10. Such a large blue shift is also found in β-naphthoquinone, as may be seen in Table 3 and Fig. 14. In all the three α-diketones in Table 2 except 1-phenyl-1,2-propanedione and benzil, the two carbonyl groups are assumed to be nearly coplanar. This large blue shift is assumed to be due to a strong CT interaction of the n–π type between ethyl ether in EP on one hand, and α-diketones and β-naphthoquinone on the other hand, in the rigid glass state. In a previous work[2] we found that the $n \rightarrow \pi^*$ bands of *o*-quinones in dioxane at room temperature shift greatly to the blue relative to those in *n*-heptane, while those in ethyl ether shift only a little to the blue. In that work this large blue shift in *o*-quinones in dioxane was attributed to the strong CT interaction of the n–π type between dioxane and *o*-quinones, while the small blue shift in ethyl ether was attributed to a weakening of the CT interaction of the n–π type due to steric hindrance caused by the chains of ethyl ether.

It may be concluded from the theoretical considerations that an oxygen atom in dioxane coordinates itself to some point between two adjacent carbonyl carbon atoms in *o*-quinones in the CT interaction of the n–π type. This conclusion is supported by the results obtained by the X-ray crystal analyses of parabanic acid and chloranil.[7] It may be assumed on the basis of these results that the large blue shift in the α-diketones and β-naphthoquinone in EP mentioned above is due to a strong CT interaction of the n-π type between ethyl ether on the one hand, and α-diketones and β-naphthoquinone on the other hand, at 77°K, an interaction similar to that between dioxane and *o*-quinones at room temperature. This strong CT interaction of the n–π type between ethyl ether and α-diketones and β-naphthoquinone at 77°K is assumed to be ascribable to a weakening of the above-mentioned steric hindrance due to a weakening of thermal motion of the chains of ethyl ether, relative to that in the liquid state.

In camphorquinone a similar strong CT interaction cannot be expected, since the close approach of an oxygen atom in ethyl ether to the carbonyl carbon atoms in camphorquinone is prevented by steric hindrance. Therefore, the small red shift in camphorquinone in EP shown in Table 2 may be due to a reinforced van der Waals interaction between camphorquinone and EP at 77°K relative to that at room temperature. In EPA and ME, a hydrogen bond between camphorquinone and alcohols is assumed to be formed at 77°K as well as in the liquid state. Therefore, the effect of the hydrogen-bond formation on the shift of the $n \rightarrow \pi^*$ band at 77°K in camphorquinone is contrary to that in the phenyl carbonyl compounds shown in Table 1 and may be characteristic of camphorquinone.

As for 1-phenyl-1,2-propanedione and benzil, the molecules are assumed to be greatly twisted about the (O=)C–C(=O) bond due to the strong steric hindrance.[8] Therefore, any CT interaction of the n–π type between EP and 1-phenyl-1,2-propanedione and benzil may be weak. The twisting angles in these molecules in the rigid glass state may be somewhat different from those in the liquid state. At this stage further discussions about their $n \rightarrow \pi^*$ bands cannot be undertaken.

As for the quinones in Table 3, the blue shift at 77°K in α-naphthoquinone and 2-methylanthraquinone may be interpreted in the same manner as that in Table 1, while the red shift at 77°K in *p*-benzoquinone is rather puzzling. In the $n \rightarrow \pi^*$ band of β-naphthoquinone, a large blue shift and a large enhancement of its absorption intensity at 77°K relative to those in the liquid state are found, as is shown in Table 3 and Fig. 14. The former fact has already been discussed together with the situation in α-diketones. The latter fact may be due to the increased mixing of the (n, π^*) state with the low-energy (π, π^*) state at 77°K, where the both states are energetically closer to each other relative to those in the liquid state, as is shown in Fig. 14, because of the large blue shift of the $n \rightarrow \pi^*$ band mentioned before and the red shift of the $\pi \rightarrow \pi^*$ band at the longer wavelengths (the tail of which band may be seen in the figure) at 77°K relative to those in the liquid state.

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[6] W. D. Kumler, L. A. Strait and E. L. Alpen, *J. Am. Chem. Soc.*, **72**, 1463 (1950).

[7] D. R. Davies, J. J. Blum, *Acta Cryst.*, **8**, 129 (1955); S. S. C. Chu, G. A. Jeffrey and T. Sakurai, *ibid.*, **15**, 661(1962).

[8] I. Bernal, *Nature*, **200**, 1318 (1963); P. H. Cureton, C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, **1961**, 4447; H. Hirokawa and T. Ashida, *Acta Cryst.*, **14**, 77 (1961).