BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1673—1679(1972)

The *n*-*π** Absorption and Phosphorescnce of Terephthalaldehyde

Yoshio MURAKAMI, Ryoichi SHIMADA and Yoshiya KANDA
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka

(Received December 17, 1971)

The $n \rightarrow \pi^*$ absorption spectrum of terephthalaldehyde (TPA) has been studied. The $f_{n\rightarrow\pi^*}$-value observed in cyclohexane at room temperature was 1.3×10^{-3}, which was 2.4 times that of benzaldehyde (BA). Vibrational analyses of the absorption and phosphorescence spectra of TPA indicate that the CHO-torsional, CHO-wagging, aldehyde H-wagging, and out-of-plane ring deformation vibrations are important in the vibronic perturbation between (n,π^*) and (π,π^*) states. The spectral structures and the results of CNDO computations of the $f_{n\rightarrow\pi^*}$-values of the $n \rightarrow \pi^*$ absorptions of TPA and BA suggest that the intensity enhancement in the TPA absorption is due to an increase in the vibronic perturbation between (n,π^*) and (π,π^*) states as well as to an increase in the electronically-allowed character in TPA in comparison with that in BA.

Since McMurry's study was published in 1941, a number of investigations have been carried out on the singlet-singlet electronic $n \rightarrow \pi^*$ systems of various aliphatic and aromatic carbonyls. Especially, the $n \rightarrow \pi^*$ absorptions of benzaldehyde and its derivatives have been a major object of interest.

It has been shown that the $n \rightarrow \pi^*$ transition of benzaldehyde is electronically allowed by the formal destruction of the C_{2v} symmetry of its parent molecule, formaldhyde, but a significant amount of the intensity is induced by $\pi \rightarrow \pi^*$ transitions through vibronic interaction between (n,π^*) and (π,π^*) states.

From the nature of the vibronic interactions, the out-of-plane vibrations of the CHO group are known to be important in promoting vibronic intensification.[1-4] Goodman *et al.* found out-of-plane CHO-torsional, CHO-wagging, and ring deformation vibrations in the $n \rightarrow \pi^*$ absorption and concluded that these vibrations are most effective in the intensification.[5-10]

It is interesting to study the $n \rightarrow \pi^*$ absorption of terephthalaldehyde(TPA), which is composed of a benzene ring and two CHO groups. TPA gives an absorption spectrum in the near ultraviolet region quite similar to that of benzaldehyde(BA), but the intensity of the $n \rightarrow \pi^*$ absorption is about 2.4 times greater than that of BA. Two main sources of the intensification of the $n \rightarrow \pi^*$ absorption in TPA may be considered to be (1) an increase in the intrinsic

---

[1] E. C. Lim and Y. H. Li, *J. Chem. Phys.*, **50**, 4925 (1969).

[2] E. C. Lim, "Molecular Luminescence," ed. by E. C. Lim, Benjamin, New York (1969), p. 469.

[3] E. C. Lim, Y. H. Li, and R. Li, *J. Chem. Phys.*, **53**, 2443 (1970).

[4] R. Shimada and L. Goodman, *ibid.*, **43**, 2027 (1965).

[5] J. M. Hollas, E. Gregorek, and L. Goodman, *ibid.*, **49**, 1745 (1968).

[6] R. Zwarich and L. Goodman, *Chem. Phys. Lett.*, **7**, 609 (1970).

[7] R. Zwarich, J. Smolarek, and L. Goodman, *J. Mol. Spectry.*, **38**, 336 (1971).

[8] M. Koyanagi, R. Zwarich, and L. Goodman, *Chem. Phys. Lett.*, **9**, 74 (1971).

[9] M. Koyanagi and L. Goodman, *ibid.*, **9**, 636 (1971).

[10] M. Koyanagi and L. Goodman, *J. Chem. Phys.*, **55**, 2959 (1971).

$n\rightarrow\pi^*$-allowed character and (2) an increase in vibronic interaction between the (n,π^*) and (π,π^*) states. TPA has two nearly degenerate (n,π^*) states; one gives an electronically-allowed transition, and the other, a forbidden $n\rightarrow\pi^*$ transition. The forbidden transition may be also perturbed by $\pi\rightarrow\pi^*$ transitions, and this perturbation may contribute to the intensity-enhancement of the $n\rightarrow\pi^*$ absorption.

The purpose of this paper is to discuss the nature of the $n\rightarrow\pi^*$ absorption of TPA and to show the probable sources for the intensification of the absorption.

The phosphorescence spectrum of TPA will also be studied because the absorption and phosphorescence are both due to the $n\rightarrow\pi^*$ transition and because their spectral structures are very similar to each other. The information obtained from the study of the phosphorescence spectrum of TPA will be useful in understanding the nature of the $n\rightarrow\pi^*$ absorptions.

Experimental

The TPA was prepared through the dehydration reaction of tetrabromo-*p*-xylene, which had been synthesized by means of *p*-xylene and bromine.[11] The crude TPA was purified by repeated recrystallization from 10% hot methanol and by repeated vacuum sublimation. Cyclohexane, methylcyclohexane, ethyl ether, isopentane, and ethanol were purified by ordinary methods.[12]

The near-ultraviolet absorption spectrum of TPA was studied in cyclohexane at room temperature and in EPA at 77°K with a Shimadzu multipurpose recording spectrophotometer MPS-50L and in the vapor with a recording spectrophotometer made of a Bausch & Lomb 500-mm grating monochromator, an RCA 1P28 photomultiplier tube, an RCA amplifier WV-84C, and a recorder. A 500-W xenon short-arc lamp and a tungsten lamp were used as the continuous-light sources. The vapor pressure of TPA in a vapor cell 45 cm in length was controlled by changing the temperature of the cell from 80 to 100°C. The infrared spectrum was recorded with a Hitachi-Perkin-Elmer infrared spectrophotometer, type 225, for the 200—4000 cm^{-1} region in the KBr disk. The Raman spectrum of the TPA crystal was recorded in the 250—4000 cm^{-1} region with a JRS-U1 laser Raman spectrophotometer equipped with a JEOL argon-ion laser, JLG-A4. The depolarization factor of the Raman lines was also measured in ethanol.

The phosphorescence spectra were studied in methylcyclohexane at 4.2 and 77°K with a Hilger E2 spectrograph. The degree of polarization of the phosphorescence was measured in EPA at 77°K by the usual method.[13]

Results and Discussion

Phosphorescence. The near-ultraviolet absorption spectra of TPA and BA[4] observed in EPA at 77°K are shown in Fig. 1. By analogy with the BA absorption, the three main absorption bands of TPA appearing in the 3900—3200, 3200—2800, and 2800—2300 Å regions can be ascribed to ${}^1U(n,\pi^*)\leftarrow S_0$, ${}^1L_b(\pi,\pi^*)\leftarrow S_0$, and ${}^1L_a(\pi,\pi^*)\leftarrow S_0$ transitions respectively.

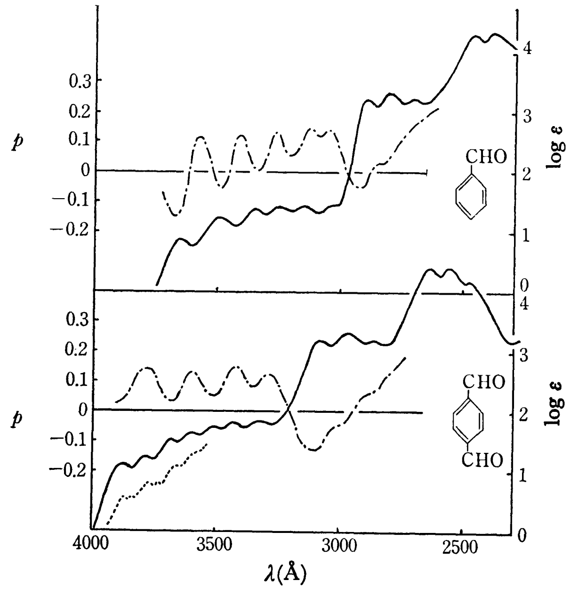

Fig. 1. The absorption spectra in EPA at 77°K (——) and the excitation polarization spectra (–·–·) obtained relative to the O–O band of the phosphorescence of BA and TPA in EPA at 77°K. The $n\rightarrow\pi^*$ absorption spectrum of TPA observed in the vapor is also shown (------).

TPA emits a weak blue-green phosphorescence with a lifetime of 2.01×10^{-2} sec in EPA at 77°K. The phosphorescence is negatively polarized relative to the ${}^1L_b(\pi,\pi^*)$ excitation and positively polarized relative to the ${}^1L_a(\pi,\pi^*)$ excitation, as can be seen in Fig. 1. The polarized phosphorescence spectrum is shown in Fig. 2; it has been observed with respect to the excitation into the O–O band at 2700 Å of the ${}^1L_a(\pi,\pi^*)$ system in EPA at 77°K. The most remarkable feature of the spectrum is a progression of about 1700 cm^{-1}; this frequency can be assigned to the totally symmetric C=O stretching vibration. The shortest wavelength band at 4350 Å was taken as the O–O band. The separation between this band and the longest-wavelength band at 3880 Å in the S′←S absorption observed in EPA at 77°K, which was taken as the O–O band of the ${}^1U(n,\pi^*)\leftarrow S_0$ absorption system, is about 2600 cm^{-1}. These characteristic features of the phosphorescence are consistent with the lowest triplet state of TPA being a ${}^3U(n,\pi^*)$ state.

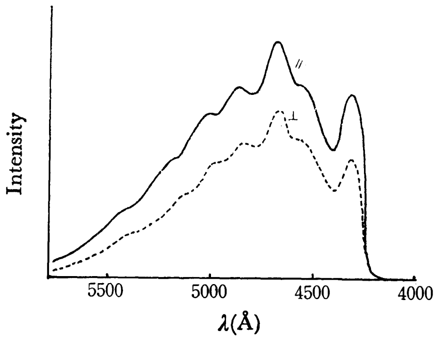

Fig. 2. The polarized phosphorescence spectrum of TPA in EPA at 77°K. Excitation was made into the O–O band of the ${}^1L_a(\pi,\pi^*)$ band.

---

[11] J. M. Snell and A. Weissberger, "Organic Syntheses," Coll. Vol. III, (1955), p. 788.

[12] Y. Kanda, "Zikken Kagaku Koza," 2nd Ser. Vol. XI, ed. by S. Nagakura, Maruzen, Tokyo (1965), p. 85.

[13] Y. Murakami, R. Shimada, and Y. Kanda, "Molecular Luminescence," ed. by E. C. Lim, Benjamin, New York (1969), p. 119.

The phosphorescence spectrum was also observed in methylcyclohexane at 4.2°K. A part of the spectral structure is given in Fig. 3, along with the phosphorescence spectrum and the phosphorescence polarization spectra measured with respect to the excitation into the O–O bands of the $^1L_b(\pi,\pi^*)$ and $^1L_a(\pi,\pi^*)$ systems in EPA at 77°K. The phosphorescence observed in methylcyclohexane at 77°K gives almost the same spectrum as that observed in EPA at 77°K. The spectrum observed in methylcyclohexane at 4.2°K shows a well-resolved fine structure. The shortest-wavelength band at 4331.8 Å, which is the strongest in the spectrum, was taken as the O–O band of the system. The observed vibrational frequencies are given in Table 1, along with their intensities. The infrared and Raman spectral data are given in the same table. Clearly polarized Raman bands are indicated by a letter, *p*.

The prominent vibrational frequency of 1715 cm^{-1}, which constitutes the main progression in the phos-

Table 1. The vibrational analysis of the phosphorescence spectrum of TPA and the corresponding vibrational frequency in BA

IR		Raman			Phosphorescence			Assignment[15]	Corresponding vibrational frequency in BA[7,10]	
$\tilde{\nu}$(cm^{-1})	Int.	$\tilde{\nu}$ (cm^{-1})	Int.	Pol.	Design.	$\tilde{\nu}$ (cm^{-1})	Int.		IR & Raman $\tilde{\nu}$(cm^{-1})	Phos. $\tilde{\nu}$(cm^{-1})
						O–O	s			
					a	70	m			
					b	150	s	ϕ-CHO-torsion	133	141
					c	235	m	ϕ-CHO-wag	245	245
		257	m							
		326	w		d	320	vw			
400	w	392	m		e	405	vw	ν_{16a}	388	
474	m									
526	m									
		634	m							
		687	w	*p*						
		707	w		f	705	w	ν_4	688	685
774	s									
818	s				g	810	w	ν_{10a}	806	817
828	w*sh*	824	vw							
		872	s	*p*	h	870	w	ν_1	1004	1004
988	vw				i	970	m	ν_5	978	978
1009	m	1020	w		j	1010	m	aldehyde H-wag	1010	1008
1013	m									
1090	w									
1096	w				k	1105	vw			
		1150	s	*p*	l	1170	m	ν_{9a}	1164	
		1166	vw							
1197	s									
		1210	s	*p*						
1300	m	1298	w		m	1295	w	ν_{14}	1292	
1335	w									
1369	m									
1388	m									
1422	w*sh*	1408	m		n	1415	m	aldehyde C–H bend	1395	1412
1429	w									
1494	m*sh*	1491	vw							
1500	m									
		1586	m	*p*						
		1615	vs	*p*	o	1610	s	ν_{8a}	1601	1600
1633	s*sh*									
1658	s*sh*	1661	vw							
1689	vs									
1696	vs	1695	vs	*p*						
		1708	vs	*p*	p	1715	s	ν(C=O)	1694	1698
		1729	m*sh*							
1832	vw									
					q	1870	w	ν(C=O)+CHO-torsion		

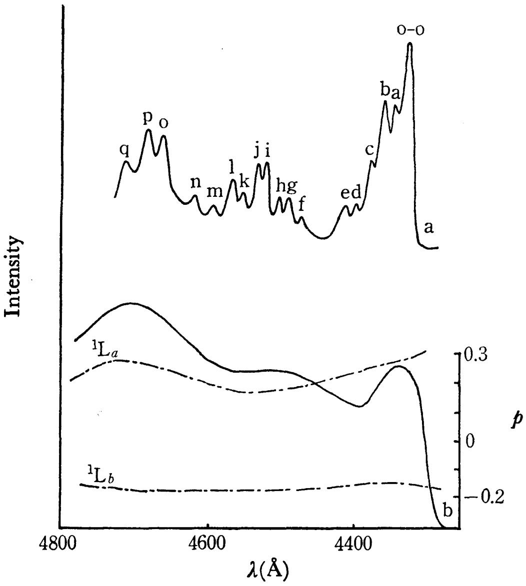

Fig. 3. A part of the phosphorescence spectra (——) of TPA at 4.2°K, a, and in EPA at 77°K, b. The phosphorescence polarization spectra (–··–) were obtained with respect to the O–O bands of the ^1L_a and ^1L_b bands.

phorescence spectrum, was assigned to the totally symmetric C=O stretching vibration. Two strong and polarized Raman bands were observed in the C=O stretching frequency region. These are 1695 and 1708 cm^{-1} in frequency and are nearly equal in intensity. This doublet was attributed to a Fermi resonance between a totally symmetric combination and the C=O stretching vibration. The in-plane CHO-bending vibration is expected to appear in the 230—240 cm^{-1} region. A combination of the overtone of this vibration and the ring-CHO stretching vibration, to which a strong and polarized Raman band of 1210 cm^{-1} was assigned, gives a frequency of about 1700 cm^{-1}. The C=O stretching vibration may be mechanically coupled with this combination vibration through the carbonyl carbon atom. Fermi resonances in the C=O stretching vibration are observed in various carbonyl compounds. The fairly strong bands at 150, 235, 970, and 1010 cm^{-1} were assigned to the out-of-plane CHO-torsional, CHO-wagging, ring deformation, ν_5,[14] and aldehyde H-wagging vibrations respectively. The other bands, at 870, 1170, 1415, and 1610 cm^{-1}, were ascribed to the totally symmetric vibrations, ν_1, ν_{9a}, aldehyde C–H bending, and ν_{8a} respectively. The degree of polarization of the phosphorescence, measured relative to the ^1L_b excitation, is negative and is approximately uniform throughout the phosphorescence region, while the degree of polarization measured relative to the ^1L_a excitation gives a minimum around the 1000 cm^{-1} region, although the overall value is positive, as can be seen in Fig. 3. This observation is consistent with the above vibrational assignment. Detailed vibrational analyses of the infrared and Raman spectra will be reported in the near future.

It should be noted that only a few vibrational frequencies were observed in both the infrared and Raman spectra. Such a mutually exclusive relation between infrared and Raman spectra must hold only for the *trans*-form of this molecule. However, the distance between two CHO groups is long enough for there to be a possibility that TPA has both *trans*- and *cis*-conformations. In this connection, the two conformations are calculated to have almost the same ground-state energy, as can be seen in Table 2. Although the CHO plane may deviate from the plane of the benzene ring by repulsion between H atoms of the benzene ring and H and O atoms of the carbonyl group, the deviation may be minimized by the conjugation of the π-electrons. Thus, the TPA molecule may be assumed to have an almost planar structure in the ground state. The *trans*-form of the TPA molecule belongs to the C_{2h} point group and the *cis*-form belongs to the C_{2v} point group. The z axis was taken to be perpendicular to the molecular plane and the y axis to be along the long axis for the C_{2h} point group, while the z axis was taken to be along the C_2 axis and the y axis to be perpendicular to the molecular plane for the C_{2v}.

TPA has two low-lying $^3U(n,\pi^*)$ states, $^3A_u(n,\pi^*)$ and $^3B_g(n,\pi^*)$ states for the *trans*-form, and $^3B_2(n,\pi^*)$ and $^3A_2(n,\pi^*)$ states for the *cis*-form. The electronically-allowed $n\leftarrow\pi^*$ character of the phosphorescence clearly indicates that the lowest triplet state in the *trans*-form is a $^3A_u(n,\pi^*)$ state; thus, the lowest triplet in the *cis*-form is a $^3B_2(n,\pi^*)$ state. CNDO SCF CI calculations, which will be described later, suggest that the lowest $^3A_u(n,\pi^*)$ and $^3B_2(n,\pi^*)$ states are strongly perturbed by the $^1L_a(\pi,\pi^*)$ state, but that the perturbations by the $^1L_b(\pi,\pi^*)$ state are negligibly small, as can be seen in Table 3. In TPA, the $^3L_a(\pi,\pi^*)$ state is expected to be located just above the emitting $^3U_A(n,\pi^*)$ state; thus, the $^3U_A(n,\pi^*)$ state may be perturbed by the $^1U_A(n,\pi^*)$ state through second-order spin-orbit-vibronic coupling. The out-of-plane vibrations observed in the phosphorescence spectrum should be due to the strong vibronic coupling between the $^3L_a(\pi,\pi^*)$ and $^3U_A(n,\pi^*)$ states through b_g or a_2 vibrations. The same phenomenon was observed in the phosphorescence spectrum of BA.[8–10]

$n\rightarrow\pi^*$ Absorption. The near-ultraviolet absorption spectrum and the excitation polarization spectrum measured with respect to the O–O band of the phosphorescence spectrum of TPA in EPA at 77°K are shown in Fig. 1. The corresponding spectra of BA[4] are also given in the same figure. The $n\rightarrow\pi^*$ absorption spectrum of TPA consists of two main progressions. One starts from the longest-wavelength band, located at 3880 Å, with an interval of 1385 cm^{-1}, while the other starts from a band separated by 695 cm^{-1} from the 3880 Å band toward the shorter-wavelength side, with the same interval. The first progression has polarization minima requiring negative polarization, even though the sign of the observed polarization is positive, while the second progression shows positive polarization maxima. No band could be observed on the longer-wavelength side of the 3880 Å band at 77°K, even though a concentrated TPA solution was used. This definitely indicates that the 3880 Å band is a O–O

---

[14] The notations of the normal modes of vibrations characteristic of the benzene ring are according to Langseth and Lord.[15]

[15] A. Langseth and R. C. Lord, *Kgl. Danske Videnskab. Selskab. Math-Fys. Medd.*, **16**, 1 (1938).

band of the $n\rightarrow\pi^*$ absorption.

The absorption spectrum of TPA observed in cyclohexane at room temperature is almost the same as that observed in EPA at 77°K. The oscillator strengths of the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ absorption bands are given in Tables 2 and 3, together with the data for BA. A question immediately arises why the $f_{n\rightarrow\pi^*}$-value of TPA is 2.4 times that of BA. Three possible reasons for the intensification of the $n\rightarrow\pi^*$ absorption in TPA may be considered:

(1) The $n\rightarrow\pi^*$ absorption of TPA has a more electronically allowed character.

(2) The $n\rightarrow\pi^*$ absorption of TPA is more vibronically intensified by strong $\pi\rightarrow\pi^*$ absorptions.

(3) TPA has two CHO groups, and thus two $n\rightarrow\pi^*$ absorptions can be expected to be observed in this region, one electronically allowed and the other forbidden. The observed $n\rightarrow\pi^*$ absorption is the superposition of these two systems.

In order to study the nature of the $n\rightarrow\pi^*$ absorption of TPA in detail, the absorption spectrum was observed in the vapor phase. The $n\rightarrow\pi^*$ vapor absorption, which is given in Fig. 1, shows a rather simple spectral structure, and the individual bands are not sharp enough. The CHO plane may deviate from the plane of the benzene ring somewhat freely in the vapor phase, and this may cause the diffuseness of the spectral structure. The longest-wavelength band at 3857 Å was taken as the O–O band of the $n\rightarrow\pi^*$ absorption. A weak and diffuse band was observed at 3830 Å, separated by 180 cm^{-1} from the O–O band. This band may be ascribed to the superposition of the CHO-torsional and CHO-wagging vibrational bands, whose ground-state vibrational frequencies are 150 and 235 cm^{-1} respectively. The second band observed in the solution spectra splits into two bands in this vapor spectrum. The observed frequencies of 740 and 880 cm^{-1} were assigned to the out-of-plane ring deformation, ν_5, and aldehyde H-wagging vibrations, whose ground-state vibrational frequencies are 970 and 1010 cm^{-1} respectively. A rather strong band was observed at 3660 Å, separated by 1395 cm^{-1} from the O–O band corresponding to the third band of the solution spectra. A frequency of 1395 cm^{-1} was assigned to the totally symmetric C=O stretching vibration in the excited state.

It should be noted that the spectral structures of the n-π^* absorption and phosphorescence spectra are very similar to one another. This means that the $^1U_A(n,\pi^*)\leftarrow S_0$ transition is perturbed by the $^1L_a(\pi,\pi^*)\leftarrow S_0$ transition through exactly the same out-of-plane vibrations as are involved in the vibronic coupling between the emitting $^3U_A(n,\pi^*)$ and the low-lying $^3L_a(\pi,\pi^*)$ states. From the electronically-allowed character of the spectral structure, the $n\rightarrow\pi^*$ absorption of TPA can be ascribed to a $^1A_u(n,\pi^*)\leftarrow S_0$ transition for *trans*-TPA and to a $^1B_2(n,\pi^*)\leftarrow S_0$ transition for *cis*-TPA.

The intensities of the $n\rightarrow\pi^*$ absorptions of TPA and BA were calculated by the CNDO SCF CI method, using Pople's parameter.[16,17] In the CI calculations, seven higher-lying occupied molecular orbitals and seven lower-lying vacant molecular orbitals were employed. All the calculations were made on the basis of an assumption that the conformations of TPA and BA molecules were both planar. The geometries of the molecular structure used in the calculation were:

ring C–C = 1.396 Å, ring C–H = 1.084 Å,
ring – aldehyde C–C = 1.490 Å,
aldehyde C–O = 1.240 Å, aldehyde C–H = 1.114 Å,
ring ∠C–C–C = 120°, ring ∠H–C–C = 120°,
ring – aldehyde ∠C–C–C = 120°,
aldehyde ∠O–C–C = 123°, and
aldehyde ∠O–C–H = 120°.

The calculated state functions of the ^1L_a, ^1L_b, and ^1U ($={}^3U$ in CNDO approximation) states for the *trans*- and *cis*-forms of TPA and BA are as follows:

for *trans*-TPA,

$$\begin{aligned}\Psi_{^1B_u(\pi,\pi^*);\,L_a} &= 0.931(\phi_{24},\phi_{26}) - 0.293(\phi_{21},\phi_{27})\\ &\quad - 0.091(\phi_{24},\phi_{29}) + 0.067(\phi_{20},\phi_{31})\\ &\quad + 0.063(\phi_{23},\phi_{30}) + \cdots\\ \Psi_{^1B_u(\pi,\pi^*);\,L_b} &= 0.761(\phi_{21},\phi_{26}) + 0.619(\phi_{24},\phi_{27})\\ &\quad - 0.187(\phi_{21},\phi_{29}) + \cdots\\ \Psi_{^1A_u(n,\pi^*);\,U_A} &= 0.681(\phi_{25},\phi_{26}) + 0.600(\phi_{23},\phi_{28})\\ &\quad + 0.266(\phi_{20},\phi_{26}) + 0.259(\phi_{25},\phi_{29})\\ &\quad + 0.196(\phi_{20},\phi_{29}) + \cdots\\ \Psi_{^1B_g(n,\pi^*);\,U_F} &= 0.698(\phi_{23},\phi_{26}) + 0.556(\phi_{25},\phi_{28})\\ &\quad + 0.355(\phi_{23},\phi_{29}) + 0.302(\phi_{20},\phi_{28}) + \cdots\end{aligned}$$

for *cis*-TPA,

$$\begin{aligned}\Psi_{^1B_1(\pi,\pi^*);\,L_a} &= 0.932(\phi_{24},\phi_{26}) - 0.294(\phi_{22},\phi_{27})\\ &\quad + 0.150(\phi_{19},\phi_{28}) - 0.091(\phi_{24},\phi_{29}) + \cdots\\ \Psi_{^1A_1(\pi,\pi^*);\,L_b} &= 0.764(\phi_{22},\phi_{26}) + 0.617(\phi_{24},\phi_{27})\\ &\quad - 0.187(\phi_{22},\phi_{29}) + \cdots\\ \Psi_{^1B_2(n,\pi^*);\,U_A} &= 0.692(\phi_{25},\phi_{26}) + 0.532(\phi_{23},\phi_{28})\\ &\quad - 0.273(\phi_{21},\phi_{28}) + 0.256(\phi_{25},\phi_{29})\\ &\quad + 0.251(\phi_{20},\phi_{26}) + 0.187(\phi_{20},\phi_{29}) + \cdots\\ \Psi_{^1A_2(n,\pi^*);\,U_F} &= 0.633(\phi_{23},\phi_{26}) + 0.559(\phi_{25},\phi_{28})\\ &\quad - 0.306(\phi_{21},\phi_{26}) + 0.292(\phi_{23},\phi_{29})\\ &\quad + 0.287(\phi_{20},\phi_{28}) + \cdots\end{aligned}$$

and for BA,

$$\begin{aligned}\Psi_{^1A'(\pi,\pi^*);\,L_a} &= 0.868(\phi_{19},\phi_{21}) + 0.418(\phi_{17},\phi_{22})\\ &\quad - 0.150(\phi_{15},\phi_{23}) - 0.106(\phi_{17},\phi_{21})\\ &\quad - 0.100(\phi_{19},\phi_{23}) + \cdots\\ \Psi_{^1A'(\pi,\pi^*);\,L_b} &= 0.703(\phi_{17},\phi_{21}) - 0.645(\phi_{19},\phi_{22})\\ &\quad - 0.231(\phi_{17},\phi_{23}) - 0.144(\phi_{15},\phi_{22})\\ &\quad + 0.108(\phi_{19},\phi_{21}) + \cdots\\ \Psi_{^1A''(n,\pi^*);\,U} &= 0.776(\phi_{20},\phi_{21}) + 0.444(\phi_{20},\phi_{24})\\ &\quad - 0.351(\phi_{16},\phi_{21}) - 0.278(\phi_{16},\phi_{23}) + \cdots\end{aligned}$$

---

16) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).

17) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); *ibid.*, **44**, 3289 (1966).

TABLE 2. OBSERVED AND CALCULATED INTENSITIES OF THE $^1U_A(n,\pi^*)\leftarrow S_0$ ABSORPTIONS AND THE TOTAL ENERGIES OF THE GROUND STATES OF TPA AND BA

		$f^{\text{obs.}}_{n\to\pi^*}$	$\tilde{\nu}^{\text{obs.}}_{n\to\pi^*0\text{-}0}$ (cm^{-1})	$M^{\text{calc.}}_{n\to\pi^*}$ (D)		$f^{\text{calc.}}_{n\to\pi^*}$		Total energy of the ground state (eV)	
				Pople	Jaffé	Pople	Jaffé	Pople	Jaffé
TPA	*trans*	1.3×10^{-3}	25,750	0.193	0.141	4.52×10^{-4}	2.40×10^{-4}	−2665.8	−1273.7
	cis			0.209	0.143	5.31×10^{-4}	2.48×10^{-4}	−2665.8	−1273.7
BA		5.5×10^{-4}	27,300	0.158	0.104	3.22×10^{-4}	1.39×10^{-4}	−1973.7	− 933.4
TPA/BA	*trans*	2.4				1.4	1.7		
	cis					1.6	1.8		

TABLE 3. $f_{T\leftarrow S}$-VALUES CONTRIBUTED FROM THE TWO PERTURBING PATHS IN TPA AND BA

	Perturbing transition	$\tilde{\nu}^{\text{obs.}}_{\pi\to\pi^*0\text{-}0}$ (cm^{-1})	$f^{\text{obs.}}_{\pi\to\pi^*}$	Emitting triplet state	$f^{\text{calc.}}_{T\leftarrow S}$ a)
trans-TPA	$^1L_a(\pi,\pi^*)$-S_0	37,600	3.51×10^{-1}	$^3A_u(n,\pi^*)$	5.44×10^{-6}
	$^1L_b(\pi,\pi^*)$-S_0	32,450	2.47×10^{-2}	$^3A_u(n,\pi^*)$	1.22×10^{-9}
cis-TPA	$^1L_a(\pi,\pi^*)$-S_0	37,600	3.51×10^{-1}	$^3B_2(n,\pi^*)$	3.24×10^{-6}
	$^1L_b(\pi,\pi^*)$-S_0	32,450	2.47×10^{-2}	$^3B_2(n,\pi^*)$	1.43×10^{-9}
BA	$^1L_a(\pi,\pi^*)$-S_0	40,500	2.56×10^{-1}	$^3A''(n,\pi^*)$	2.93×10^{-6}
	$^1L_b(\pi,\pi^*)$-S_0	34,600	2.02×10^{-2}	$^3A''(n,\pi^*)$	1.18×10^{-8}

a) The $f^{\text{calc.}}_{T\leftarrow S}$-value was calculated with the following equations and observed values:

$$M_{T\leftarrow S}=M_{^1La\text{ or }^1Lb\text{-}So}\frac{<\psi_{^1La\text{ or }^1Lb}|H_{so}|\psi_{^3UA}>}{E_{^1La\text{ or }^1Lb}-E_{^3UA}}$$

$$f_{T\leftarrow S}=1.08\times10^{-5}\times\tilde{\nu}(\text{cm}^{-1})\times G\times M^2{}_{T\leftarrow S},$$

$E^{\text{TPA}}_{^3UA}=23{,}100$ cm^{-1}, and

$E^{\text{BA}}_{^3U}=25{,}150$ cm^{-1}.

These state functions were used for the calculations of the transition moments of the $n\to\pi^*$ absorptions and the spin-orbit couplings between the $^3U_A(n,\pi^*)$ states and the $^1L_a(\pi,\pi^*)$ and $^1L_b(\pi,\pi^*)$ states for TPA and BA; the results are listed in Tables 2 and 3. The calculated $f_{n\to\pi^*}$-values of TPA and BA are listed in Table 2, together with the $f_{n\to\pi^*}$-values observed in cyclohexane at room temperature. The $f_{n\to\pi^*}$-values were also calculated by the use of Jaffé's parameter;[18] the results are given in the same table. Although Jaffé's parameter gives $f_{n\to\pi^*}$-values about one half of those obtained with Pople's parameter, the ratios of the calculated $f_{n\to\pi^*}$-values of TPA to those of BA are almost all the same. The values were 1.4 and 1.7 for *trans*-TPA and 1.6 and 1.8 for *cis*-TPA with Pople's and Jaffé's parameters respectively, as is shown in Table 2.

$$f_{n\to\pi^*}\,(\textit{trans}\text{-TPA})/f_{n\to\pi^*}\,(\text{BA}) \approx 1.6 \text{ and}$$

$$f_{n\to\pi^*}\,(\textit{cis}\text{-TPA})/f_{n\to\pi^*}\,(\text{BA}) \approx 1.7.$$

The calculation shows that *cis*-TPA gives an $f_{n\to\pi^*}$-value slightly greater than that of *trans*-TPA. The molecular extinction coefficients of the O–O bands of the $n\to\pi^*$ absorptions of TPA and BA measured in cyclohexane at room temperature are 18 and 11 respectively, the ratio being 1.6: 1. This value cannot be directly equal to the ratio of the electronically-allowed characteristics of the $n\to\pi^*$ absorptions of TPA and BA because the O–O band observed in solution generally involves non-totally symmetric vibrational bands of a low frequency, and the Frank-Condon factors of the n-π^* transitions of TPA and BA may be different. The calculated and experimental ratios both give values greater than unity. Hence, this leads to the conclusion that the $n\to\pi^*$ absorption of TPA has a fairly stronger electronically-allowed character than that of BA.

It is well known that the greater part of the observed intensity of the $n\to\pi^*$ absorption of BA is vibronically induced. The ratio of the observed $f_{n\to\pi^*}$-values of TPA and BA, 2.4: 1, may suggest that the $n\to\pi^*$ absorption of TPA is much more intensified vibronically than that of BA. This may be supported by the experimental fact that the second progression of the $n\to\pi^*$ absorption of TPA, which contains vibronic bands due to the out-of-plane ring deformation, ν_5, and aldehyde H-wagging vibrations, is remarkably enhanced in intensity compared with that of BA. This may result in an increase in the degree of polarization of the first band of the second progression of TPA to +0.15 from +0.10 for BA.

It should be noted that the degree of polarization of the first progression of TPA is markedly increased compared with that of BA. The degree of polarization of the first band of the progression of BA is −0.15, while that of TPA is +0.02. It was observed in the vapor absorption that the first band of TPA contains not only the O–O band, but also vibronic bands due to the CHO-torsional and CHO-wagging vibrations. These out-of-plane vibrations may increase the degree of polarization of the first progression of TPA. Since they increase the intensity of the first band of the first progression, the experimental ratio of $\varepsilon^{\text{TPA}}_{\text{O-O}}/\varepsilon^{\text{BA}}_{\text{O-O}}$, 1.6: 1, seems a little greater than the ratio in an ideal case where no out-of-plane vibrations are involved. The calculations of the transition densities between $^1U_A(n,\pi^*)$ and $^1L_a(\pi,\pi^*)$, and between $^1U_A(n,\pi^*)$ and $^1L_b(\pi,\pi^*)$ with the state functions given above suggest that the n-π^* transition in TPA is preferentially perturbed by $^1L_a(\pi,\pi^*)$. The ratio of intensity incre-

---

[18] J. D. Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968); *ibid.*, **48**, 4050 (1968); *ibid.*, **49**, 1221 (1968).

ments of the $n \rightarrow \pi^*$ absorptions due to the vibronic perturbation in TPA and BA is given by:

$$\frac{f^{\mathrm{TPA}}_{{}^1U_A(n,\pi^*)_{\mathrm{vib}}}}{f^{\mathrm{BA}}_{{}^1U(n,\pi^*)_{\mathrm{vib}}}} = \frac{f^{\mathrm{TPA}}_{{}^1L_a}}{f^{\mathrm{BA}}_{{}^1L_a}} \cdot \frac{E^{\mathrm{TPA}}_{{}^1U_A}}{E^{\mathrm{BA}}_{{}^1U}} \cdot \frac{E^{\mathrm{BA}}_{{}^1L_a}}{E^{\mathrm{TPA}}_{{}^1L_a}}$$

$$\times \frac{\{E^{\mathrm{BA}}_{{}^1U} - E^{\mathrm{BA}}_{{}^1L_a}\}^2}{\{E^{\mathrm{TPA}}_{{}^1U_A} - E^{\mathrm{TPA}}_{{}^1L_a}\}^2} \frac{(W^{\mathrm{TPA}}_{{}^1U_A{}^1L_a})^2}{(W^{\mathrm{BA}}_{{}^1U{}^1L_a})^2} \approx 1.7 \times \frac{(W^{\mathrm{TPA}}_{{}^1U_A{}^1L_a})^2}{(W^{\mathrm{BA}}_{{}^1U{}^1L_a})^2}$$

where $W_{{}^1U{}^1L_a}$ is the vibronic interaction energy matrix element between ${}^1U$ and ${}^1L_a$ states.19) The ratio of $W^{TPA}_{{}^1U_A{}^1L_a}/W^{BA}_{{}^1U{}^1L_a}$ is suggested to be greater than unity by a rough estimation of the value of the energy matrix element. Therefore, the above relation clearly explains the increase in the vibronic intensification of the $n \rightarrow \pi^*$ absorption of TPA.

The CNDO calculation indicates that the forbidden $n \rightarrow \pi^*$ transition is also strongly perturbed by the ${}^1L_a(\pi,\pi^*) \leftarrow S_0$ transition; thus, a_u or b_2 vibrations can be expected to appear in the $n \rightarrow \pi^*$ absorption. These vibronic bands give a positive polarization and should have different vibrational frequencies from those of the b_g or a_2 vibrations which are found in the allowed $n \rightarrow \pi^*$ absorption. Therefore, the observed $n \rightarrow \pi^*$ absorption and excitation polarization spectra can be expected to have very complicated patterns if a_u or b_2 vibrations are present. The $n \rightarrow \pi^*$ absorption spectrum of TPA was carefully studied in the vapor phase and in the crystal matrix at a low temperature in order to find the vibronic bands due to the electronically-forbidden $n \rightarrow \pi^*$ transition, but no positive evidence for the existence of these bands could be found. This indicates that the enhancement of the $n \rightarrow \pi^*$ absorptions due to the forbidden $n \rightarrow \pi^*$ transition is negligible.

The authors wish to thank Mr. Anjin Matsuda for his very helpful collaboration, and Mr. Hajime Ishii for his help in the theoretical calculations. The authors are also grateful to the Japan Electron Optics Laboratory Co., Ltd., for the measurement of the Raman spectrum of TPA.

---

19) J. A. Pople and J. W. Sidman, *J. Chem. Phys.*, **27**, 1720 (1957).