Electronic Absorption Spectra and Geometry of Radical Ions of Tetraphenylethylene

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The geometry of the radical ions of tetraphenylethylene was studied by means of electronic absorption spectroscopy. The spectrum of the anion radical produced by γ-ray irradiation in frozen 2-methyltetrahydrofuran changes markedly on controlled warming. The resultant spectrum resembles the spectra of the anion radical in fluid solutions produced by potassium reduction and by pulse radiolysis. These spectra are distinctly different from the spectra of diphenylmethanide ion and of diphenylmethyl radical. From these facts it is inferred that the relaxed anion radical has a geometry in which the central ethylenic bond is twisted by an angle considerably smaller than 90°, in contrast with the near 90° twist in the dianion, and in which each bond connecting a phenyl group with an ethylenic carbon atom is twisted by a smaller angle than in the molecule. The spectrum of the cation radical produced by γ-ray irradiation in frozen matrices is similar to that of the cation radical produced by pulse radiolysis in fluid solutions and changes only slightly on controlled warming. The geometry of the relaxed cation radical is suggested to be similar to that of the molecule, in contrast with that of the anion radical.

The geometries of the tetraphenylethylene molecule (TPE), anion radical ($TPE^{-\cdot}$), and dianion (TPE^{2-}) are an interesting subject of study because of the possibility of twisting of the central ethylenic bond ("α-α' bond") as well as the bonds connecting a phenyl group with an ethylenic carbon atom ("α-1 bonds").

TPE is considered to have a propeller-like geometry, in which each phenyl group is twisted around an α-1 bond by about 35—42° out of the plane of the α-α' bond.[1)]

In order to explain the strong tendency of alkali salts of $TPE^{-\cdot}$ in ethereal solvents to disproportionate to TPE and alkali salts of TPE^{2-},[2—16)] Garst *et al.*[6—9,17,18)] and Szwarc *et al.*[10—16,19—21)] suggested the hypothesis that $TPE^{-\cdot}$ and TPE^{2-} had markedly different geometries. According to their hypothesis, $TPE^{-\cdot}$ has a geometry similar to that of TPE, while TPE^{2-} has a geometry in which two $-CPh_2^-$ groups are perpendicularly twisted around the α-α' bond; owing to the difference in the geometry, $TPE^{-\cdot}$ forms a loose solvent-separated ion pair with an alkali metal ion, while TPE^{2-} forms a tight contact ion aggregate with two metal ions.[10—14,22)] This hypothesis also accounts for the relative slowness of the disproportionation.[15,16,23)]

The suggested geometry of TPE^{2-} seems to be supported by the similarity of the electronic absorption spectrum of the dianion[24)] to those of carbanions of $R-CPh_2^-$ type (*i.e.*, 1,1-diphenyl-1-alkanides), such as 1,1-diphenyl-1-hexanide $[CH_3(CH_2)_4CPh_2^-]$[26)] and 1,1,4,4-tetraphenyl-1,4-butanediide $[Ph_2C(CH_2)_2CPh_2^{2-}]$,[31)] since this similarity would indicate that the the π-π interaction across the α-α' bond is almost completely absent in TPE^{2-}.

As to the geometry of $TPE^{-\cdot}$, however, no reliable evidence has been presented. In the present work the geometry of this anion radical as well as that of the corresponding cation radical ($TPE^{+\cdot}$) is studied by means of electronic absorption spectroscopy mainly using radiation-chemical techniques, which enable us to study counterion free systems.

Experimental

Spectra of the Radical Ions in Fluid Solutions. The electronic absorption spectrum of $TPE^{-\cdot}$ produced by alkali metal reduction is contaminated to some extent by the concomitantly produced TPE^{2-}. Therefore, the spectrum of $TPE^{-\cdot}$ has been revised several times in the literature.[2—4,6,7,10,15,23,25)] In the present work TPE was reduced by potassium in 1,2-dimethoxyethane (DME). Since the disproportionation of alkali salts of $TPE^{-\cdot}$ is endothermic,[2—4,7,10—15)] the spectrum ascribable mainly to $TPE^{-\cdot}$ was obtained by measurement at low temperature (about −50 °C) in the presence of a large excessof TPE.

Attempts to produce $TPE^{+\cdot}$ in fluid solution by oxidation with antimony(V) chloride and to measure its spectrum were unsuccessful.

Spectra of the Radical Ions Produced by Pulse Radiolysis of Fluid Solutions at Room Temperature. In order to obtain the spectra of the counterion free radical ions in fluid solutions at room temperature, pulse radiolysis measurements were made. Solutions of TPE were irradiated with 1—2-μs pulses of a 2.5-MeV electron beam with a peak current of 80 mA. Spectra immediately after pulses are assignable to the solute anion if degassed 2-methyltetrahydrofuran (MTHF) or ethanol is used as solvent, and to the solute cation if aerated acetone is used as solvent.[32)]

Spectra of the Radical Ions Produced by γ-Ray Irradiation of Frozen Solutions at 77 K. It is known that unambiguous spectra of radical ions can be obtained by γ-ray irradiation of rigid solutions at low temperature.[33—35)] The details of experimental procedure have been described in previous papers,[35—38)] so only minimum essential information on the experimental conditions will be given here.

TPE was dissolved in MTHF, *s*-butyl chloride (BuCl), or a Freon mixture (FM: an equivolume mixture of trichlorofluoromethane and 1,2-dibromo-1,1,2,2-tetrafluoroethane), to a concentration of 15—60 mol m^{-3}, unless otherwise indicated. The solution was degassed, frozen to a glassy solid at 77 K in liquid nitrogen, and irradiated with γ-rays from ^{60}Co to the dose of $(1—3)\times 10^{19}$ eV g^{-1}. The measurement of the spectra was carried out by the use of a Cary 14RI spectrophotometer. The spectrum obtained with the MTHF solution can be assigned to TPE$^{-\bullet}$ and the spectrum obtained with the BuCl solution, as well as that obtained with the FM solution, to TPE$^{+\bullet}$.[34,35)

The spectra after "illumination (photobleaching)" or after "controlled warming" of γ-irradiated solutions were also measured. Illumination was made by using a tungsten lamp and glass filters. Controlled warming was carried out by taking the γ-irradiated solution out of the liquid nitrogen for a limited time (a few seconds) and then refreezing it at 77 K.

Molecular Orbital Calculation

A semiempirical SCF-MO-CI calculation of π electronic states of the radical ions was made for various geometries by the use of a method developed by Longuet-Higgins and Pople.[39) The details of the calculation procedure are substantially the same as those described in a previous paper.[38)

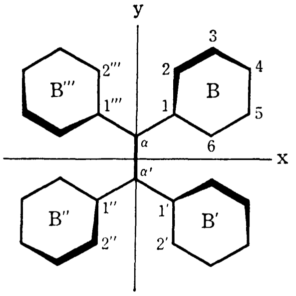

Fig. 1. The carbon skeleton of TPE.

The carbon skeleton of TPE and the numbering of the carbon atoms are illustrated in Fig. 1. All the carbon atoms were assumed to be trigonal. The dihedral angle between the σ-bond planes centered on atoms α and α', for example, is denoted by $\theta_{\alpha\alpha'}$. The calculation was made only for geometries belonging to symmetry group D_2 or D_{2h} with the relation $\theta_{\alpha 1}=\theta_{\alpha' 1'}=\theta_{\alpha' 1''}=\theta_{\alpha 1'''}$. Such a geometry in which $\theta_{\alpha 1}=A°$ and $\theta_{\alpha\alpha'}=B°$ is represented as (A, B).

As a matter of course, the MO calculation based on the π electron approximation becomes less valid as the planarity of the system is lost. However, the calculation is useful as a limited guide for rough characterization of the absorption bands and for qualitative prediction of the relation between the bands and the geometry of the system.

Results and Discussion

Designation of Spectra and of Geometries. For the sake of convenience, the electronic absorption spectra of a radical ion measured under different conditions are designated as follows: The spectrum of a radical ion immediately after its production by γ-ray irradiation in a frozen matrix is designated as F (*frozen*), that after illumination as P (*photobleached*), that after controlled warming as W (*warmed*), and that in a fluid solution as R (*relaxed*). The same designations also apply to the geometries of the radical ion under the respective conditions. In addition, the geometry of the parent neutral molecule is designated as N (*neutral*).

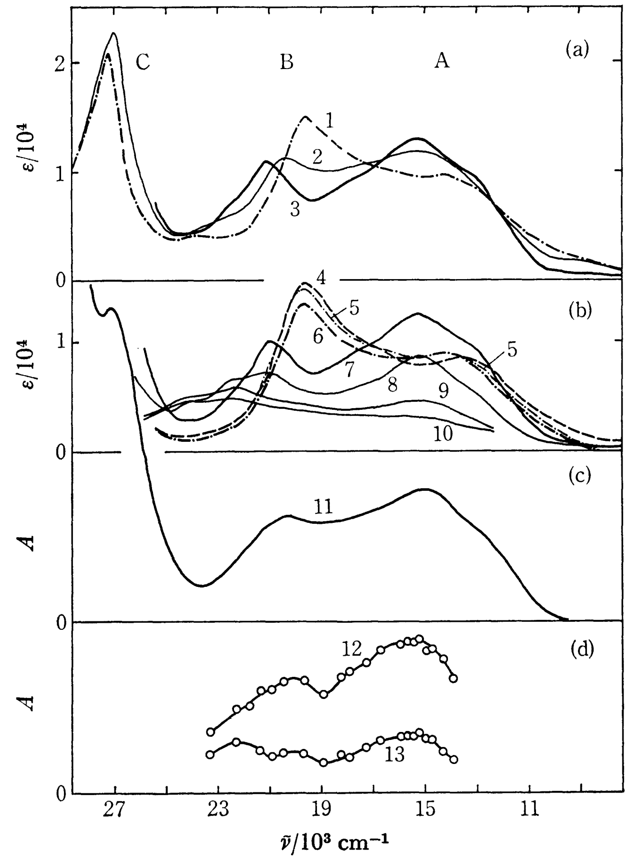

Fig. 2. Electronic absorption spectra of TPE$^{-\bullet}$.
----: Spectrum F, ——: spectrum W or R, -·-·-: spectrum P.
(a) Curve 1: spectrum of a sample obtained by γ-ray irradiation of a dilute solution of TPE in MTHF at 77 K and subsequent illumination with light of $\lambda > 700$ nm. Curve 2: spectrum obtained after controlled warming of the sample for curve 1. Curve 3: spectrum of a sample obtained by γ-ray irradiation and subsequent controlled warming. (b) Curve 4: spectrum F. Curve 5: spectrum obtained after illumination of the sample for curve 4 with light of $\lambda > 620$ nm. Curve 6: spectrum obtained after subsequent illumination with light of $\lambda > 450$ nm. Curve 7: spectrum obtained after controlled warming of the sample for curve 6. Curves 8, 9, and 10: spectra obtained after successive warming of the sample for curve 7. (c) Curve 11: spectrum of TPE$^{-\bullet}$ produced by potassium reduction of TPE in DME at −50 °C. (d) Spectra obtained by radiolysis of a saturated solution of TPE in degassed ethanol at room temperature with a 1-μs electron pulse. Curve 12: spectrum at the end of the pulse. Curve 13: spectrum at 6 μs after the pulse.

The Anion Radical. Assignment of Absorption Bands: Representative spectra of TPE$^{-\bullet}$ measured under various conditions are shown in Fig. 2, and relevant data are shown in Table 1. The values of molar absorption coefficient (ε) for spectra F were determined on the basis of the fact that the yield of the electron from the solvent per unit energy absorbed, $G(e^-)$, is 2.55 for MTHF,[35,37,38) and those for spectra P and W were determined on the assumption that the concentration of the anion radical did not vary on illumination

TABLE 1. DATA ON ELECTRONIC ABSORPTION SPECTRA OF $TPE^{-\cdot}$

Spectrum		Band C		Band B		Band A	
Class	No. in Fig. 2	$\frac{\lambda_{max}}{nm}$	$\frac{\varepsilon}{10^4}$	$\frac{\lambda_{max}}{nm}$	$\frac{\varepsilon}{10^4}$	$\frac{\lambda_{max}}{nm}$	$\frac{\varepsilon}{10^4}$
F	4			511	1.54	*ca.* 750	0.85
P	1	368	2.08	512	1.49	*ca.* 700	0.95
P	6			508	1.33	713	0.90
W	2	371	2.27	496	1.13	650	1.19
W	3			476	1.09	652	1.30
R(K/DME)	11	372		498		670	
R(Li/THF)[a]		375	2.35	495	0.85	660	1.13
R(Pulse)	12			*ca.* 500		*ca.* 655	

a) Taken from Ref. 15.

or on controlled warming.

Most of the spectra shown in Fig. 2 cover only the visible region, because the intense absorption by TPE in the near-ultraviolet region obscures the absorption by $TPE^{-\cdot}$ in the same region. By reducing the concentration of TPE in the MTHF solution, part of the electrons produced upon γ-ray irradiation survived scavenging by TPE and became trapped electrons, which exhibited an absorption in the near-infrared region.[37] The absorption, however, could be eliminated by illuminating the γ-irradiated sample with red light. The spectrum of $TPE^{-\cdot}$ which appeared after the illumination extends to the near-ultraviolet region (Curve 1 in Fig. 2). The main bands are designated as A, B, and C, as shown in Fig. 2.

According to the results of the MO calculation, the π bond order of each α-1 bond increases in going from TPE to $TPE^{-\cdot}$. Therefore, the resistance to torsion of the bond will be stronger in $TPE^{-\cdot}$ than in TPE. This, in turn, suggests that the torsion angle of the bond, $\theta_{\alpha 1}$, is possibly smaller in $TPE^{-\cdot}$ than in TPE. Thus, as a tentative model for geometry F of $TPE^{-\cdot}$, geometry (30, 0) was adopted, instead of geometry (35—42, 0) assumed for TPE.[1] The result of the MO calculation for geometry (30, 0) is shown in Table 2, which includes all the transitions having oscillator strength (f) larger than 0.01 and having transition energy (ΔE) smaller than 4.5 eV. By comparison between Fig. 2 and Table 2, bands A, B, and C are ascribed to transitions 2, 7, and 8, respectively.

As is seen in Table 2, transitions 2, 7, and 8 can be well approximated as one-electron excitations. The orbitals involved can be approximately expressed as follows:

$$(b_1)\quad \psi_{13} \approx a\phi_{+1}(E) - b[\phi_{+1}(B) + \phi_{+1}(B') + \phi_{+1}(B'') + \phi_{+1}(B''')]$$

$$(b_3)\quad \psi_{14} \approx a\phi_{-1}(E) + b[\phi_{-1}(B) - \phi_{-1}(B') - \phi_{-1}(B'') + \phi_{-1}(B''')]$$

$$(a)\quad \psi_{15} \approx a[\phi_{-1}(B) - \phi_{-1}(B') + \phi_{-1}(B'') - \phi_{-1}(B''')]$$

$$(b_1)\quad \psi_{21} \approx b\phi_{+1}(E) - a[\phi_{-1}(B) + \phi_{-1}(B') + \phi_{-1}(B'') + \phi_{-1}(B''')]$$

In these expressions, a and b represent coefficients bearing the relation $a > b > 0$; $\phi_{+1}(E)$ and $\phi_{-1}(E)$ represent the bonding and the antibonding π orbital of the central ethylenic bond (the $\alpha-\alpha'$ bond), respectively; $\phi_{+1}(B)$ and $\phi_{-1}(B)$, for example, represent the following π orbitals of benzene ring B (see Fig. 1):

$$\phi_{+1}(B) = 12^{-1/2}(2\chi_1 + \chi_2 - \chi_3 - 2\chi_4 - \chi_5 + \chi_6)$$

$$\phi_{-1}(B) = 12^{-1/2}(2\chi_1 - \chi_2 - \chi_3 + 2\chi_4 - \chi_5 - \chi_6)$$

Comparison of Spectra and Inference of Geometries: The spectrum of a DME solution of the potassium salt of $TPE^{-\cdot}$ at −50 °C (Curve 11 in Fig. 2) is very similar to the spectra of tetrahydrofuran (THF) solutions of the lithium and the sodium salt of $TPE^{-\cdot}$ reported by Lundgren *et al.*[15] The latter two spectra are virtually identical, and do not vary with temperature. Furthermore, the enthalpy changes on the dissociation of the ion pairs of $TPE^{-\cdot}$ with the alkali metal cations have small negative values.[15] From these facts the following inferences are drawn: The alkali salts of $TPE^{-\cdot}$ form loose solvent-separated ion pairs in THF and probably in DME also; the spectra of the ion pairs and the spectrum of $TPE^{-\cdot}$ free from the counterion are almost identical, suggesting that the effect of the counterion in the ion pairs on the spectrum of $TPE^{-\cdot}$ is very small and that the geometry of $TPE^{-\cdot}$ in the ion pairs is similar to the geometry of $TPE^{-\cdot}$ free from the counterion in the fluid solutions. Thus, the spectra of ethereal solutions of alkali salts of $TPE^{-\cdot}$ can be considered to directly reflect geometry R of $TPE^{-\cdot}$.

TABLE 2. RESULTS OF THE MO CALCULATION FOR $TPE^{-\cdot}$ OF GEOMETRY (30, 0)

Transition[a]	ΔE/eV	$\tilde{\nu}/10^3$ cm^{-1}	λ/nm	f	P[b]	Character[c]	$\Delta P_{\alpha 1}$[d]	$\Delta P_{\alpha\alpha'}$[e]
2	1.583	12.76	784	0.337	x	0.977(14—15)	−0.061	+0.149
7	2.062	16.62	602	0.168	y	0.970(14—21)	−0.101	+0.177
8	3.025	24.38	410	0.277	y	0.957(13—14)	+0.105	−0.333
11	4.207	33.91	295	0.031	x	0.673(14—23)	−0.029	+0.070
12	4.295	34.62	289	0.057	y	0.659(14—25)	−0.039	+0.068

a) Transitions are numbered in the order of increasing transition energy. b) The polarization of the transition. For the coordinate axes, see Fig. 1. c) The wave function of the excited state of the transition. Only the electron configuration whose coefficient in the wave function is the largest is shown, together with the coefficient. Symbol (i—j) denotes the electron configuration arising from the ground configuration by promotion of an electron from the ith π SCF-MO (ψ_i) to the jth one (ψ_j). The orbital index i runs from 1 for the lowest orbital to 26 for the highest one in the order of increasing energy. The coefficient of the ground configuration in the wave function of the ground state is 0.993. d) The change in the π bond order of the α-1 bond ($P_{\alpha 1}$) on the transition. The value of $P_{\alpha 1}$ in the ground state is 0.331. e) The change in the π bond order of the α-α' bond ($P_{\alpha\alpha'}$) on the transition. The value of $P_{\alpha\alpha'}$ in the ground state is 0.659.

Transient spectra of $\mathrm{TPE}^{-\bullet}$ produced by pulse radiolysis of a degassed ethanol solution of TPE at room temperature (Curves 12 and 13 in Fig. 2) resemble the spectra of alkali salts of $\mathrm{TPE}^{-\bullet}$ in ethereal solutions. Therefore, the geometry of $\mathrm{TPE}^{-\bullet}$ produced by pulse radiolysis is probably similar to that of $\mathrm{TPE}^{-\bullet}$ produced by alkali metal reduction. It is inferred that $\mathrm{TPE}^{-\bullet}$ produced by pulse radiolysis in fluid solution takes the relaxed geometry within the time interval of a pulse width.

The end-of-pulse spectrum of a degassed MTHF solution of TPE closely resembles that of the ethanol solution, except for the appearance of an absorption band at about 500 nm in the former, a band which is ascribed to a relatively long-lived chemical species other than $\mathrm{TPE}^{-\bullet}$.

The spectra of γ-irradiated MTHF frozen solutions of TPE (spectra F of $\mathrm{TPE}^{-\bullet}$; Curve 4 in Fig. 2) are markedly different from spectra R of $\mathrm{TPE}^{-\bullet}$. Controlled warming of the frozen solutions distinctly changed the color of the solutions from purple to dark blue. The spectra after the warming, *i.e.*, spectra W (Curves 3 and 7 in Fig. 2), resemble spectra R. These facts indicate that $\mathrm{TPE}^{-\bullet}$ produced in frozen solutions nearly retains the geometry of the neutral TPE (geometry N) owing to the rigidness of the environment, and that during the process of controlled warming the geometry of $\mathrm{TPE}^{-\bullet}$ is relaxed to a geometry (geometry W) which is almost identical with geometry R. This means that geometry R of $\mathrm{TPE}^{-\bullet}$ is distinctly different from geometry N, in opposition to the aforementioned hypothesis proposed by Garst *et al.* and by Szwarc *et al.* Since the same spectral change from F to W was observed both for solutions of concentration of about 50 mol m^{-3} and for much more dilute solutions, and since spectra W closely resemble spectra R, the spectral change cannot be due to formation of chemical species other than $\mathrm{TPE}^{-\bullet}$, such as dimer anions.

Thus, geometry F is inferred to be nearly similar to geometry N, although it may have been partially relaxed towards geometry R, and the spectral change from F to W is interpreted as a result of the geometrical change from F to W. In the spectral change, band A shifts to shorter wavelengths and increases in intensity, band B shifts to shorter wavelengths and decreases in intensity, and band C shifts to longer wavelengths and increases in intensity. This spectral change is in qualitative agreement with what is expected from the result of the MO calculation shown in Tables 3 and 4 if the geometrical change occurs in such a way that $\theta_{\alpha 1}$ becomes smaller and/or $\theta_{\alpha\alpha'}$ becomes larger. Such a geometrical change is conceivable, in view of the result of the MO calculation that on the change from TPE to $\mathrm{TPE}^{-\bullet}$ the π bond orders of the α-1 bond and of the α-α' bond increases and decreases, respectively.[40]

Table 3. Dependence of transitions in $\mathrm{TPE}^{-\bullet}$ on torsion angle $\theta_{\alpha 1}$

Geometry	Transition 8		Transition 7		Transition 2	
	ΔE/eV	f	ΔE/eV	f	ΔE/eV	f
(0, 0)	2.587	0.415	2.234	0.009	1.680	0.276
(15, 0)	2.801	0.346	2.302	0.102	1.723	0.346
(30, 0)	3.025	0.277	2.062	0.168	1.583	0.337
(45, 0)	3.470	0.209	1.654	0.193	1.328	0.301

Table 4. Dependence of transitions in $\mathrm{TPE}^{-\bullet}$ on torsion angle $\theta_{\alpha\alpha'}$

Geometry	Transition 8		Transition 7		Transition 2	
	ΔE/eV	f	ΔE/eV	f	ΔE/eV	f
(30, 0)	3.025	0.277	2.062	0.168	1.583	0.337
(30, 15)	2.941	0.299	2.116	0.161	1.626	0.331
(30, 30)	2.616	0.301	2.247	0.152	1.753	0.316
(30, 45)	2.497	0.170	2.171	0.236	1.962	0.279

Even in geometry W, $\theta_{\alpha\alpha'}$ cannot be too large. If $\theta_{\alpha\alpha'}$ were so large that the π-π interaction across the α-α' bond were negligibly small, the spectrum of $\mathrm{TPE}^{-\bullet}$ would be the superposition of the spectra of a 1,1-diphenyl-1-alkanide ion and of a 1,1-diphenylalkyl radical. Solvent-separated ion aggregates formed of 1,1-diphenyl-1-alkanides and alkali metal cations exhibit an intense absorption band which has its maximum at about 495—501 nm;[26,31] diphenylmethyl radical exhibits a weak band with its maximum at 460 nm and an intense band with its maximum at 335 nm.[41] The observed spectra of $\mathrm{TPE}^{-\bullet}$ are definitely different from the superposition of such absorptions.

Angles $\theta_{\alpha 1}$ and $\theta_{\alpha 1'''}$, for example, cannot be simultaneously 0° because of the steric interference of the geminal phenyl groups. Therefore, it is considered that, in going from TPE to the relaxed $\mathrm{TPE}^{-\bullet}$, $\theta_{\alpha 1}$'s (*i.e.*, $\theta_{\alpha 1}$, $\theta_{\alpha' 1'}$, $\theta_{\alpha' 1''}$, and $\theta_{\alpha 1'''}$) decrease from about 35—42° not to 0° but to an angle appreciably larger than 0°, while $\theta_{\alpha\alpha'}$ increases from 0° not to 90° as in TPE^{2-} but to an angle considerably smaller than 90°. By consulting the result of the MO calculation (*cf.* Tables 3 and 4), a geometry in which $\theta_{\alpha 1}$'s are about 15—30° and $\theta_{\alpha\alpha'}$ is about 0—30° is proposed as a plausible geometry of the relaxed $\mathrm{TPE}^{-\bullet}$. Thus, it is concluded that the geometry of the relaxed $\mathrm{TPE}^{-\bullet}$ is different from the geometries of both TPE and TPE^{2-}.

Extensive warming until the rigid MTHF matrix became a viscous fluid brought about a change of the color of the solution to greenish blue and a homogeneous diminution of the absorption by $\mathrm{TPE}^{-\bullet}$ with a concomitant appearance of new peaks at 445 and 413 nm (see Curves 9 and 10 in Fig. 2). The new absorption is attributable to 1,1,2,2-tetraphenylethyl radical formed by neutralization of $\mathrm{TPE}^{-\bullet}$ with a proton produced upon γ-ray irradiation.[35] Part of the absorption at about 450 nm in the spectrum at 6 μs after the pulse obtained by pulse radiolysis of an ethanol solution of TPE (Curve 13 in Fig. 2) may be attributed to the tetraphenylethyl radical.

Illumination of the γ-irradiated MTHF frozen solution with light of $\lambda > 630$ nm and with light of $\lambda > 420$ nm only slightly changed the spectrum. Thus, the change from spectrum F to spectrum P (Curves 5 and 6 in Fig. 2) is much smaller than the change from F to W. However, the tendencies induced by illumination and by warming are similar. This suggests that illumination may cause a local heating of the matrix to allow the limited relaxation of the radical ions.

Controlled warming of samples exhibiting spectrum P changed the spectrum to spectrum W (Curve 7 in Fig. 2), which was almost identical with that obtained by direct controlled warming of γ-irradiated samples.

The Cation Radical. Assignment of Absorption Bands: Spectra of TPE$^{+\cdot}$, so far unknown in the literature, were measured under various conditions, and representative ones are shown in Fig. 3. Relevant data are given in Table 5. The molar absorption coefficient cannot be precisely evaluated for spectra F of cation radicals.[35] The values of the molar absorption coefficients shown in Fig. 3 and Table 5 were tentatively determined on the assumption that all the positive charges produced in the matrix by γ-ray irradiation were transferred to TPE molecules to produce TPE$^{+\cdot}$. The main bands are designated as A and B, as shown in Fig. 3.

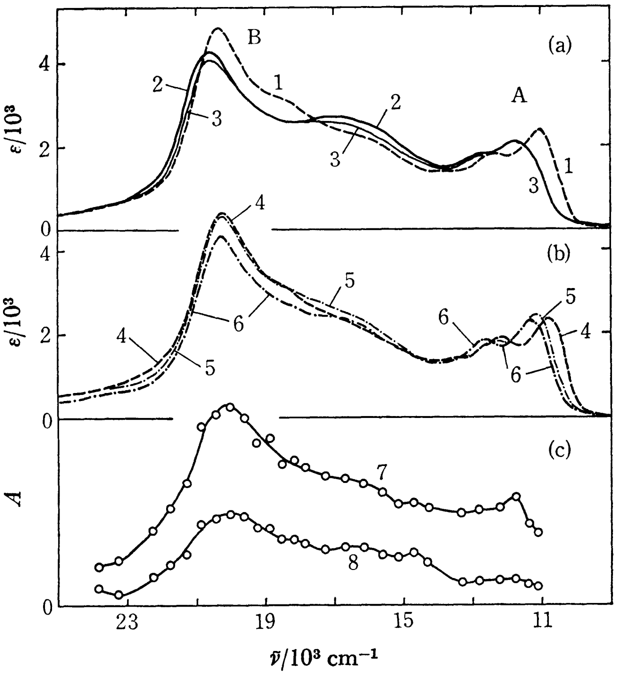

Fig. 3. Electronic absorption spectra of TPE$^{+\cdot}$.
(a) Curve 1: spectrum of a sample obtained by γ-ray irradiation of a solution of TPE in FM at 77 K. Curve 2: spectrum obtained after controlled warming of the sample for curve 1. Curve 3: spectrum obtained after repeated controlled warming of the same sample. (b) Curve 4: spectrum of a sample obtained by γ-ray irradiation of a solution of TPE in BuCl at 77 K. Curve 5: spectrum obtained after illumination of the sample for curve 4 with light of $\lambda > 660$ nm. Curve 6: spectrum obtained after illumination of the sample for curve 5 with light of $\lambda > 370$ nm. (c) Spectra obtained by pulse radiolysis of a solution of TPE in aerated acetone at room temperature. Curve 7: spectrum at the end of the pulse. Curve 8: spectrum at 5 μs after the pulse.

Table 5. Data on electronic absorption spectra of TPE$^{+\cdot}$

Spectrum		Solvent	Band B		Band A	
Class	No. in Fig. 3		$\lambda_{\max}$/nm	ε/10^3	$\lambda_{\max}$/nm	ε/10^3
F	4	BuCl	494	4.85	929	2.33
F	1	FM	492	4.85	907	2.41
P	6	BuCl	493	4.28	887	2.26
W	2	FM	484	4.23	853	2.08
R(Pulse)	7, 8	Acetone	*ca.* 500		*ca.* 850	

Prolonged γ-ray irradiation for 20—30 min of dilute (2—4 mol m^{-3}) frozen solutions of TPE in FM and in a 5: 1 mixture of 3-methylpentane and BuCl gave spectra of TPE$^{+\cdot}$ which exhibited a band having its maximum at 358 nm (band C). The intensity of band C is comparable to that of band B.

The result of the MO calculation for TPE$^{+\cdot}$ is quite similar to that for TPE$^{-\cdot}$, as should be the case because of the pairing properties of π orbitals of the alternant hydrocarbon. Similarly to the case of TPE$^{-\cdot}$, bands A, B, and C are ascribed to transitions 2, 7, and 8, respectively. As is seen in Table 6, these transitions can be well approximated as one-electron transitions. Of the orbitals involved, ϕ_{13} and ϕ_{14} are similar to the corresponding orbitals of TPE$^{-\cdot}$, and ϕ_6 and ϕ_{12} can be approximately expressed as follows:

$$(\mathrm{b_3})\quad \phi_6 \approx b\phi_{-1}(\mathrm{E}) + a[\phi_{+1}(\mathrm{B}) - \phi_{+1}(\mathrm{B'}) - \phi_{+1}(\mathrm{B''}) + \phi_{+1}(\mathrm{B'''})]$$

$$(\mathrm{b_2})\quad \phi_{12} \approx a[\phi_{+1}(\mathrm{B}) + \phi_{+1}(\mathrm{B'}) - \phi_{+1}(\mathrm{B''}) - \phi_{+1}(\mathrm{B'''})]$$

The behavior of transitions 2, 7, and 8 with the change in geometry is expected to be quite similar to that of the corresponding transitions in TPE$^{-\cdot}$.

Comparison of Spectra and Inference of Geometries: Spectrum F of TPE$^{+\cdot}$ (Curves 1 and 4 in Fig. 3) is similar as a whole to spectrum F of TPE$^{-\cdot}$ (Curve 4 in Fig. 2). Thus, geometries F of TPE$^{+\cdot}$ and of TPE$^{-\cdot}$ seem to be similar.

In contrast with the case of TPE$^{-\cdot}$, spectrum F of TPE$^{+\cdot}$ changes only slightly both on controlled warming and on illumination [*cf.* Fig. 3, (a) and (b)]. The spectra of TPE$^{+\cdot}$ produced by pulse radiolysis of solutions of TPE in aerated acetone at room temperature (spectrum R; Curves 7 and 8 in Fig. 3) are similar to the spectra of TPE$^{+\cdot}$ in rigid matrices, especially to spectra W (Curves 2 and 3 in Fig. 3). This indicates that geometry R of TPE$^{+\cdot}$ is only slightly different

Table 6. Results of the MO calculation for TPE$^{+\cdot}$ of geometry (30, 0)[a]

Transition	ΔE/eV	$\tilde{\nu}/10^3$ cm^{-1}	λ/nm	f	P	Character	$\Delta P_{\alpha 1}$	$\Delta P_{\alpha\alpha'}$
2	1.576	12.70	787	0.297	x	0.968(12—13)	−0.061	+0.148
7	2.063	16.63	601	0.141	y	0.959(6—13)	−0.096	+0.167
8	3.015	24.30	412	0.381	y	0.942(13—14)	+0.098	−0.312

a) See footnotes of Table 2. The coefficient of the ground configuration in the wave function of the ground state is 0.993. The values of $P_{\alpha 1}$ and $P_{\alpha\alpha'}$ in the ground state are 0.331 and 0.660, respectively.

from geometry F and probably from geometry N.

A detailed comparison of the spectra, however, reveals that there are small, but significant, differences among the spectra of $TPE^{+\cdot}$ measured under different conditions. Especially, in going from spectrum F to spectrum W, both bands A and B shift to shorter wavelengths (*cf.* Table 5), probably indicating that, in going from geometry F to geometry W, $\theta_{\alpha 1}$'s become slightly smaller and/or $\theta_{\alpha\alpha'}$ becomes slightly larger. Both bands A and B are located at slightly shorter wavelengths in spectrum F of the FM solution (Curve 1 in Fig. 3) than in spectrum F of the BuCl solution (Curve 4 in Fig. 3). This fact suggests that the FM glass at 77 K is softer than the BuCl glass at 77 K[35)] and that $TPE^{+\cdot}$ in the former is relaxed to some extent immediately after its production, while $TPE^{+\cdot}$ in the latter is almost unrelaxed.

In conclusion, the geometries of relaxed $TPE^{-\cdot}$ and $TPE^{+\cdot}$ are considerably different. This is a rather unexpected finding, because the π bond orders of each bond in the anion and the cation of an alternant hydrocarbon should be equal and hence one would not expect a significant difference for the geometries of the two ions within the framework of π electron approximation. However, a few similar examples are found in the literature: While the geometry of the anion radical of cyclooctatetraene is inferred to be planar,[42,43)] the geometry of the corresponding cation radical is suggested to be similar to that of the neutral cyclooctatetraene, a tub form;[35)] according to Ishizu *et al.*,[44)] the torsion angle of the coannular bond (the 1-1′ bond) of the cation radical of 2,2′,4,4′,6,6′-hexamethylbiphenyl is close to that of the parent neutral molecule (about 70°), while that of the anion radical of 2,2′,6,6′-tetramethylbiphenyl is much smaller (45—50°) (although Sullivan and Fong[45)] have cast some doubt on this conclusion). It is of interest that in all these examples, including the present case, the geometry of the cation radical is inferred to be similar to that of the parent neutral molecule while that of the anion radical is considered to be different from that of the molecule.

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