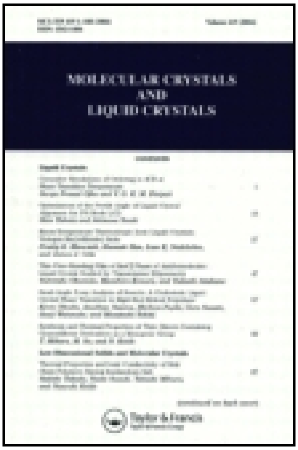

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Design of Conjugated Aromatic Unsaturated Molecules for Photonics to Control Trans to cis Isomerization Under Irradiation

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Design of Conjugated Aromatic Unsaturated Molecules for Photonics to Control trans to cis Isomerization under Irradiation

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Molecular design is discussed for conjugated aromatic unsaturated molecules composed of aromatic ring - double bond - benzene ring (Ar-X=Y-Ph) to control either being durable for a purpose such as the harmonic generation or facilely inducing morphological change of materials such as LB film under light irradiation. For the former purpose, either substitution of aromatic rings of low excitation energies such as anthracene or perylene or substitution of ferrocene ring on a trans CH=CHPh double bond is suitable by preventing trans to cis isomerization. For the latter purpose, use of various C=N and N=N bonds will generally be suitable, since trans to cis isomerization of these bonds still takes place except C=NOMe even with substitution of an aromatic ring of low excitation energy.

Keywords: molecular design; photochemical trans cis isomerization; C=C bond; C=N bond; N=N bond

INTRODUCTION

Photochemical trans to cis isomerization of the N=N bond can be used to control alignment of liquid crystals and functionalize Langmuir-Blodgett (LB) films[1, 2]. The N=N bond isomerizes even on graphite surface as revealed by STM spectroscopy[3]. As to C=N bonds, many azomethine compoounds used as dyes and charge transport materials in electrophotography are known to degrade in polymer matrices during exposure to light often by the way of trans to cis isomerization[4, 5].

On the other hand, for the second or third harmonic generation, molecules should not change under irradiation. As to C=C bonds, it is revealed that substitution of aromatic rings with low excitation energies such as anthracene on the ethylenic bond suppresses trans to cis isomerization and induces only cis to trans one-way isomerization[6, 7, 8].

On designing conjugated molecules for photonics, it is often undertaken to incorporate aromatic or hetero-aromatic rings and an unsaturated bond, for example, in a structure such as Ar-X=Y-Ar, where Ar means an aromatic or a hetero-aromatic ring and X=Y represents a double bond. Depending on purpose, one intends either to keep these molecules unchanged during irradiation without undergoing isomerization around the double bond or to induce the isomerization. This paper aims to discuss design of conjugated aromatic unsaturated molecules which can control either to induce or to prevent photochemical isomerization of unsaturated bonds based on consideration of the results from our and other groups.

RESULTS AND DISCUSSION

C=C Bonds

Many ethylenic compounds undergo isomerization between their trans (^{1}t) and cis isomers (^{1}c) (mutual isomerization) under irradiation as extensively studied for 1,2-diphenylethene (stilbene)[9, 10]. However, we have found that substitution of large aromatic rings of low excitation energies such as anthracene or azulene on carbon atoms of C=C and C=NOMe bonds retard or completely suppress trans to cis isomerization and leads to one-way isomerization solely from cis to trans isomers at the triplet state[6, 11].

Table I collects data to examine how the ènergy of aromatic groups effects the isomerization of the double bond in series of trans isomers of arylethylenes, trans ArCH=CHPh (trans styrylarenes), under direct excitation. The aromatic groups are arranged in the order of decreasing the singlet excitation energies, E_S, of the aromatic hydrocarbons (ArH), that is, phenyl (Ph), biphenylyl (Bi), naphthyl (Np), phenanthryl (Phe), fluoranthenyl (Flu), chrysenyl (Chr), pyrenyl (Py), anthryl (Ant), perylenyl (Per), azulenyl (Az) and ferrocenyl (Fc); and the quantum yield for trans to cis isomerization, $\Phi_{t\text{-}c}$, and the lifetime of the singlet excited state of the trans ethylenic compounds, τ_{St} (when a singlet excited state is composed from two fluorescent rotamers, their lifetimes are indicated.), are listed.

To estimate roughly the rate constants of the trans to cis isomerization occuring at the singlet excited state, $k^S_{t\text{-}c}$, $\Phi_{t\text{-}c}$ is simply divided by τ_{St}[12], and the estimated values are included in the table. The estimated $k^S_{t\text{-}c}$ values are now plotted against the E_S values of the aromatic rings, ArH, in Figure 1.

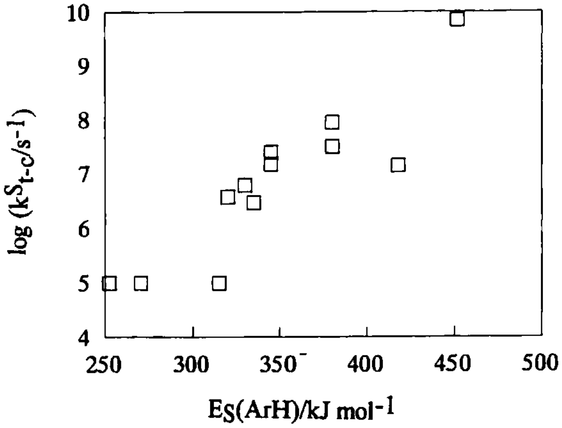

FIGURE 1 Effect of singlet excitation energies of aromatic rings, E_S(ArH), on rate constants of trans to cis isomerization occuring at the singlet excited state, $k^S_{t\text{-}c}$, of trans ArCH=CHPh.

TABLE I Photochemical Data of trans ArCH=CHPh: Singlet excitation energies of the aromatic rings, $E_S(ArH)$, quantum yields for trans to cis isomerization, $\Phi_{t\text{-}c}$, lifetimes of the singlet excited state of the trans isomers, τ_{St}, and estimated rate constants of the trans to cis isomerization occuring at the singlet excited state, $k^S_{t\text{-}c}$.

Ar	$E_S(ArH)$/kJ mol^{-1}	Φt-c	τ_{St}/ns	$k^S_{t\text{-}c}$/s^{-1}	Ref.
Ph	452	0.50	7×10^{-2}	7×10^{9}	9
2-Bi	418	0.37	25.9	1.4×10^{7}	8
1-Np	380	0.16	1.8	8.9×10^{7}	8
2-Np	380	0.16	5.2/27.6	3.1×10^{7b}	c
1-Phe	340	0.13	8.5	1.5×10^{7}	8
9-Phe	340	0.13	5.3	2.5×10^{7}	d
8-Flu	335	0.029	9.7	3.0×10^{6}	6
3-Chr	330	<0.1	16.3	$<6.1 \times 10^{6}$	6
1-Py	320	<0.02	5.3	3.8×10^{6}	6
1-Ant	315	0	4.7	0	6
2-Ant	315	0	9.1/28.6	0	6
9-Ant	315	0	3.6	0	8
3-Per	270	0	3.52	0	6
1-Az	252^{a}, 170	~0	~1^{a}	~0	11
Fc		~0		~0	6

a. the second excited state; b. obtained using $\tau_{St} = 5.2$ ns; c. G. Bartocci, F. Masetti, U. Mazzucato and G. Marconi, *J. Chem. Soc., Faraday Trans. 2*, **80**, 1093 (1984); d. G. Bartocci, F. Masetti, U. Mazzucato, A. Spalletti, I. Baraldi and F. Momicchioli, *J. Phys. Chem.*, **91**, 4733 (1987).

Figure 1 and Table I clearly indicate that with decrease of Es of the aromatic rings subustituted on the ethylenic carbon both $\Phi_{t\text{-}c}$ and $k^S{}_{t\text{-}c}$ tend to decrease, and when Es is lower than 320 kJ mol^{-1} isomerization does not take place at all.

Figure 2 is depicted to show schematically concepts of the potential energy surfaces of the isomerization at the ground, the singlet excited state and the triplet state for stilbene, PhCH=CHPh, as a representative comound which undergoes isomerization between trans and cis isomers (mutual isomerization) (real curves in Figure 2) and for 2-AntCH=CHPh (3-PerCH=CHPh behaves in a similar way at the triplet state) as a representative compound which does not isomerize at all from the trans to cis isomer but isomerizes only from the cis to trans isomer at the singlet[8, 13] and the triplet excited states[6, 8] (dotted curves in Figure 2). In this figure, the triplet surfaces are depicted mostly based on our experimental results[6]; however, the singlet excited surfaces are drawn to show concepts fitting experimental facts[6, 8, 13] as discussed later.

With E_S higher than 320 kJ mol^{-1}, that is, Ar = Ph, Bi, Np, Phe, Flu and Chr in Table I, the trans ethylenic compounds isomerize mostly at the singlet excited state preceding to crossing to the triplet state as thoroughly investigated for stilbene (Ar = Ph)[9, 10]. Thus, both the trans ($^1t^*$) and cis excited states ($^1c^*$) quickly twist around the double bond to give a more stable perpendicularly twisted state ($^1p^*$) followed by its deactivation to the ground state(^1p) giving a mixture of cis and trans isomers as drawn as real curves in Figure 2[9, 10].

However, when E_S of ArH is equal to or lower than 320 kJ mol^{-1}, that is, when Ar = 1-Py, 1-Ant, 2-Ant, 9-Ant, 3-Per and 1-Az, isomerization hardly or never takes place, whereas with Ar = 1-Py (E_S = 320 kJ mol^{-1}) the trans compound isomerizes in polar media[14, 15].

No occurence of the isomerization means that $k^S{}_{t\text{-}c}$ must be lower than one thousandth of rate constants for the other competing processes such as fluorescence emission and intersystem crossing to the triplet state, accordingly, lower than 10^5 s^{-1}, when the singlet excited state has a lifetime of 10 ns. Therefore, the values of $k^S{}_{t\text{-}c} = 0$ in Table I are tentatively plotted as $k^S{}_{t\text{-}c} = 10^5$ s^{-1} in Figure 1. Moreover, in these cases, after the singlet excited state crosses to the triplet state, still isomerization does not occur at the triplet state competing with deactivation to the ground state as revealed for Ar = 1-Ant, 2-Ant and 3-Per[6].

The above very low rate constants for isomerization mean that the isomerization needs to overcome an activation barrier as observed in cis to trans isomerization of several arylethylenes at the triplet state[6]. If rate constants for isomerization of excited states follow the Arrhenius type equation and the preexponential factor is assumed as 10^{11}-10^{13} s^{-1}, isomerization with a rate constant of 10^5 s^{-1} at ambient temperature is to proceed with an activation enegy of 35-47 kJ mol^{-1}.

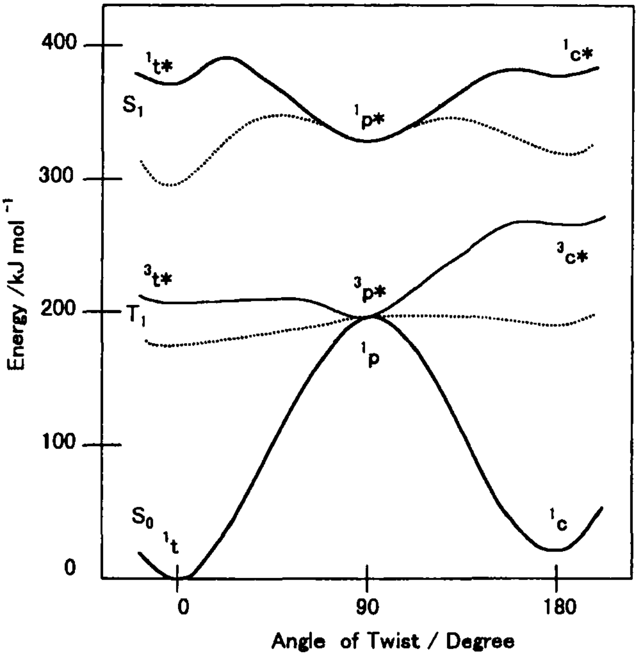

FIGURE 2 Schematic potential energy surfaces of the ground state (S_0), the singlet excited state (S_1) and the triplet state (T_1) of ArCH=CHPh along the twisting angle of the double bond. For the excited states, real and dotted curves are for Ar = Ph and 2-Ant, respectively.

With Ar groups of low excitation energies, at the singlet excited state as well as the triplet state, excitation must mostly be populated at the moiety of the lowest excitation energy, namely at the Ar goup, neither at the ethylenic bond nor at the Ph goup. This leads to stabilization of such excited states compared to those of stilbene and results in high activation barriers to be overcome for isomerization from the trans to cis isomer as depicted as dotted curves in Figure 2.

FcCH=CHPh listed in Table I exhibits a unique feature not only to prevent trans to cis isomerization but also to retard cis to trans isomerization. Ferrocene has low singlet and triplet excitation energies. Furthermore, presence of ferrocene ring containing iron accelerates intersystem crossing from the singlet excited state to the triplet state and subsequently to the ground state. These properties seem favorable for using this type of compounds, such as FcCH=CHAr (Ar: 4-nitrophenyl), as non-linear optial materials[16].

C=N and N=N Bonds

Azobenzene, PhN=NPh, and N-benzylideneaniline, PhCH=NPh, generally exist as trans isomers at ambient temperature, and under irradiation isomerize to their cis isomers, which, though higher in energy than the trans isomers (ca. 55 kJ mol^{-1} for azobenzene), are stable at liquid nitrogen temperature but facilely revert at ambient temperature to the trans isomers overcoming an activation barrier of nearly 85-100[17, 18] and 65-70 kJ mol^{-1}[19], respectively. Most N=N and C=N compounds behave in a similar way.

An exceptional case is oxime ethers, ArCR=NOMe (R = H or alkyl), of which not only trans but also cis isomers are stable at ambient temperature. In this class of compounds, presence of an electronegative oxygen atom leads the adjacent unsaturated nitrogen atom to take more rigid configuration than the nitrogen atom adjacent to a carbon atom such as =NPh. Therefore, ArCR=NOMe behaves similar to arylethylenes different from other C=N compounds.

The N=N and C=N bonds have lone pair electrons on their nitrogen atoms, and show an n,π* absorption in addition to π,π* absorptions. Both trans and cis PhN=NPh exhibit an n,π* absorption band at 380 - ca.500 nm and a π,π* absorption band with a maximum at 330 nm for the trans and 275 nm for the cis isomer[17]. Excitation of either the n,π* band with visible light or the π,π* band with ultraviolet light leads to isomerization in different quantum yields. PhCH=NPh also shows absorption at wavelengths longer than 400 nm[19].

Photochemical isomerization of azobenzene takes place very rapidly. The singlet excited states of many azo and azomethine compounds scarcely fluoresce, except some aryloxime ethers described below, ArCR=NOMe[6], and undergo isomerization much more rapidly than fluorescence emission.

Thus, trans PhN=NPh shows very weak fluorescence (quantum yield: $<10^{-4}$) decaying in a lifetime of ca. 25 and <5 ps from the first (n,π*) and the second (π,π*) excited state, respectively[20]. According to recent femtosecond spectroscopy the singlet excited state undergoes isomerization in nearly or less than 1 ps at ambient temperature[21, 22], much more rapidly than that of trans-stilbene.

Isomerization of C=N and N=N bonds can proceed not only by the way of twisting or rotation around the double bond as the isomerization of the C=C bond, but also by the way of inversion of a substituent on nitrogen atoms in the plane of the double bond. In the latter mechanism, isomerization takes place passing through an intermediate conformation where the double bond and the single bond connecting the substituent with the nitrogen atom are linear and the hybridization of the nitrogen atom changes from sp^2- to sp-hybridization. Moreover, the resulting intermediate state, either a perpendicularly twisted state or a linearly inverted state, can be stabilized by additional conjugation between the lone pair orbital at the nitrogen atom and the twisted moiety at both the ground and the excited states[17, 18, 23]. This additional conjugation certainly contributes to reduction of the activation energies for cis to trans isomerization in the ground state than that for the C=C bonds.

As described above, substitution of anthracene ring with low excitation energies on C=C bond completely suppressed the trans to cis isomerization. In contrast, effect of substitution of aromatic rings on N=N and C=N bond isomerization has not been much known. This led us to examine the effect of 2-Ant on N=N and C=N bonds. The results are now indicated in Table II which collects the effect of substitution of 2-Ant group at N=NPh, CH=NPh, N=CHPh and CMe=NOMe on their trans to cis isomerization under direct irradiation and triplet sensitization together with the lifetimes of their singlet excited states and the triplet states as indices for reactivity in comparison to that at CH=CHPh bond.

As to the series of ArCR=NOMe (R = H or Me), we found a similar trend to ArCH=CHPh; substitution of 2-Ant suppressed and that of 1-Py retarded to some extent trans to cis isomerization. The singlet state of trans 2-AntCMe=NOMe does not isomerize but emits fluorescence and crosses to the triplet state which subsequently deactivates to the ground state[6, 24]. However, substitution of 9-Ant did not suppress trans to cis isomerization on direct irradiation, but, on triplet sensitization, suppressed trans to cis isomerization and led to solely cis to trans isomerization[25]. The above difference between 2-Ant and 9-Ant substitution suppressing or allowing

TABLE II Effect of substitution of 2-anthryl group at several types of double bond on their trans to cis isomerization at ambient temperature on direct irradiation and on triplet sensitization and the lifetimes of the singlet excited state, τ_{St}, and the triplet state, τ_{Tt}, of the trans isomers.

Compound	Direct irradiation		Triplet sensitization	
	Effect[a]	τ_{St}/ns	Effect[a]	$\tau_{Tt}/\mu s$
2-AntCH=CHPh	suprn.	9.1/28.6[b,d]	suprn.	ca. 190[d]
2-AntCMe=NOMe	suprn.	5.6/8.3[b,d,e]	suprn.	90[b, e]
2-AntCH=NPh	no suprn.	n.d.[c]	suprn.	2[f]
2-AntN=CHPh	no suprn.	n.d.[c]	no suprn.	<0.2[f]
2-AntN=NPh	no suprn.	n.d.[c]	no suprn.	n.d.[c,f]

a. Suprn. and no suprn. represent suppression and no suppression, respectively; b. Lifetimes of two fluorescent rotamers; c. too short to be determined; d. Ref. 6; e. Ref. 24; f. Ref. 26.

trans to cis isomerization on direct excitation, respectively, could be attributed to lower energy of $^1p^*$ of the latter than the former due to higher conjugative property of the latter group. This effect is keeping with observation of lower activation energy for cis to trans one-way isomerization of 9-AntCH=CH*t*-Bu than for 2-AntCH=CH*t*-Bu[6].

Substitution of 2-Ant on the carbon atom of CH=NPh did not suppress trans to cis isomerization on direct irradiation, but suppressed the isomerization on triplet sensitization[26], whereas 9-Ant did not suppress on both direct irradiation and triplet sensitization[27]. Substitution of 2-Ant on the nitrogen atoms of N=NPh and N=CHPh was not effective to suppress the isomerization on both direct irradiation and triplet sensitization[26].

Now we consider reason why substitution of 2-Ant at N=NPh, N=CHPh and CH=NPh is ineffective in completely suppressing trans to cis isomerization of these double bonds in contrast to the effect to CH=CHPh and CH=NOMe in which the nitrogen atom takes as rigid configuration as the ethylenic carbon as mentioned before.

First, in these compounds, the absorption band at the longest wavelength showed a character of n,π^* absorption. For example, trans and cis 2-AntN=NPh exhibited absorption extended to 520 and 540 nm, respectively[28]. This is in contrast to the absorption of trans 2-AntCH=NOMe which showed similar spectral profiles to that of 2-AntCH=CHR (R = H, alkyl) and was not extended to much longer wavelength than 400 nm[24]. Therefore, the lowest singlet excited state of 2-AntN=NPh will be rich in n,π^* character; as a result the excitation will not be so much populated at the anthracene ring as in the excited states of 2-AntCH=CHPh and 2-AntCH=NOMe. Second, at the intermediate state of isomerization, as mentioned before, the lone pair orbital on nitrogen atoms can conjugate with the π orbital of the twisted moiety.

These two factors will attenuate the effect of low excitation energy of 2-Ant group substituted on N=NPh, CH=NPh and N=CHPh bonds, therefore, allowing facile isomerization of the excited states.

As to the triplet state, triplet energy of azobenzene was estimated as 190-200 kJ mol^{-1}[29], which is not much different from that of trans-stilbene, 205 kJ mol^{-1}[10]. Although 2-AntN=NPh did not give observable transient absorption of the triplet state with nanosecond spectroscopy, trans

2-AntCH=NPh showed absorption of the triplet state decaying with a lifetime of 2.0 μs[26]. This relatively long lifetime corresponds to the aforementioned inactivity of this triplet state for isomerization and shows the presence of too high activation barries for this state to overcome for the isomerization. This is in keeping with the results of computation of the potential energy surface of this compound, which shows the presence of relatively high energy barrier at the triplet state[30]. On the other hand, the triplet state of trans 2-AntN=CHPh decayed with a much shorter lifetime, less than 200 ns[26], accompanied by the isomerization.

The above difference in the reactivity of the triplet state between 2-AntCH=NPh and 2-AntN=CHPh may result from difference of the extent of the conjugation of the aryl group with the double bond. In the ground state of PhCH=NPh, the Ph group on the carbon atom is planar with the plane of the CH=N bond in gas phase as determined by electron diffraction[31], or nearly planar as twisted only ca. 10° from the plane in crystal according to X-ray crystallography[32]; on the other hand, the Ph group on the nitrogen atom is twisted from the plane more than 50° in gas phase, crystal and solution as determined by electron diffraction[31], X-ray crystallography[32], electronic absorption and photoelectron spectroscopy[33].

Accordingly, it is not unreasonable to suppose that 2-Ant group can take more planar conformation with the double bond in trans 2-AntCH=NPh than in trans 2-AntN=CHPh. This will stabilize the triplet state of the former to a higher extent than that of the latter, therefore, giving higher activation energy of isomerization for the former triplet state than for the latter.

Therefore, in the triplet state, different from the singlet state, low triplet excitation energy of anthracene ring (175 kJ mol^{-1}) seems effective in stabilizing the triplet state as seen in trans 2-AntCH=NPh and, though in lesser extent, trans 2-AntN=CHPh, but not effective to stabilize the triplet state of trans 2-AntN=NPh, which facilely isomerizes.

It is to be noted that, in the singlet excited state, contribution of the n,π* configuration to the lowest excited state will diminish the effect of relatively low lying excited state of anthryl moiety and accelerate the isomerization; however, on intersystem crossing from the singlet excited state to the triplet state, π,π* state of the anthryl group will lower in much larger energy than the n,π* state due to the well-known different energy gap between the π,π* and the n,π* states[34].

CONCLUSION

On design of conjugated aromatic unsaturated molecules such as Ar-X=Y-Ph as materials for photonics used under light irradiation, to prepare molecules durable for chemical action of light, substitution of either aromatic rings of low excitation energies such as anthracene and perylene or ferrocene ring containing on a C=C double bond can suitably prevent trans to cis isomerization of ArCH=CHPh. On the other hand, to attempt to induce morphological change of materials such as liquid crystals and LB films, various C=N and N=N bonds will generally be suitable, since these bonds isomerize even with substitution of the above aromatic rings.

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