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Solvent Effects on the Intensity of the nπ* Absorption Spectra of 1-Phenylethylenetrithiocarbonate and *p*-Benzoquinones

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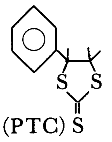
Synopsis. The nπ* absorption intensities of 1-phenylethylene trithiocarbonate (**1**), *p*-benzoquinone (**2**), and 2,5-di-*t*-butyl-p-benzoquinone (**3**) in nonpolar solvents are compared with the theoretical ones calculated by the use of Abe's formula, in which the Onsager-cavity field is used. For **3**, the theoretical intensities are well correlated with the observed ones, whereas for the others there are discrepancies, especially for **1**. These discrepancies are attributed to strong dispersion-force interactions with the solvents.

Experimental data about solvent effects on the intensity of the electronic absorption spectra are still scarce. Previously, however, we found that the intensity of the nπ* absorption spectrum of *p*-benzoquinone (PBQ) in carbon disulfide is far stronger than that in heptane.[1] Recently, we also found that the intensification of the thiocarbonyl nπ* absorption spectrum of 1-phenylethylene trithiocarbonate (PTC) in carbon disulfide is greater than that of PBQ. In the studies of the solvent effects on the intensity of the nπ* absorption spectra PTC is favorable in that the nπ* absorption spectrum is at far longer wavelengths than the longest wavelength ππ* absorption spectrum and in that the steric hindrance about the thiocarbonyl group is small.



(PTC)

Experimental

Measurements. The absorption spectra have been obtained by means of a Cary 14 self-recording spectrophotometer. The integrated absorption intensities of the spectra were obtained by measuring the weight of the section papers, on which the areas are the same as those surrounded by the absorption curves and the baselines. In order to minimize errors which might be caused by any unevenness of the quality of the section papers used, they were calculated from the ratio of the weight of a portion of an absorption spectrum to that of a polygon[2] inscribed in it. In this method, the errors were within 0.4%.

Materials. The PTC (Toyotama Kogyo Co.) was purified by vacuum sublimation (mp 85.0—86.0 °C). The PBQ (Tokyo Kasei Kogyo Co.) was purified by sublimation (mp 115.0—116.0 °C). The 2,5-di-*t*-butyl-*p*-benzoquinone (2,5-PBQ) (Tokyo Kasei Kogyo Co.) was twice recrystallized from cyclohexane (mp 152.7 °C). All the solvents employed, *i.e.*, cyclohexane, benzene, carbon tetrachloride, and carbon disulfide, were of a spectro-grade (all from Wako Pure Chemical Industries Co. except for the carbon disulfide of E. Merck), and were used without further purification. GR-grade 1-methylnaphthalene (Tokyo Kasei Kogyo Co.) was purified by vacuum distillation.

Results and Discussion

The long-wavelength absorption spectra of PTC in several nonpolar solvents in Fig. 1 can safely be assigned to the thiocarbonyl nπ* spectrum[1,3] from their positions and from the intensity and solvent effects on their positions; this nπ* transition has previously been thought to be essentially forbidden, like that of quinones,[1] in view of the weak intensity of these spectra. The intensity of the nπ* spectra of PTC and quinones is thought to be essentially due to the vibronic mixing of the nπ* and the closest allowed ππ* state.[4]

In Tables 1 and 2, the ratios of the *f*-values (oscillator strengths) of the nπ* spectra in various nonpolar solvents and that in cyclohexane are compared with those obtained by means of Abe's formula,[5]

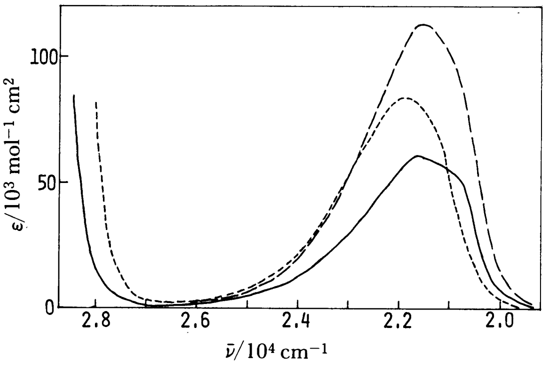


Fig. 1. The nπ* absorption spectra of 1-phenylethylene trithiocarbonate in nonpolar solvents. ——: Cyclohexane, ----: benzene, —–—: carbon disulfide.

TABLE 1.[a)] 1-PHENYLETHYLENE TRITHIOCARBONATE ($f_{C_6H_{12}}=3.60\times10^{-4}$)

Solvent	n_D^{20}	$\bar{\nu}_{max}$	ε_{max}	$f_x/f_{C_6H_{12}}$	
		cm^{-1}	10^3 mol^{-1} cm^2	Obsd	Theoret.
Cyclohexane	1.426	21650	60.5	1.00	1.000
Carbon tetrachloride	1.460	21800	80	1.21	0.978
Benzene	1.501	21900	84	1.19	0.949
1-Methyl-naphthalene	1.617	22000	101.5	1.28	0.864
Carbon disulfide	1.628	21600	112.5	1.35	0.841

a) f_x denotes the *f*-value in the solvent X.

TABLE 2.[a] *p*-BENZOQUINONE (**1**) ($f_{C_7H_{16}}=1.73\times10^{-4}$) AND 2,5-di-*t*-BUTYL-*p*-BENZOQUINONE (**2**) ($f_{C_6H_{12}}=2.68\times10^{-4}$)

	Solvent	n_D^{20}	$\bar{\nu}_{max}$	f_x/f_{HC}[b]	
			cm^{-1}	Obsd	Theoret.
1	Heptane	1.388	21850	1.00	1.000
	Carbon tetrachloride	1.460	21850	1.02	0.943
	Carbon disulfide	1.628	21750	1.04	0.811
2	Cyclohexane	1.426	21850	1.00	1.000
	Carbon tetrachloride	1.460	21900	0.98	0.972
	Carbon disulfide	1.628	21750	0.84	0.839

a) f_X denotes the *f*-value in the solvent X. b) f_{HC} denotes $f_{C_7H_{16}}$ in **1** and $f_{C_6H_{12}}$ in **2**.

derived with the Onsager-cavity field, on the basis of the quantum-mechanical theory. In obtaining the observed *f*-values, the factor of $(1/n_D^{20})^2$[2] (n_D^{20}: refractive index of the D-line at 20 °C) is included.[5,6] In Abe's work,[5] the formula derived with the Onsager-cavity field best reproduced the observed results among the many formulas thus far derived by many authors. In 2,5-PBQ, the observed results are close to the theoretical ones, while in PTC and PBQ the observed results are far from the theoretical ones, especially in PTC. The above results can be interpreted as follows.

In 2,5-PBQ, solvent molecules can hardly ever approach the carbonyl oxygen atoms because of the heavy steric hindrance caused by the two *t*-butyl groups. In PBQ, the hydrogen atoms attached to the α-carbon atoms cause something of a steric hindrance to the approach of solvent molecules to its carbonyl oxygen atoms. On the other hand, in PTC there is no such steric hindrance. Moreover, in PTC the bond length of the thiocarbonyl C–S bond is longer than that of the C–O bonds of PBQ, and the 3p lone-pair orbital of the sulfur atom is far more spread outward than the 2p lone-pair orbital of the oxygen atoms of PBQ. Therefore, solvent molecules can approach more easily to the thiocarbonyl sulfur atom of PTC than to the oxygen atoms of PBQ.

From the above discussion, the before-mentioned discrepancy of the observed results from the theoretical ones may be concluded to be essentially related to the approachability of solvent molecules to these heteroatoms. As the main interaction between nonpolar solvent molecules and these heteroatoms, which causes the intensification of the nπ* spectra, any interaction but the dispersion-force interaction can hardly ever be cited. Previously Koyanagi[7] theoretically proved that the dispersion-force interaction between solvents and a solute may cause mixing between a forbidden state and the allowed states of the solute, resulting in an intensification of the forbidden spectrum, and later Koyanagi *et al.*[7,8] experimentally showed this on the nπ* absorption spectra of carbonyl compounds. The dispersion-force interaction is very sensitive to the distance between the component molecules. Moreover, it becomes, in general, stronger with decreases in the ionization potentials of the component molecules. The ionization potential of the 3p lone-pair electron of the thiocarbonyl sulfur atom in PTC is considerably lower than that of the 2p lone-pair electrons of the carbonyl oxygen atoms in PBQ. Consequently, the dispersion-force interaction of PTC with solvents may be considerably stronger than that of PBQ. Therefore, the main cause of the before-mentioned discrepancy of the observed results may be attributed to the strong dispersion-force interaction of PTC and PBQ with the nonpolar solvents.

Generally speaking, the blue-shift of an nπ* spectra in a solvent relative to that in saturated hydrocarbons shows that there are some specific interactions between the solvent and the solute, such as hydrogen-bond formation and charge-transfer and electrostatic interactions.[1] The nπ* spectrum of PTC in carbon disulfide is at almost the same position as that in cyclohexane.[1] This fact may show that specific interactions between carbon disulfide and PTC are very small. Therefore, the remarkable enhancement of the nπ* absorption intensity of PTC in carbon disulfide can hardly ever be attributed to the complex formation between carbon disulfide and PTC.

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