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PHOTOTRANSFORMATIONS IN NONHOMOGENEOUS MEDIA: cis-trans-ISOMERIZATION OF OLEFINS IN INCLUSION COMPOUNDS.

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Abstract - In order to elucidate photophysical and steric factors influencing extent and reaction pathway of a reaction process involving inclusion compounds the photoisomerization of cis- or trans- stilbene and cis- or trans- methylcinnamate has been studied in cavities of deoxycholic acid or Ni(II)-(4-picoline)$_4$-(NCS)$_2$. The observed isomerization yields have been correlated with the excitation energy transfer processes which occur between host and guest molecules as well as with the symmetry properties of the various species involved during the isomerization process.

INTRODUCTION

The use of host-guest inclusion compounds to carry out phototransformations in the solid state may be of value particularly in regio and stereospecific syntheses.[1] However, the achievement of significant results in this scarcely studied field is strictly dependent on the knowledge of the photophysical and stereochemical factors influencing any photochemical process which occurs in the cavities of a host-guest inclusion compound.

This paper deals with a specific phototransformation, the cis-trans-isomerization of olefins, in solution and in inclusion compounds. The purpose is to study the photophysical and stereochemical factors which determine the course of this reaction process.

It seems useful to briefly outline the characteristics of these factors.

1 - Host-Guest Electronic Energy Transfer

It has been shown that in molecular organic crystals and aggregates, where a "strong coupling" exists between the molecules, the phenomena consequent to light irradiation, i.e., the electronic energy transfer processes, involve excitons[2]. For a host-guest inclusion compound, where a "very weak coupling" exists between the host and guest molecules,[3,4] any energy transfer between host and guest molecules involves resonance coulombic multipolar or short-range exchange energy transfers. In addition, any energy transfer process strongly depends on the anisotropy of the interaction between host and guest molecules.[4] On these premises, a certain number of excitation decay functions have been developed which represent the spreading of the electronic excitation vs. time in an inclusion compound.[5] In fact, on the basis of the unit cell parameters of a specific inclusion compound it is possible to compute all short-range interactions between the species and the consequent energy transfer processes. These functions represent various possible conditions: i.e., host molecules which absorb light radiation with transfer of excitation to unexcited guest molecules, host molecules inert to radiation which is absorbed directly by guests with consequent excited guest → unexcited guest energy migration, etc..[5,6]

The knowledge of the spreading of excitation energy vs. time in a particular inclusion compound may afford an estimate of the extent of a specific phototransformation. For instance, the yield of naphthalene obtained by U.V. irradiation of the inclusion compound $Ni(II)-(4\text{-picoline})_4-(NCS)_2$ and 2-Bromo-naphthalene is significantly larger than that obtained by irradiating the inclusion compound formed by the same host and 1-Bromo-naphthalene as a guest.[7] For the two inclusion compounds the photophysical properties of the guests are rather similar and obviously no difference exists for the host moiety. However, the unit cells of the two inclusion compounds belong to different space groups with significant differences in the host-guest spatial relative orientations. Hence, numerical calculations based on these structures lead to different plots of excitation spreading vs. time for the two complexes which correctly correlate with the observed extent of naphthalene yields i.e., the rate of energy transfer from the host to 2-Bromo-naphtalene is about 10 times larger than that from the same excited host to 1-Bromo-naphtalene.[6,7]

2 - Steric Effects

A reaction involving an inclusion compound may be represented as a multistep process:

$$H + G \rightarrow [G]_H \xrightarrow{h\nu} [Exc]_H \rightarrow [P]_H \rightarrow H + P$$

where the symbols H, G and P represent the host, guest and product, respectively, and the symbols in square brackets represent the guest, transition state and product included in the host cavity, respectively.

With reference to this reaction process the following symmetry considerations have been suggested.[5] First, the mere existence of an inclusion compound, like $[G]_H$, $[Exc]_H$ or $[P]_H$ implies that at least the included species fits inside the host cavity. However, in case no common symmetry element exists between the host cavity site and the guest, a disordered structure has been observed for the inclusion compound. On the other hand when one or more symmetry elements exist in common between the host cavity site and the guest, an ordered structure has been observed for the inclusion compound, and a higher efficiency occurs for the reaction step involved with respect to the disordered structure.[8,9] Finally, when a single reaction step involves a change of the host cavity[10] all the symmetry elements present in the lower symmetry structure should be present in the higher symmetry structure i.e., they are in a group-subgroup relation. If more than one subgroup is possible, the more symmetric corresponds to the more probable reaction pathway. Examples of these symmetry considerations will be given in the next paragraph.

3 - The cis- trans- Isomerization of Olefins

The following systems have been irradiated by U.V. light:

a) cis-stilbene and trans-stilbene in cyclohexane.
b) cis-stilbene and trans-stilbene in deoxycholic acid.
c) cis-stilbene and trans-stilbene in $Ni(II)-(4\text{-picoline})_4(NCS)_2$.
d) cis-methyl-cinnamate and trans-methyl-cinnamate in deoxycholic acid.
e) cis-methyl-cinnamate and trans-methyl-cinnamate in $Ni(II)-(4\text{-picoline})_4(NCS)_2$.

These systems were chosen in order to correlate the results obtained in this work with significant results generated elsewhere on similar systems involving different inclusion compounds.[9,11]

RESULTS AND DISCUSSION

The cis- and trans-photoisomerization of the various systems is summarized in Table I. The following observations are noteworthy.

i- In solution, a final photostationary ratio is reached at a dose of 3.6×10^{18} quanta from either cis-stilbene or from trans-stilbene.

ii- When cis- or trans-stilbene is irradiated in cavities of deoxycholic acid or $Ni(II)-(4\text{-picoline})_4(NCS)_2$ the only observed conversion is a cis → trans isomerization, (only minor conversion of the trans to cis isomer is observed).

iii- When cis- or trans-methyl-cinnamate is irradiated in deoxycholic acid or in $Ni(II)-(4\text{-picoline})_4(NCS)_2$, cis $\rightleftarrows$ trans isomerization occurs.

iv- The per cent conversion of cis-stilbene to trans-isomer, when included in deoxycholic acid, reaches a steady state of 48% at a dose of 1.1×10^{20} quanta cm^{-2}. On the other hand, when cis-stilbene is included in $Ni(II)-(4\text{-picoline})_4(NCS)_2$ the trans isomer increases with the dose.

Table II shows the conversion yields for the inclusion compounds when irradiated by gamma rays. The behaviour is analogous to that previously reported for U.V. irradiation.

Independent results obtained for the same guests included in tri-ortho-thymotide[9] (TOT) or in ß-cyclodextrin[11] (ß-CD) are summarized in table III.

It is apparent that a similar behaviour is displayed by all the systems studied, i.e.:

i- cis → trans photoisomerization is the favoured reaction path for both cis-

TABLE I. Photoisomerization of cis/trans Olefins.

System	Isomerization Product (Per cent conversion)		Irradiation Dose (Quanta cm^{-2})
1. In cyclohexane:			
a) trans-stilbene	cis isomer	38%	3.6×10^{18}
b) cis-stilbene	trans isomer	48%	"
c) trans-cinnamate	cis isomer	64%	"
d) cis-cinnamate	trans isomer	30%	"
2. In deoxycholic acid:			
a) trans-stilbene	cis isomer	0.01%	1.1×10^{20}
b) cis-stilbene	trans isomer	48%	"
c) trans-cinnamate	cis isomer	30%	"
d) cis-cinnamate	trans isomer	28%	"
3. In Ni(II)-complex:			
a) trans-stilbene	cis isomer	0.2%	3.2×10^{20}
b) cis-stilbene	trans isomer	80%	"
c) trans-cinnamate	cis isomer	30%	"
d) cis-cinnamate	trans isomer	30%	"

TABLE II. Isomerization of cis/trans Stilbene Under Gamma Irradiation.

System	Isomerization Product (Per cent conversion)		Irradiation Dose (MRads)
1. In deoxycholic acid:			
a) trans-stilbene	cis isomer	0.1%	60
b) cis-stilbene	trans isomer	75%	"
2. In Ni(II)-complex:			
a) trans-stilbene	cis isomer	0.1%	60
b) cis-stilbene	trans isomer	65%	"

TABLE III. Photoisomerizations of cis/trans Olefins in Inclusion Compounds.

Guest	Isomerization product	Hosts			
		DCA	Ni(II)-complex	TOT	β-CD
1) trans-stilbene	cis isomer	0.01%	0.2%	0%	5%
2) cis-stilbene	trans isomer	48%	80%	100%	90%
1) trans-cinnamate	cis isomer	30%	-	50%	55%
2) cis-cinnamate	trans isomer	28%	-	50%	45%

and trans-stilbene; no photochemical trans → cis conversion is observed in the case of trans-stilbene.

ii- cis ⇄ trans photoisomerization occurs for cis- or trans-cinnamate esters;

iii- a cis ⇄ trans photoisomerization is observed whenever stilbenes are irradiated in solution.

These experimental results give the opportunity for a thorough discussion of the action of the photophysical and steric factors outlined in the introduction.

1 - Photophysics of Isomerization.

With reference to the photophysical behaviour of the host molecules under U.V. irradiation, TOT or $Ni(II)(4\text{-picoline})_4(NCS)_2$ absorb and ß-CD or DCA are inert to radiation, at the employed irradiation wave lenght of ca. 350 nm.

On the basis of known structural and photophysical properties of the involved species, the following estimate for the extent of isomerization in these systems may be suggested:

i- In the case of TOT or $Ni(II)(4\text{-picoline})_4(NCS)_2$ inclusion compounds, guest molecules are excited by energy transfer from the excited host molecules. The extent of isomerization increases steadly with the dose.

ii- In the case of the DCA complex the spreading of excitation depends on the guest molecules in the host channels and their spatial distribution. The extent of isomerization is lower than that observed in the previous case i; it reaches a steady-state at a given irradiation dose, which depends on the efficiency of excitation energy migration among the guest molecules stacked in the host channels.

iii- in the case of ß-CD the excitation is directly absorbed by the guests which are only partially inserted in the ring-like host cavities, as shown by molecular CPK models.[11] Hence, the extent of conversion is a direct function of the radiation absorbed by the guests and increases steadly with the dose.

2 - Stereochemistry of Isomerization

The possibility of correlating the observed isomerizations with the symmetry properties of the various systems will now be investigated.

The empty host cavity sites of TOT and $Ni(II)\text{-}(4\text{-picoline})_4(NCS)_2$ complexes belong to the symmetry group $C_i = \{E, i\}$, i.e. they are centrosymmetric; trans-stilbene belongs to the symmetry group $C_{2h} = \{E, C_2, i, \sigma_h\}$; cis-stilbene to the group $C_{2v} = \{E, C_2, \sigma'_v, \sigma_v\}$ and trans- or cis-cinnamate esters belong to the group $C_s = \{E, \sigma_h\}$. The resultant symmetry group of two bodies of different shapes treated as a single system, (as in the case of an empty cylinder which contains a sphere or in the case of a host-guest complex), is equal to the largest common subgroup of the symmetry groups of the constituent bodies.[12] If the following symbols are adopted: H for TOT or $Ni(II)\text{-}(4\text{-picoline})_4(NCS)_2$, t-ST for trans-stilbene and c-ST for the cis-isomer, t-CIN and c-CIN for the two cinnamate esters, Scheme 1 shows the multistep reaction processes for the systems studied.

The following observations deserve comment.

i- For trans-stilbene, both TOT and Ni(II)-(4-picoline)$_4$(NCS)$_2$ inclusion complexes belong to the C_i symmetry group. The cis-stilbene inclusion compounds belong to a lower symmetry group $C_1 = \{E\}$, with no other symmetry element except its Identity. In relation to this fact, it was observed that cis-stilbene is included in disordered positions in the host cavities.[9]

ii- For both cis- and trans-stilbene the favoured isomerization pathway is towards the more symmetric structure, i.e. a C_i complex. This pattern correlates with the observed reaction products.

iii- In the case of cis- or trans- cinnamates both isomers are included and isomerized by irradiation with no change of symmetry in the various steps: as a consequence, no favoured pattern of isomerization exists and is experimentally observed.

iv- The structure of the $\left[\mathrm{Exc}\right]_H$ should take into account the symmetry of the transition state from the guest to the product.[13] For trans-stilbene, which remains unchanged during irradiation, it seems reasonable that C_{2h} symmetry exists for the transition state corresponding to the free molecule symmetry. Hence, for a C_i host cavity site $C_i \cap C_{2h} = C_i$ excited-complex symmetry results. On the other hand, cis-stilbene, which belongs to C_{2v} symmetry, isomerizes to its trans isomer and its transition state involves a twisted molecular structure of $C_2 = \{E, C_2\}$ or $C_1 = \{E\}$ symmetry. Hence, in cis-stilbene a $C_i \cap C_2 = C_1$ or $C_i \cap C_1 = C_1$ excited-complex symmetry results.

Scheme 2 reports the reaction process in the case of DCA-olefins complexes. Here, the host cavity site symmetry is $D_2 = \{E, C_2^x, C_2^y, C_2^z\}$. The symmetries of the various reaction steps and correlation with experimental observations are analogous to those examined for the previous two inclusion compounds.

As far as the structure of $\left[\mathrm{Exc}\right]_{DCA}$ is concerned, it seems reasonable to assume for trans-stilbene a transition state of C_{2h} symmetry and for cis-stilbene a transition state of C_2 or C_1 symmetry. Accordingly, $\left[\mathrm{Exc}\right]_{DCA}$ should belong to $D_2 \cap C_{2h} = C_2$ symmetry for trans-stilbene and to $D_2 \cap C_2 = C_2$ or $D_2 \cap C_1 = C_1$ symmetry for the cis isomer. However, the observed cis → trans conversion, with practically no starting cis isomer remaining after irradiation, rules out the possibility of a C_2 symmetry which should generate both trans and cis isomers in similar yields.

The reaction process in the case of ß-CD-olefins has been thoroughly discussed with the help of molecular CPK models[11]. From these models it may be inferred that a trans → cis isomerization of stilbene is restricted by the ß-CD cavity, in particular by an interaction between a phenyl ring and the rim of the cavity On the other hand, when trans-cinnamate ester is the guest, a trans → cis isomerization may occur because of the lack of steric hindrance.

The symmetry associated with the various reaction steps may not only help to explain the path of a multistep reaction process but also the overall

SCHEME 1 -The Photoisomerization Process in TOT and Ni(II)-(4-picoline)$_4$(NCS)$_2$ Inclusion Compounds.

$$\begin{tikzcd}
 & & & \underset{(C_i)}{[\text{Exc}_1]_H} \arrow[r] & \underset{(C_i)}{[\text{t-ST}]_H} \\
\text{1-} & \underset{(C_i)}{\text{H}} + \underset{(C_{2h})}{\text{t-ST}} \arrow[r] & \underset{(C_i)}{[\text{t-ST}]_H} \arrow[ur, "h\nu"] \arrow[dr] & & \\
 & & & \underset{(C_1)}{[\text{Exc}_2]_H} \arrow[r] & \underset{(C_1)}{[\text{c-ST}]_H}
\end{tikzcd}$$

$$\begin{tikzcd}
 & & & \underset{(C_i)}{[\text{Exc}_1]_H} \arrow[r] & \underset{(C_i)}{[\text{t-ST}]_H} \\
\text{2-} & \underset{(C_i)}{\text{H}} + \underset{(C_{2v})}{\text{c-ST}} \arrow[r] & \underset{(C_1)}{[\text{c-ST}]_H} \arrow[ur, "h\nu"] \arrow[dr] & & \\
 & & & \underset{(C_1)}{[\text{Exc}_2]_H} \arrow[r] & \underset{(C_1)}{[\text{c-ST}]_H}
\end{tikzcd}$$

$$\begin{tikzcd}
 & & & & {[\text{t-CIN}]_H \ (C_1)} \\
\text{3-} & \underset{(C_i)}{\text{H}} + \underset{(C_s)}{\text{t-CIN}} \arrow[r] & \underset{(C_1)}{[\text{t-CIN}]_H} \arrow[r, "h\nu"] & \underset{(C_1)}{[\text{Exc}]_H} \arrow[ur] \arrow[dr] & \\
 & & & & {[\text{c-CIN}]_H \ (C_1)}
\end{tikzcd}$$

$$\begin{tikzcd}
 & & & & {[\text{t-CIN}]_H \ (C_1)} \\
\text{4-} & \underset{(C_i)}{\text{H}} + \underset{(C_s)}{\text{c-CIN}} \arrow[r] & \underset{(C_1)}{[\text{c-CIN}]_H} \arrow[r, "h\nu"] & \underset{(C_1)}{[\text{Exc}]_H} \arrow[ur] \arrow[dr] & \\
 & & & & {[\text{c-CIN}]_H \ (C_1)}
\end{tikzcd}$$

SCHEME 2 - The Photoisomerization Process in DCA Inclusion Compounds.

$$\begin{tikzcd}
 & & & \underset{(C_2)}{[\text{Exc}_1]_{\text{DCA}}} \arrow[r] & \underset{(C_2)}{[\text{t-ST}]_{\text{DCA}}} \\
\text{1-} & \underset{(D_2)}{\text{DCA}} + \underset{(C_{2h})}{\text{t-ST}} \arrow[r] & \underset{(C_2)}{[\text{t-ST}]_{\text{DCA}}} \arrow[ur, "h\nu"] \arrow[dr] & & \\
 & & & \underset{(C_1)}{[\text{Exc}_2]_{\text{DCA}}} \arrow[r] & \underset{(C_2)}{[\text{c-ST}]_{\text{DCA}}}
\end{tikzcd}$$

$$\begin{tikzcd}
 & & & \underset{(C_2)}{[\text{Exc}_1]_{\text{DCA}}} \arrow[r] & \underset{(C_2)}{[\text{t-ST}]_{\text{DCA}}} \\
\text{2-} & \underset{(D_2)}{\text{DCA}} + \underset{(C_{2v})}{\text{c-ST}} \arrow[r] & \underset{(C_2)}{[\text{c-ST}]_{\text{DCA}}} \arrow[ur, "h\nu"] \arrow[dr] & & \\
 & & & \underset{(C_1)}{[\text{Exc}_2]_{\text{DCA}}} \arrow[r] & \underset{(C_2)}{[\text{c-ST}]_{\text{DCA}}}
\end{tikzcd}$$

$$\begin{tikzcd}
 & & & & {[\text{t-CIN}]_{\text{DCA}} \ (C_1)} \\
\text{3-} & \underset{(D_2)}{\text{DCA}} + \underset{(C_s)}{\text{t-CIN}} \arrow[r] & \underset{(C_1)}{[\text{t-CIN}]_{\text{DCA}}} \arrow[r, "h\nu"] & \underset{(C_1)}{[\text{Exc}]_{\text{DCA}}} \arrow[ur] \arrow[dr] & \\
 & & & & {[\text{c-CIN}]_{\text{DCA}} \ (C_1)}
\end{tikzcd}$$

$$\begin{tikzcd}
 & & & & {[\text{t-CIN}]_{\text{DCA}} \ (C_1)} \\
\text{4-} & \underset{(D_2)}{\text{DCA}} + \underset{(C_s)}{\text{c-CIN}} \arrow[r] & \underset{(C_1)}{[\text{c-CIN}]_{\text{DCA}}} \arrow[r, "h\nu"] & \underset{(C_1)}{[\text{Exc}]_{\text{DCA}}} \arrow[ur] \arrow[dr] & \\
 & & & & {[\text{c-CIN}]_{\text{DCA}} \ (C_1)}
\end{tikzcd}$$

product yield. In fact, by comparing Table III with Schemes 1 and 2, it may be observed how the largest yields of isomerization occur when the symmetry of the transition state complex matches the host cavity site symmetry.

CONCLUSION

Phototransformations with guest olefins in inclusion compounds formed by different host molecules have been studied in an attempt to carefully investigate the influence of photophysical and stereochemical factors on reaction pathways and yields.

It seems reasonable to draw the following conclusions:

i- Provided the photophysics of the excited states of the host and guest molecules as well as the lattice parameters for an inclusion complex are available, it is possible to make reasonable assumptions on the kind of host-guest energy transfer processes which occur under irradiation and to evaluate the extent of a specific reaction process.[5-7]

ii- Simple considerations based on the symmetry of the host cavity site as well as on the symmetry of the guest and product may suggest the favoured reaction pathway.

iii- These studies on the photophysics and stereochemistry of a photoreaction process in an inclusion compound may be extended to other processess which occur in molecular cavities as, for instance, in reactions in zeolites,[14] in enzymatic clefts,[15] etc.

EXPERIMENTAL

Products. cis-stilbene was purchased from EGA CHEMIE and trans-stilbene from FLUKA. They were further purified using VPC on a column of E301 on chromosorb W, at 150°C. Trans-methyl-cinnamate was purchased from SIGMA Chem. Co. and further purified by VPC on the same column, at 120°C. Cis-methyl-cinnamate was prepared by U.V. irradiation of a benzene solution of the trans-isomer and further purified by VPC. Deoxycholic acid was purchased from EGA Chemie. $Ni(II)-(4-picoline)_4(NCS)_2$ was prepared as previously described.[7]

Inclusion compounds. The inclusion compounds with the Ni(II)-complex were prepared as previously described. The inclusion compounds with deoxycholic acid were prepared by adding to a methanolic solution of DCA the appropriate guest. For both compounds, the obtained crystals were carefully washed with spectral grade benzene and analyzed for their host-guest ratio.

Irradiation and analysis of the inclusion compounds. The various solid compounds were irradiated as layers of known width between two quartz plates inside a four-ring U.V. Hanovia lamp, at irradiation doses up to 4 x 10^{20} quanta cm^{-2}, at ca. 350 nm.

The irradiated compounds were dissolved in methanol and analyzed by VPC on the same columns employed for purification.

The gamma irradiations were carried out using a Co-60 source, (Gammacell, of the Atomic Energy of Canada), for doses up to 100 MRad.

Per cent conversions from the starting isomers were computed by VPC. They are averages from three irradiation runs carried out on inclusion compounds obtained from different preparations in order to ascertain the reproducibility for the various systems. The observed standard deviations, at any dose, were about 5%.

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