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Photochromic Properties of Unsymmetric Mono- and Bis(phenylazo)naphthalenes

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To utilize the reversible photochromic system of phenylazonaphthalenes in a design of functional molecule, the photochromic behaviors of various substituted phenylazonaphthalenes have been investigated. Introduction of substituents onto ortho positions with respect to the azo group retarded the rate of thermal cis-to-trans isomerization. The retardation effects were greatly dependent on both the number and position of the ortho substituents. To investigate the reterdation effects of ortho substituents, the activation parameters were determined; the results suggest that the steric hindrance among the ortho substituents and the two nitrogen lone pairs of the azo group becomes far more severe in an inversional transition-state than in the ground cis-state, which leads to the remarkable slow cis-to-trans isomerization. On the basis of the kinetic data of various phenylazonaphthalenes, the complicated isomerization behaviors of unsymmetric bis(phenylazo)naphthalenes have been elucidated.

Since Hartley[1)] had first isolated the cis-isomer of azobenzene in 1938, the photochemical and thermal cis-trans isomerization of azobenzene derivatives has attracted considerable attention for many years because of its both theoretical and practical significance. In general the cis-isomers of azobenzenes are unstable and thermally revert to the trans-isomers by a first-order process in the dark. The mechanism of the remarkably facile thermal isomerization of cis-isomers has been the subject of numerous experimental and theoretical investigations.[2—15)] Two opposing mechanisms (rotation and inversion) have been proposed, however, in the present stage it seems to be agreed that most cis-azobenzenes without strong push-pull substituents proceed via an inversion mechanism.

On the other hand, recently, the reversible photochromic system of azobenzenes has been utilized to design a variety of functional molecules.[16—19)] To get higher capabilities of the functional molecules, the thermal stability of cis-isomers produced by irradiation of trans-isomers is sometimes required. However, azobenzene derivatives are generally less stable than azobenzene itself in the cis-forms: para-substitutions invariably accelerate the thermal cis-to-trans isomerization rate, regardless of the nature of the substituents, whereas ortho-substitutions produce complicated results, both acceleration and retardation effects being observed.[9)] Some azobenzenes substituted with alkyl,[9)] alkoxy,[20)] or halogeno[21,22)] groups at ortho positions have been found to be unusually stable, however, the effect of the ortho substituents is still obscure.

For the enormous researches on the isomerization of azobenzene derivatives, there are only several reports on that of phenylazonaphthalenes. With a view to utilize the reversible photochromic system of phenylazonaphthalenes in a design of functional molecule, we have examined the isomerization behavior of a variety of substituted phenylazonaphthalenes. Firstly, the substituent effect on the photochemical and thermal cis-trans isomerization of phenylazonaphthalenes are examined. Then, on the basis of the kinetic data of phenylazonaphthalenes, the complicated isomerization behaviors of unsymmetric bis(phenylazo)naphthalenes are elucidated.

Experimental

Measurements. All the melting points are uncorrected. The visible spectra were measured using a Hitachi 220A spectrophotometer. The ^{1}H NMR spectra were taken by using a Hitachi Model R-90H spectrometer and chemical shifts were recorded in parts per million (ppm) on the δ scale from tetramethylsilane as an internal standard. The elemental analyses were recorded on a Yanaco CHN recorder MT-2. The HPLC (high performance liquid chromatography) was carried out by using a JASCO 875-UV Intelligent UV-VIS detector equipped with a JASCO 880-PU and JASCO Cosmosil Packed Column (5C$_{18}$).

Materials. 1-Phenylazonaphthalene (**1a**) was prepared by condensing of nitrobenzene with 1-naphthylamine in the presence of sodium hydroxide at 180 °C.[23)] 1-Methoxy-4-(substituted phenylazo)naphthalenes (**1b**—**j**) and 2-methoxy-1-(substituted phenylazo)naphthalenes (**1k**—**n**) were prepared by the diazo coupling from the corresponding substituted anilines and 1- or 2-naphthol and the methylation of the resulting azo compounds was worked up with trimethylsulfonium hydroxide according to the literature.[24)]

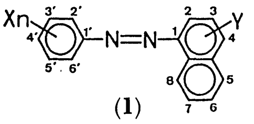
1-Methoxy-2-(*p*-tolylazo)naphthalene (**2**) was prepared by condensing 1,2-naphthoquinone with *p*-tolylhydrazine and the methylation of the resulting azo compound was worked up by using trimethylsulfonium hydroxide. The crude products obtained by the above reactions were purified by column chromatography (silica gel using benzene or xylene as eluents), and then recrystallized from ethanol. The physical and spectral data of these *trans*-phenylazonaphthalenes are shown in Table 1.

1-Methoxy-2,4-bis(substituted phenylazo)naphthalenes (**3a**—**c**) were prepared by the diazo coupling of 2 mole ratio of the corresponding substituted benzenediazonium salts with 1-naphthol, the resulting bisazo compounds were methylated by using trimethylsulfonium hydroxide. The crude products were purified by column chromatography (silica gel or activated alumina using benzene or xylene as eluents), and then recrystallized from ethanol.

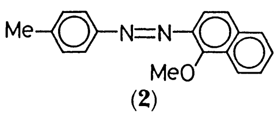
The physical and spectral data are as follows: **3a**, mp 141—142 °C. λ_{max} (benzene) 344 nm (ε 31400) 387 nm (ε 23600). ^{1}H NMR (CDCl$_3$) δ=2.42 (s, 6H, -CH$_3$), 4.45 (s, 3H, -OCH$_3$), 7.14—9.05 (m, 13H, aromatic protons). Found: C, 75.89; H, 5.74; N, 14.08%. Calcd for $C_{25}H_{22}N_4O$: C, 76.12; H, 5.62; N, 14.20%; **3b**, mp 155—157 °C. λ_{max} (benzene) 363 nm (ε 35600). ^{1}H NMR (CDCl$_3$) δ=3.88 (s, 6H, -OCH$_3$), 4.44 (s, 3H, -OCH$_3$), 6.8—9.0 (m, 13H, aromatic protons). Found: C, 70.07; H, 4.94; N, 12.99%. Calcd for $C_{25}H_{22}N_4O_3$: C, 70.41; H, 5.20; N, 13.14%; **3c**, mp 133—134 °C. λ_{max} (benzene) 333 (ε 23800), 361^{sh} (ε 20200), 488 nm (ε 2400). ^{1}H NMR (CDCl$_3$) δ=2.47 (s, 6H, -CH$_3$), 2.51 (s, 6H, -CH$_3$), 4.38 (s, 3H, -OCH$_3$), 7.16—9.0 (m, 11H, aromatic protons). Found: C, 76.69; H, 6.28; N, 13.50%. Calcd for $C_{27}H_{26}N_4O$: C, 76.75; H, 6.20; N, 13.26%.

Kinetic Measurements and Determination of Isomeric Composition of Mono- and Bis(phenylazo)naphthalenes. An appropriate amount of the sample was dissolved in a benzene containing 0.2% piperidine[25] in the dark. The solution was transferred to a 1 cm square cell put in cell holders thermostated at constant temperature, and was irradiated with a Black-Ray lamp (λ_{max} 366 nm) (UV-21, San Gabriel, CA911778 U.S.A.). The thermal cis-to-trans isomerization rate of phenylazonaphtalenes (**1a**—**n** and **2**) was

Table 1. Physical and Spectral Data of Trans-Phenylazonaphthalenes



(1)



(2)

No.	Compound Substituent		Mp/°C (lit.$^{b)}$)	Vis (benzene) λ_{max}/nm (ε_{max})		^{1}H NMR (CDCl$_3$) δ/ppm
	Xn	Y		π-π*	n-π*	
1a	H	H	67—70 (63.5, 69,70)	375(12900)	460(850)	7.25—9.10(m, 12H)
1b	H	4-MeO	84—85 (82, 83)	393(17900)	—	4.06(s, 3H, -OCH$_3$) 6.80—9.03(m, 10H)
1c	4-Me	4-MeO	99—101 (103—104, 100—101)	391(20800)	—	2.43(s, 3H, -CH$_3$) 4.04(s, 3H, -OCH$_3$) 6.79—9.06(m, 10H)
1d	4-MeO	4-MeO	130—132 (134)	393(21700)	—	3.86(s, 3H, -OCH$_3$) 4.02(s, 3H, -OCH$_3$) 6.79—9.00(m, 10H)
1e	4-Cl	4-MeO	126—128	410(21500)	—	4.01(s, 3H, -OCH$_3$) 6.76—9.01(m, 10H)
1f	4-NO$_2$	4-MeO	168—170 (169)	435(20100)	—	4.09(s, 3H, -CH$_3$) 6.76—9.05(m, 10H)
1g	2-Et	4-MeO	93—93.5	395(17800)	—	1.35(t, 3H, -CH$_3$) 3.23(q, 2H, -CH$_2$-) 4.04(s, 3H, -OCH$_3$) 6.80—9.10(m, 10H)
1h	2-MeO	4-MeO	125—126 (121—122)	400(18300)	—	4.04(s, 6H, -OCH$_3$×2) 6.80—8.50(m, 10H)
1i	2,6-Me$_2$	4-MeO	57—60	383(15400)	470(1340)	2.46(s, 6H, -CH$_3$) 4.06(s, 3H, -OCH$_3$) 6.81—8.95(m, 9H)
1j	2,6-Et$_2$	4-MeO	oil	378(13900)	470(1280)	1.20(t, 6H, -CH$_3$) 2.81(q, 4H, -CH$_2$-) 4. 06(s, 3H, -OCH$_3$) 6.81—9.01(m, 9H)
1k	4-Me	2-MeO	61—63 (68)	377(9400)	472(2010)	2.44(s, 3H, -CH$_3$) 3.95(s, 3H, -OCH$_3$) 7.28—8.38(m, 10H)
1l	4-MeO	2-MeO	108—109.5 (107)	373(11700)	467(2520)	3.87(s, 3H, -OCH$_3$) 3.93(s, 3H, -OCH$_3$) 7.00—8.32(m, 10H)
1m	4-Cl	2-MeO	63.5—65 (65)	387(10200)	480(2290)	3.96(s, 3H, -OCH$_3$) 7.2—8.48(m, 10H)
1n	2-MeO	2-MeO	97—98 (93—94)	384(8300)	482(1700)	3.97(s, 3H, -OCH$_3$) 4.01(s, 3H, -OCH$_3$) 6. 90—8.50(m, 10H)
2			72—74 (74—77)	384(14100)	—	2.42(s, 3H, -CH$_3$) 4.37(s, 3H, -OCH$_3$) 7.1—8.5(m, 10H)

a) Satisfactory elemental analyses were obtained for all the compounds. b) Beilstein.

followed by measuring the absorbance recovery at the absorption maximum of the trans-isomer with a spectrophotometer. The rate constant was estimated by the first order kinetic analysis.

The isomeric composition of the photostationary mixture was determined by HPLC analysis. In the case of bis(phenylazo)naphthalenes (**3a**—**c**), the thermal isomerization rates of the photo-products (cis-cis, trans-cis, and cis-trans isomers) were estimated on the basis of the decreasing curves of the corresponding isomers (refer to Fig. 4).

Results and Discussion

Photochemical and Thermal Cis-Trans Isomerization of Phenylazonaphthalenes. We have prepared a variety of substituted phenylazonaphthalenes whose physical and spectral data measured in the trans-forms are listed in Table 1. The absorption spectra of the parent compound (**1a**) exhibits typical π-π* and n-π* absorption bands. In the spectra of most para-substituted compounds (**1b**—**h**) the n-π* absorption is buried underneath the intense longest-wavelength π-π* absorption band. On the contrary, some ortho-substituted compounds (**1i**—**n**) exhibit well separated π-π* and n-π* absorption bands. It is known that in the absorption spectra of trans-azobenzenes *p*-substituents cause a blue shift in the n-π* band and a red shift in the first π-π* band and that *o*-substituents cause opposite changes. With the aid of calculations by using semiempirical INDO/1 methods, Forber et al.[15] elucidated that the effects caused by the *p*-substituents are electronic in nature and those caused by the *o*-substituents contain a steric component: the introduction of 2,6-dialkyl groups into azobenzene causes a strong repulsion between the ortho substituent and the distant nitrogen lone pair of the azo group, which is the origin of the red shift in the n-π* band and the blue shift in the π-π* band.

We have investigated the photochemical and thermal cis-trans isomerization of the substituted phenylazonaphthalenes. When a solution of the *trans*-phenylazonaphthalene was irradiated with a Black-Ray lamp (λ_{max} 366 nm), a photostationary trans-cis mixture was obtained within 5 minutes, subsequent standing the solution in the dark resulted in gradual reversal to the trans-isomer by a first-order process. The cis-isomers of these compounds were stable enough to permit chromatographic separation, so that the isomeric composition of the photo-stationary mixtures could be determined by HPLC analysis. The thermal cis-to-trans isomerization rate was estimated from the absorbance recovery at the absorption maximum of the trans-isomer. These results obtained in benzene are summarized in Table 2. Both the isomeric composition in the photostationary state and the thermal cis-to-trans isomerization rate were drastically affected by the substituents. Para substitutions accelerated the rate, while ortho substitutions retarded the rate and the retardation effect tended to increase in degree depending on both the number and position of the ortho substituents. Namely, as seen in the compounds (**1g** and **1h**), the introduction of one ortho substituent onto the phenyl ring did not alter the isomerization rate greatly. However, as seen in the compounds (**1i**—**n**, and **2**), the introduction of one methoxy group at ortho position onto the naphthyl ring or 2′,6′-disubstituents onto the phenyl ring retarded the rate effectively. It was found that the rate retardation effect by ortho substituents on the phenylazonaphthalene tends to increase in the following order; 1-substituent on the naphthyl ring in **2**<2-substituent on the naphthyl ring in **1**<2′,6′-disubstituent on the phenyl ring. To investigate the difference in the retardation effect of ortho substituents, we determined the activation parameters about several phenylazonaphthalenes. A plot of $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ is presented in Fig. 1. A good fit line can be

Table 2. Isomeric Composition in the Photostationary State and First-Order Rate Constant (k) in the Thermal Cis-to-Trans Isomerization of Phenylazonaphthalenes at 30 °C

Compound	Isomers in photostationary state		Rate constant 10^3k/min^{-1}
	cis/%	trans/%	
1a	72.3	27.7	5.22
1b	38.7	61.3	21.4
1c	54.5	45.5	34.9
1d	60.9	39.1	62.6
1e	44.8	55.2	39.8
1f	21.9	78.1	57.8
1g	45.0	55.0	28.1
1h	55.1	44.9	14.3
1i	35.5	64.5	0.472
1j	33.1	66.9	0.484
1k	54.2	45.8	0.678
1l	58.4	41.6	0.903
1m	53.2	46.8	1.05
1n	50.2	49.8	0.599
2	87.5	12.5	1.86

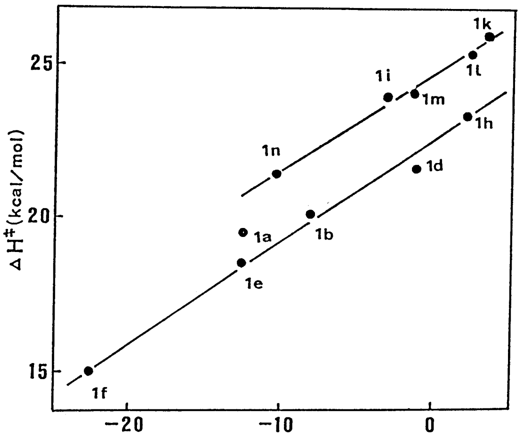
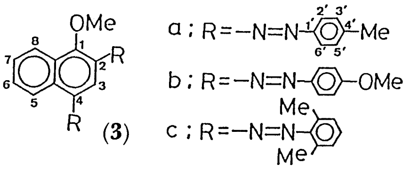


Fig. 1. $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ for the thermal cis-to-trans isomerizations of phenylazonaphthalenes.

drawn through the phenylazonaphthalenes (**1b**, **1d—f**, and **1h**) which have para-substituent and/or one-ortho-substituent on the phenyl ring. However, the phenylazonaphthalenes (**1i**, **1k—n**) which have 2-methoxy group on the naphthyl ring or 2′,6′-dialkylated phenyl ring lie far above the line and seem to describe an another line. A similar trend has been reported by Otruba and Weiss[14] who measured the activation energy for cis-to-trans thermal isomerization of various "low-bipolarity" azobenzenes in a cholesteric phase and in several other solvents and observed that most of azobenzenes were on a straight line, however, the 2,6-dimethylated azobenzenes fell consistently above it and described a separate, nearly parallel slope line. The good accordance between the above results suggests that the isomerization mechanism of our phenylazonaphthalenes are the same as that of "low-bipolarity" azobenzenes which has been concluded to proceed via an inversional mechanism, and that the introduction of 2-methoxy group onto the naphthyl ring leads to the same effects on the isomerization rate as does the 2,6-dimethyl groups onto the phenyl ring; the 2-methoxy and naphthyl ring parts would be sterically correspond to the 2,6-dialkyl groups. These results suggest that, in these ortho blocked azo-compounds, the steric hindrance among the ortho substituents and the two nitrogen lone pairs of the azo group becomes far more severe in an inversional transition-state than in the ground cis-state, which leads to the remarkable slow cis-to-trans isomerization.

Photochemical and Thermal Cis-Trans Isomerization of Bis(phenylazo)naphthalenes. Though the photochemical and thermal isomerization of azobenzenes has been examined widely, there are only a few reports on that of disazobenzenes. In 1939 Cook et al.[20] have first identified the possible geometric isomers of bisazo compounds, cis-cis, cis-trans, and trans-trans isomers. Recently, Itoho and co-workers have reported the kinetics and mechanism of the photochemical and thermal isomerization of some symmetric bisazo compounds, and have proposed two mechanisms, simultaneous(cis-cis→trans-trans)[26a] and consecutive (cis-cis→cis-trans→trans-trans)[26b] routes for the isomerization of bisazo compounds.

In this paper, we have elucidated a complicated isomerization behavior of unsymmetric bis(phenylazo)naphthalenes, 1-methoxy-2,4-bis(substituted phenylazo)naphthalenes (**3a—c**), on the basis of the kinetic data of a variety of substituted patterns of phenylazonaphthalenes summarized in Table 2. As shown in Fig. 2, the irradiation of a benzene solution of trans-trans-isomer of 1-methoxy-2,4-bis(*p*-tolylazo)naphthalene (**3a**) with a Black-Ray lamp (λ_{max} 366 nm) resulted in the trans-cis photostationary state within 5 minutes. The HPLC analysis of the isomeric mixture in the photostatlonary state showed the existence of four isomers (A, B, C, and D), the amounts of which changed gradually with subsequent standing the solution in the dark; three isomers (A, B, and C) corresponding to the photochemical isomerization products (cis-cis, trans-cis, and cis-trans isomers) disappeared one by one, and the final chromatogram was accordance with the one before irradiation: the trans-trans isomer was completely reproduced to the start-



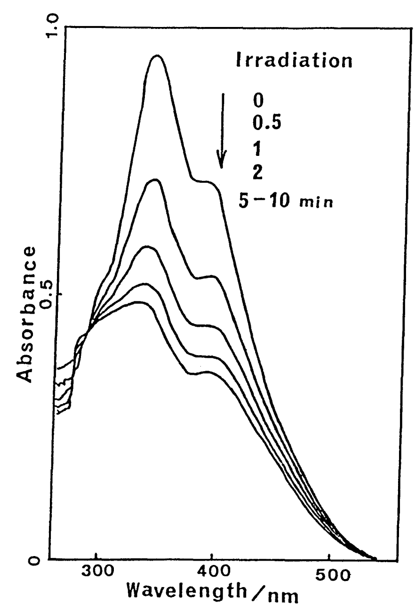


Fig. 2. Changes in the absorption spectra of **3a** (3.01×10^{-5} mol dm^{-3}) by irradiation with a Black-Ray lamp.

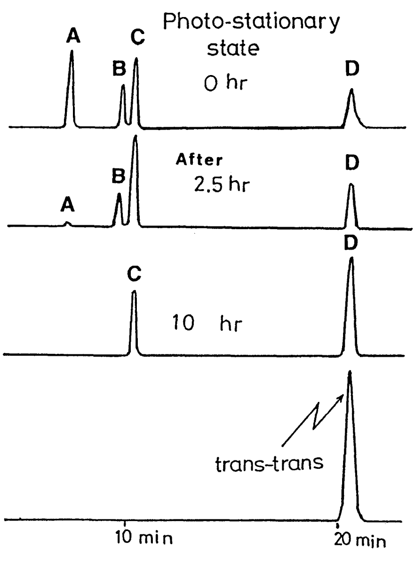


Fig. 3. Changes in the HPLC chromatograms of **3a**.

ing amounts (Fig. 3). Therefore, the quantitative measurements could be performed by using benzylideneaniline as internal standard. The changes in the isomeric composition of the irradiated solution with time in the dark at 30 °C are shown in Fig. 4. It was estimated that in the photostationary state the composition of the mixture was A (28.2%), B (19.0%), C (27.2%), and D (25.6%). In the rapid decreasing region of the most unstable A-isomer, C-isomer increased remarkably, reached to a maximum and then decreased gradually, whereas, in the same region the effect on a decreasing curve of B-isomer was small. These results imply that A-isomer converts more easily into C-isomer than into B-isomer, because of a big difference in the thermal cis-to-trans isomerization rates between the 2- and 4-(*p*-tolyl)azo groups in **3a**. To know which *p*-tolylazo group (2- or 4-position) has larger stability in the cis-form, we refer to the cis-to-trans isomerization rates of the corresponding two isomeric *p*-tolylazonaphthalenes, 1-methoxy-4-(*p*-tolylazo)naphthalene (**1c**) and 1-methoxy-2-(*p*-tolylazo)naphthalene (**2**), as models. As seen in Table 2, the thermal cis-to-trans isomerization rate constants of **1c** and **2** are 3.49×10^{-2} min^{-1} and 1.86×10^{-3} min^{-1}, respectively; the 4-(*p*-tolylazo) group isomerizes ca. 18.8 times faster than the 2-(*p*-tolylazo)

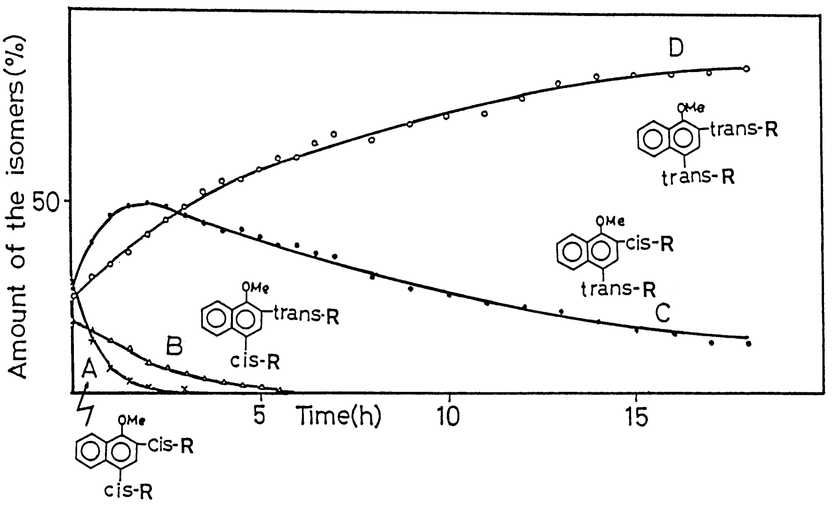


Fig. 4. Changes in isomeric composition (%) vs. time for the thermal cis-to-trans isomerization of **3a** at 30 °C.

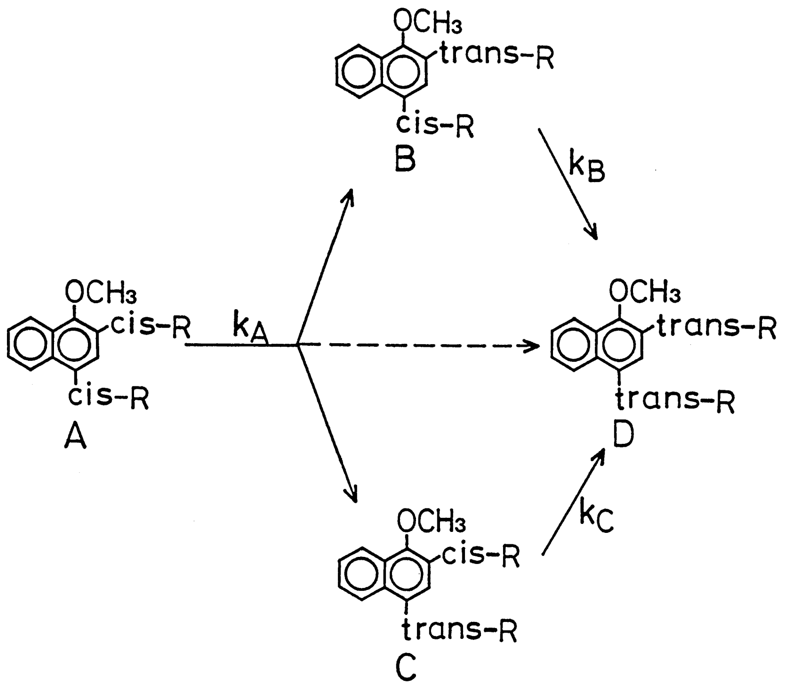


Fig. 5. Possible routes for the thermal cis-to-trans isomerization of bis(phenylazo)naphthalenes (**3**).

group. It was assumed from these kinetic data that the isomers A, B, and C correspond to the cis-cis-, trans-cis-, and cis-trans-forms as shown in Fig. 4, respectively. As shown in Fig. 5 there are three possible routes for the disappearence of A-isomer, namely, A→B, A→C, and A→D. We could not determine the exact individual rate constants for these three paths. The diminishing rate constants of A-, B-, and C-isomers could be calculated and shown in Table 3 together with the results obtained by using **3b** and **3c** as starting materials. The C-isomers are more stable than B-isomers in every case, which is consistent with the expectation that the cis-2-azo groups isomerize slower than the cis-4-azo groups and thence support the assignment of the geometries for the B- and C-isomers.

The thermal cis-to-trans isomerization rate was also considerably affected by the substituents introduced onto the phenyl rings. The similar substitution effects as seen in the phenylazonaphthalenes were obserbed. Namely, 4′-methoxy group accelates the rate, while 2′,6′-dialkyl groups drastically retard the rate. Comparing with three bisazo compounds (**3a**—**c**), the stability of each three geometric cis-isomers (A, B, and C) were always in the following order: **3b**<**3a**≪**3c**. Furthermore, by comparing rate constants (k_B(**3a**), k_C(**3a**), k_B(**3b**), and k_B(**3c**)) with the rate constants (k(**1c**), k(**2**), k(**1d**), and k(**1i**)) of the corresponding phenylazonaphthalenes shown in Table 2, it was found that cis-forms of azo groups are more stable in bis(phenylazo)naphthalenes (**3**) than in phenylazonaphthalenes (**1** and **2**). Especially, in the case of **3c** trans-cis-(B) and cis-trans-isomer(C) were found to be marvelously stable. Isomeric compositions of bis(phenylazo)naphthalenes (**3a**—**c**) in photostationary state obtained by irradiation with various light sources are shown in Table 4. As bis(phenylazo)naphthalenes have strong broad absorption over UV-VIS region(refer to Fig. 2), the photoisomerization proceeded efficiently even on exposure to sun light. These informations are useful for designing new functional molecules based upon a reversible photochromic system of phenylazonaphthalenes.

Table 3. Diminishing Rate Constants (k_A, k_B, and k_C) for the Thermal Cis-to-Trans Isomerization of Bis(phenylazo)naphthalene at 30 °C

Compound	10^3k_A/min^{-1}	10^3k_B/min^{-1}	10^3k_C/min^{-1}
3a	28.6	10.7	1.50
3b	48.3	13.2	2.24
3c	2.93	0.189	0.0648

Table 4. Isomeric Composition of Bis(phenylazo)naphthalenes in the Photostationary State on Various Light Sources

Compound	Light source	% of isomers			
		A	B	C	D
3a	B.L.[a)]	28.2	19.0	27.2	25.6
	H.L.[b)]	20.6	24.4	26.0	29.0
	S.L.[c)]	19.3	24.9	26.6	29.2
3b	B.L.[a)]	32.4	19.7	24.3	23.6
3c	B.L.[a)]	21.7	7.5	23.5	47.3

a) Black-Ray lamp ($\lambda_{max}\approx$366 nm). b) 400W High-pressure mercury lamp ($\lambda\geq$300 nm). c) Sun light.

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