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Semiempirical Calculation of the Triplet–Triplet Absorption Spectra of 2-Anthrylethylenes Undergoing Photochemical One-Way Isomerization

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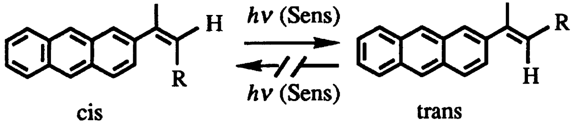
Synopsis. Semiempirical PPP-SCF-SCI calculations support the assignment of the triplet–triplet absorption spectra of 2-anthrylethylenes to the planar trans conformations, which act as a key intermediate in adiabatic cis-to-trans one-way isomerization on the triplet energy surface.

Although the photochemical isomerization of olefins has generally been believed to occur mutually between their cis and trans isomers, we have shown that olefins substituted with aromatic nuclei with low triplet energies, like anthracene, undergo a cis-to-trans one-way isomerization in the triplet state (Scheme 1).[1] The transient absorption spectroscopy showed that in 2-anthrylethylenes, 2-AntCH=CHR (2-Ant: 2-anthryl; R: ^{t}Bu, Me, Ph and 2-naphthyl (2-Np)), the cis triplet (^{3}c*) which formed initially underwent twisting around the double bond overcoming an energy barrier at the perpendicular conformation (^{3}p*) to attain the trans triplet (^{3}t*), which subsequently deactivated to the ground-state trans isomer; on the triplet energy surface, ^{3}t* is the most stable conformation. This is in sharp contrast to the triplet state of olefins, such as stilbene, which undergo mutual isomerization, where ^{3}p* is the funnel to deactivate to the ground-state cis and trans isomers.[2]

Olefins substituted with a naphthyl moiety also undergo mutual isomerization; however, ^{3}t* is the transient intermediate observed in transient spectroscopy. It appears to be in equilibrium with ^{3}p* from which deactivation takes place, thus leading to mutual isomerization.[3] In an investigation of the triplet states of 2-anthryl- and 2-naphthyl-ethylenes by transient spectroscopy we assigned the observed absorptions to a conformation of ^{3}t* rather than ^{3}p* based on experimental evidence.[3,4]

We now report the results of a relatively simple semiempirical calculation of the transition energies and oscillator strengths of the triplet–triplet absorption spectra of planar 2-anthryl- and 2-naphthyl-ethylenes as well as those of the doublet–doublet absorption spectra of 2-anthrylmethyl and 2-naphthylmethyl radicals as models of the twisted conformation, together with supplementary measurements of the transient absorption of related species to support our previous assignment.[1,4)]



R= ^{t}Bu, Ph, 2-Np (2-Naphthyl), Me

Scheme 1.

Experimental

Materials. 2,3-Butandione was purified by a fractional distillation. Solvent benzene and carbon tetrachloride (Dotite Spectrozol) were used as received.

2-(Bromomethyl)anthracene.[4] Anthraquinone-2-carboxylic acid (25 g, 0.10 mol) was reduced by zinc dust (160 g, 2.4 mol) and concentrated ammonia water (27 %, 200 ml) to give 2-anthracenecarboxylic acid (31.4 g, 61 %). 2-Anthracenecarboxylic acid (5 g, 23 mmol) was treated with thionyl chloride and then allowed to react with methanol to give methyl 2-anthracenecarboxylate (3.5 g, 65 %). The methyl ester was reduced by $LiAlH_4$ in ether to give 2-anthrylmethanol (2.0 g, 65 %). 2-(Bromomethyl)anthracene was obtained from 2-anthrylmethanol (1.8 g, 15 mmol) by treating with phosphorus tribromide (1 g, 3.7 mmol) in $CHCl_3$ at 0 °C in the presence of a few drops of pyridine (2.2 g, 94%).

2-(Iodomethyl)anthracene.[5,6] Red phosphorus (0.1 g, 3.2 mmol) was suspended in a $CHCl_3$ solution (50 ml) of 2-anthrylmethanol (0.3 g, 1.5 mmol), and a solution of iodine (0.2 g, 0.8 mmol) in $CHCl_3$ (10 ml) was added dropwise. Then, the reaction mixture was allowed to reflux for 4 h. After cooling down to room temperature, $CHCl_3$ (100 ml) was added to the reaction mixture; it was then poured into water. The organic layer was separated, washed with water, and dried with anhydrous sodium sulfate. Evaporation of the solvent gave a crude product of 2-(iodomethyl)anthracene which was purified by flash column chromatography (silica gel) with $CHCl_3$.

Laser Flash Photolyses. Laser flash photolyses were performed by using a nitrogen laser (National Research Group Inc., 5-ns fwhm, 4mJ/pulse) for excitation at 337 nm, a XeCl excimer laser (Lambda Physik EMG-101, 10-ns fwhm, 150 mJ/pulse) for excitation at 308 nm, and a XeCl excimer laser-pumped dye laser (Lambda Physik FL3002, Stilbene 3) for excitation at 425 nm, and a pulsed xenon arc (Wacom KXL-151, 150 W) as a monitoring light source. The excitation beam was passed through suitable ND filters (Toshiba) and the monitoring light was passed through a cut-off filter (Corning 3-72, 3-73 or 3-74). The data were analyzed on a personal computer (Sharp MZ-2000 or NEC PC-9801 VX). Sample solutions in benzene or carbon tetrachloride were prepared and degassed by three to five freeze-pump-thaw cycles, or argon or nitrogen purging in a Pyrex

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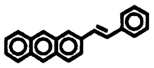
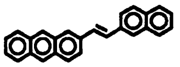
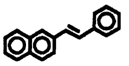
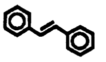
Table 1. Calculated Triplet Excitation Energies (E_T), Bond Orders of Double Bonds (P), Wavelengths (λ), and Oscillator Strengths (f_{calcd}) of T–T Absorption of Hydrocarbons and D–D Absorptions of Free Radicals

Compound	E_T a)	P	λ/nm (f_{calcd})		
	34		220 (1.85)	287 (0.43)	398 (0.59)
			257 (1.10) 454 (0.00)	319 (0.16) 729 (0.00)	386 (0.17)
	38	0.92	232 (1.45)	417 (0.64)	552 (0.06)
	36	0.83	297 (0.75)	441 (0.72)	599 (0.30)
	33	0.80	307 (0.58)	453 (0.63)	617 (0.42)
			226 (1.21)	267 (0.06)	336 (0.11)
	53	0.79	407 (0.68)	719 (0.11)	
	44	0.32	389 (1.40)	562 (0.28)	
	46	0.24	366 (1.38)	427 (0.11)	

a) In kcal mol^{-1}.

tube attached to a 1 cm×1 cm quartz cuvette with a graded seal.

Molar Extinction Coefficients of Triplet–Triplet Absorption. To determine the molar extinction coefficients (ε_T) of T–T absorption of 2-AntCH=CH^{t}Bu, 2,3-butandione (4.0×10^{-2} mol dm^{-3}) was excited at 425 nm in the presence of various concentrations of *cis*- and *trans*-2-AntCH=CH^{t}Bu, and anthracene as a standard in argon-purged benzene. The absorbance immediately after the laser pulse (ΔA_0) was determined at 430 and 445 nm. In a plot of ΔA_0 against the concentration of 2-AntCH=CH^{t}Bu, ΔA_0 increased with increasing concentration of 2-AntCH=CH^{t}Bu, and reached a plateau in the higher concentration region due to quenching of nearly 100% of the triplet sensitizer. The value at the plateau was compared with that of anthracene (ε_T=4980 dm^2 mol^{-1}).[7)]

Oscillator Strengths of Triplet–Triplet Absorptions. The oscillator strengths of T–T absorptions (f_{obsd}) were determined by the following equation:[8)]

$$\begin{aligned} f_{\mathrm{obsd}} &= \frac{2303 m_e c^2}{\pi e^2 N n}\int \varepsilon \mathrm{d}\bar{\nu} \\ &\approx 4.39\times10^{-9}\int \varepsilon \mathrm{d}\bar{\nu} \\ &\approx 4.39\times10^{-9}\varepsilon_T^{\max}\Delta\bar{\nu}_{1/2}, \end{aligned}$$

where m_e is the mass of an electron, c the speed of light, e the charge of an electron, N Avogadro's number, n the refractive index of the medium employed (approximated to be unity), $\bar{\nu}_{1/2}$ the wavenumber of the transition, $\varepsilon_T^{\max}$ the molar extinction coefficient of the T–T absorption maximum, and $\Delta\bar{\nu}_{1/2}$ the full width at the half height of the absorption band.

Calculations. The energies, bond orders of the ethylenic bond, and oscillator strengths of the T–T absorptions of aromatic olefins and D–D absorptions of arylmethyl radicals were caluculated by a semiempirical PPP-SCF-SCI method. The SCF calculation was started from Hückel MO's, and a restricted open-shell SCF calculation was performed for the lowest triplet-state configuration using zero differential overlap and half-electron approximations. Ideal molecular geometries were assumed as regular planar polygons with a bond length of 140 pm. The standard parameter set used in closed-shell calculations was $\gamma_{\mu\nu}=1439.5/(132.8+R_{\nu\mu}/\mathrm{pm})$ eV, $I_\mu=0$ eV, $\beta_{\nu\mu}=-2.318$ eV, and $Z_\mu^c=1$ (Greek suffixes (μ,ν) label atomic p$_z$ orbitals). Saturated alkyl substituents (Me, ^{t}Bu) were disregarded. Details concerning the calculation have been described.[10)].

Results and Discussion

Table 1 lists the calculated values of the triplet excitation energies (E_T), the bond orders (P) of the double bond in the lowest triplet state, and the transition wavelengths (λ) and oscillator strengths (f) of the T–T absorption. Figure 1 is drawn to compare the calculated wavelengths and oscillator strengths with the observed spectra. Figure 1 also depicts the D–D absorption spectra of the 2-anthrylmethyl radicals observed upon pulsed laser excitation of 2-(bromomethyl)anthracene and 2-(iodomethyl)anthracene in carbon tetrachloride. Table 2 compares the calculated oscillator strengths with those estimated from the observed T–T absorption.

Our assignment of the observed T–T absorption of

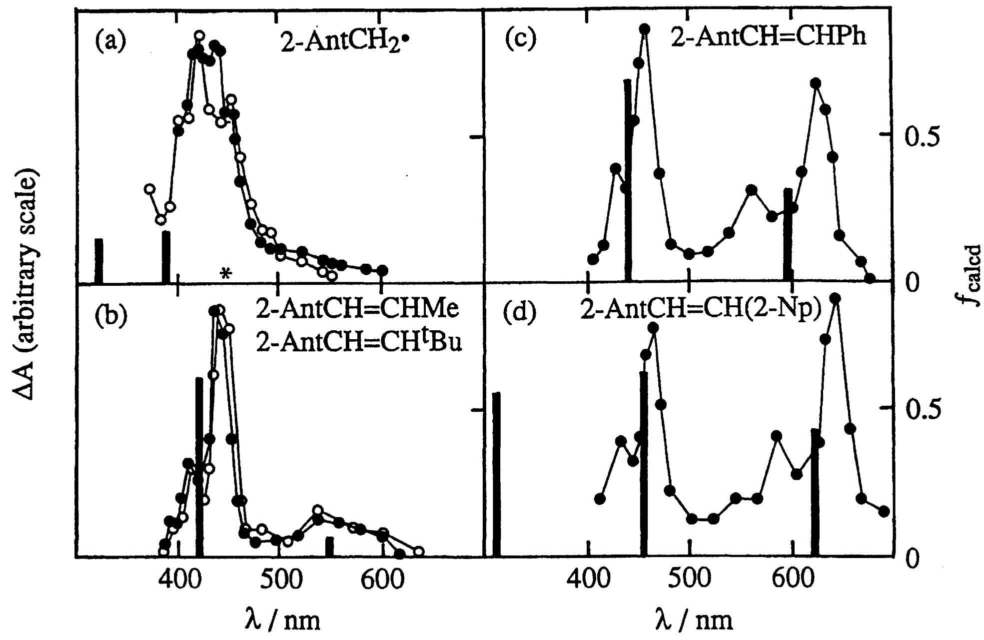


Fig. 1. $T_n \leftarrow T_1$ and $D_n \leftarrow D_1$ absorption spectra (ΔA) measured and calculated wavelengths and oscillator strengths (f_{calcd}: bar indication). (a) 2-Anthrylmethyl radical (1.6 μs after the laser excitation) generated from photolyses of 2-(bromomethyl)- (solid circles) and 2-(iodomethyl)- (open circles) anthracene in CCl_4, * mark indicates the position of a forbidden transition by calculation, (b) *trans*-2-AntCH=CHMe (20 μs, open circles) and *trans*-2-AntCH=CH^{t}Bu (39 μs, solid circles), (c) *trans*-2-AntCH=CHPh (20 μs, solid circles), (d) *trans*-2-AntCH=CH(2-Np) (20 μs, solid circles).

Table 2. Determined (f_{obsd}) and Calculated (f_{calcd}) Oscillator Strengths of 2-Anthrylethylenes

Compound	$\lambda^{\max}$	$\varepsilon_t^{\max}$	f_{obsd}	f_{calcd}	$f_{\mathrm{obsd}}/f_{\mathrm{calcd}}$
	nm	dm^2 mol^{-1}			
2-AntCH=CH^{t}Bu	415	1800	}0.29	0.64	0.45
	445	4500			
2-AntCH=CHPh	430	3000	}0.47	0.72	0.65
	460	6000$^{a)}$			
	560	2100	}0.30	0.30	1.00
	620	4100$^{a)}$			
2-AntCH=CH(2-Np)	430	2600	}0.38	0.63	0.60
	465	5000$^{a)}$			
	580	3400	}0.42	0.42	1.00
	640	6200$^{a)}$			

a) Ref. 11.

the 2-anthrylethylenes to $^3t^*$, rather than $^3p^*$, was based on the following facts: (1) The observed absorptions at the longest wavelength are shifted to longer wavelength with a change of R=^{t}Bu and Me to Ph and 2-Np in 2-AntCH=CHR,[4,11] whereas the $^3p^*$ states of these olefins should have the longest wavelength absorptions, irrespective of the substituent R, at nearly the same wavelength corresponding to the absorption of 2-anthrylmethyl radicals. (2) The observed absorptions have lifetimes that are more than a thousand-times longer (on the order of 100 μs)[4,11] than those expected for $^3p^*$ (for example, 60 ns for stilbene $^3p^*$),[12] since the energy gap between $^3t^*$ and the ground state of the trans isomer is large, whereas it is expected to be small between $^3p^*$ and the perpendicular conformation of the ground state.

Concerning item (1), the present spectral results for the 2-anthrylmethyl radical, which shows an absorption maximum at around 430 nm, provide clear support for our previous assignment.[4]

Figure 1 shows that the calculated wavelengths and intensities of the T–T absorption of 2-anthrylethylenes are generally in agreement with those observed; the calculated wavelengths tend to be shorter than those observed. Table 2 indicates that the calculated oscillator strengths are of the same order as those estimated from the observed T–T absorptions.

For anthracene the calculated wavelength is also shorter than the observed value.[8] The results calculated for the planar triplet states of 2-vinylanthracene, as a model of 2-AntCH=CHMe and 2-AntCH=CH^{t}Bu, well reproduce the presence of stronger absorptions at 400—450 nm and a weaker one around 550 nm.

The calculations predict strong absorptions at 441 and 599 nm for 2-AntCH=CHPh and at 453 and 617 nm for 2-AntCH=CH(2-Np); the former correspond to the observed absorptions at 460 and 620 nm, and the latter to those at 465 and 640 nm, respectively. It is noteworthy that the calculations well reproduce the bathochromic shift of both the shorter- and longer-wavelength absorptions accompanied by a considerable increase in intensity for the latter absorption upon the replacement of R=Me or ^{t}Bu by Ph and 2-Np.

The present calculation tends to give slightly lower triplet excitation energies (E_T) of the 2-anthrylethylenes than those observed, though the calculated E_T values are of the same order as those observed (E_T=42.5, 41.5, and 41.3 kcal mol^{-1} for R=H (^{t}Bu), Ph, and 2-Np, respectively)[1,4] (1 kcal=4.184 kJ). The calculated bond orders (P) indicate that the excitation is largely localized in the anthracene moiety and that the double-bond character of the ethylenic bond is retained.

For a comparison, the absorption spectra of the planar triplet states of stilbene and 2-naphthylethylenes were calculated together with the corresponding arylmethyl radicals. Table 1 indicates that the present calculation also affords reasonable results. Thus, the calculated wavelength of 407 nm for 2-vinylnaphthalene is close to that observed (426 nm),[13] and for 2-styrylnaphthalene the calculated wavelengths of 389 and 562 nm are close to the observed stronger absorption at 395 nm and the weaker one at 560 nm.[14] Those absorption bands are shifted to longer wavelengths than the absorption of 2-naphthylmethyl radicals as a model of ^{3}p* (observed at 375 nm[15] and calculated at 336 nm). The decrease in the calculated E_T values from 2-vinylnaphthalene to 2-styrylnaphthalene agrees with that regarding the observed E_T values of 53[3,16] for the former to 49 kcal mol^{-1}[17] for the latter. Also, the absorption at 366 nm, calculated for the planar triplet of *trans*-stilbene, is close to the observed 378-nm absorption assigned to ^{3}t*.[12,18]

The lower double-bond orders observed for stilbene and 2-styrylnaphthalene compared with 2-anthrylethylenes and 2-vinylnaphthalene indicate that the excitation is spread over the entire molecule when the double bond is conjugated with two benzene rings, as in stilbene, and with a benzene and a naphthalene ring, as in 2-styrylnaphthalene, whereas the excitation tends to remain in the aromatic nucleus[1] in 2-anthrylethylenes and 2-vinylnaphthalene. This is in keeping with the observations that ^{3}p* is the most stable conformation in stilbene and related ethylenes,[2,19] but that ^{3}t* is the most stable conformation in 2-vinylnaphthalene and 2-anthrylethylenes.

In conclusion, the present work shows that PPP-SCF-SCI calculations are useful to assign T–T absorptions of arylethylenes to their proper conformations.

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19) The values for E_T, P, and $\lambda(f)$ for cis-isomers of 2-AntCH=CHPh and 2-NpCH=CHPh were calculated as follows. E_T: 35, P: 0.82, $\lambda(f)$: 302 (0.51), 446 (0.57) and 613 (0.23) for *cis*-2-AntCH=CH–Ph, and E_T: 44, P: 0.34, $\lambda(f)$: 299 (0.49), 417 (0.61) and 606 (0.21) for *cis*-2-NpCH=CHPh. These values are, however, not included in Table 1, since they cannot be compared with those observed due to too short lifetimes of their ^{3}c*'s to be observed.