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Light-Induced Geometric Isomerization of 1,2-Diphenylcyclopropanes Included within Y Zeolites: Role of Cation−Guest Binding[†]

Lakshmi S. Kaanumalle,[‡] J. Sivaguru,[‡] R. B. Sunoj,[§] P. H. Lakshminarasimhan,[‡]
J. Chandrasekhar,[§] and V. Ramamurthy*,[‡]

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, and Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India

murthy@tulane.edu

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Through a systematic study of several diphenylcyclopropane derivatives, we have inferred that the cations present within a zeolite control the excited-state chemistry of these systems. In the parent 1,2-diphenylcylopropane, the cation binds to the two phenyl rings in a sandwich-type arrangement, and such a mode of binding prevents cis-to-trans isomerization. Once an ester or amide group is introduced into the system (derivatives of 2β,3β-diphenylcyclopropane-1α-carboxylic acid), the cation binds to the carbonyl group present in these chromophores and such a binding has no influence on the cis−trans isomerization process. Cation-reactant structures computed at density functional theory level have been very valuable in rationalizing the observed photochemical behavior of diphenylcyclopropane derivatives included in zeolites. While the parent system, 1,2-diphenylcylopropane, has been extensively investigated in the context of chiral induction in solution, owing to its failure to isomerize from cis to trans, the same could not be investigated in zeolites. However, esters of 2β,3β-diphenylcyclopropane-1α-carboxylic acid could be studied within zeolites in the context of chiral induction. Chiral induction as high 20% ee and 55% de has been obtained with selected systems. These numbers, although low, are much higher than what has been obtained in solution with the same system or with the parent system by other investigators (maximum ~10% ee).

Introduction

1,2-Diphenylcyclopropane has played a central role in the quest for new methods of asymmetric induction in organic photochemistry.[1] The optically inactive *cis*-1,2-diphenylcyclopropane can be transformed into its chiral trans isomer by both singlet- and triplet-photosensitized irradiations. Following the original report by Hammond and Cole (ee 6.7%), the chiral induction on this isomerization process has been investigated by at least five independent research groups and the best ee obtained thus far is 10% (Scheme 1).[2,3] Therefore, *cis*-1,2-diphenylcyclopropane suggested itself as a benchmark system to examine the influence of the zeolite medium on the chiral induction process. Surprisingly, when this molecule was included within MY (M = alkali ion) zeolite and excited (direct excitation or triplet sensitization), no cis-to-trans isomerization resulted.[4] As opposed to the photobehavior of the above parent system, upon direct excitation and triplet sensitization, amides and esters of 2β,3β-diphenylcyclopropane-1α-carboxylic acid readily photoisomerized from cis to trans isomers within zeolites. With the help of computations based on density functional theory, we have traced this puzzling difference in

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[†] Dedicated to Professors R. G. Weiss and F. D. Lewis on the occasion of their 60th birthdays.

[‡] Tulane University.

[§] Indian Institute of Science.

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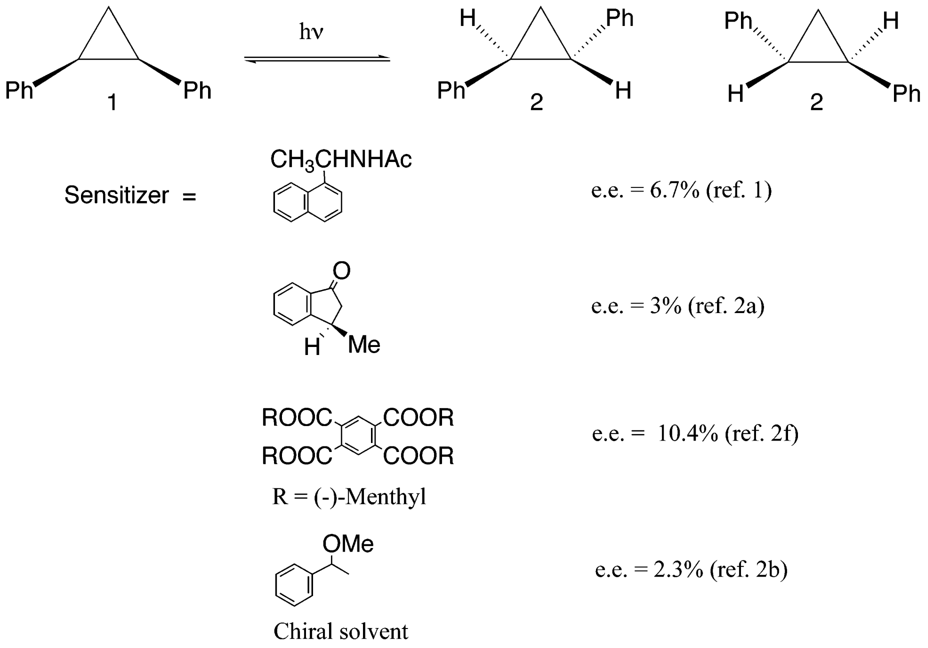
SCHEME 1



behavior between the parent, and the latter two systems to the difference in the nature of the cation interaction with these systems.

To appreciate the influence of zeolites on the photoisomerization of 1,2-diphenylcyclopropanes, a knowledge of the structure of the Y zeolite and the nature of interaction between cations present in the zeolites and the guest molecules is essential. The internal structure of the faujasite class of zeolites is characterized by a three-dimensional network of “supercages” (large voids ca. 13.6 Å in diameter within which adsorbed guest molecules are located) interconnected by tetrahedrally disposed “windows” (ca. 8 Å diameter, Figure 1).[5] Charge-compensating cations are located at three different sites (types I, II, and III) within the zeolite framework of which only the latter two are expected to be readily accessible to the interior of the supercages and hence to the adsorbed organic.[6] The Y zeolite used in this study has only types I and II sites occupied.

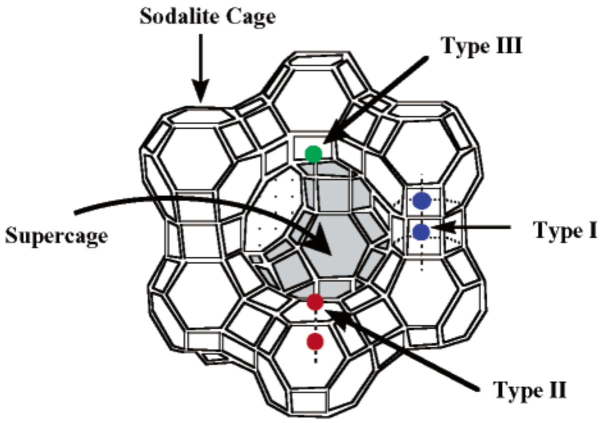


FIGURE 1. The structure of a supercage in which the organic guest is presumed to reside. Eight of these supercages constitute one unit cell of a X or Y zeolite. Cation locations are indicated as type I, type II, and type III. Type II and type III cations are present within the supercage, and type I is within the sodalite cage.

A variety of techniques have demonstrated that benzene and alkylated benzenes in NaY zeolite are preferentially adsorbed at the type II site inside the supercage.[7] Cation−π interaction (also known as cation−quadrupolar interaction)[8] has been recognized by the zeolite community for over two decades as the main force of interaction between aromatic guest molecules and the zeolite supercage. Polar aromatic molecules such as nitrobenzene are stabilized within NaY zeolite via interaction of the cation with the nitro group.[9] More importantly, in such cases, the cations are dislodged from their original type II positions. Similar cation migration from

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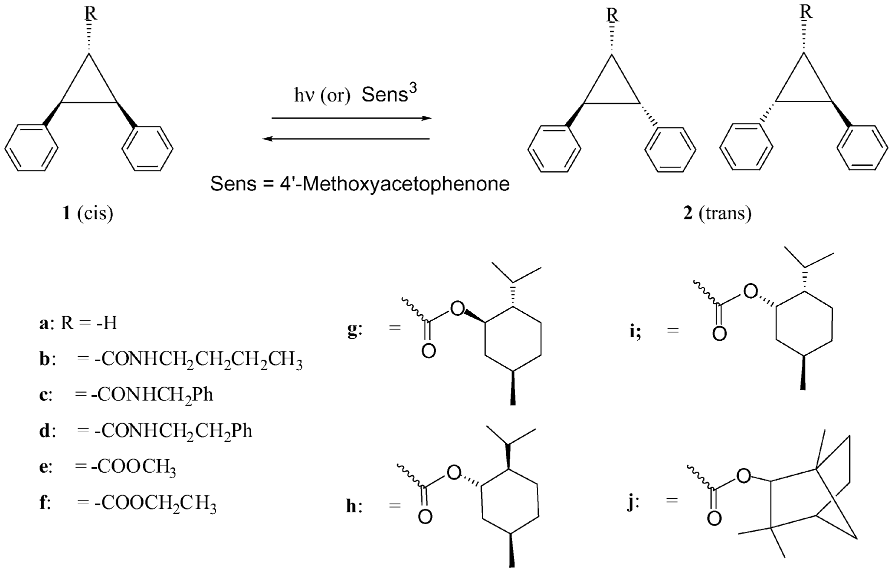
SCHEME 2



their original location has been established during the adsorption of hydroflurocarbons within NaY.[10] The main reason for dislocation of cations from their original positions is believed to be the strong cation−guest molecule interaction. Examination of the literature on guest adsorption within Y zeolites leads to two conclusions of relevance to our investigation: (a) Cation−guest interaction is important within zeolites. (b) On adsorption of organic guest molecules, cations would move from their original locations and provide a stronger interaction (than the cation zeolite wall interaction) between the cation and the guest molecule results.

The fact that 2*β*,3*β*-diphenylcyclopropane-1α-carboxylic acid derivatives behaved differently from the parent system allowed us to reach our initial goal of examining the use of a confined space (zeolite) on chiral induction during the photoisomerization of *cis*-diphenylcyclopropane derivatives to the trans isomer (Scheme 2). We present our results on several esters and amides of 2*β*,3*β*-diphenylcyclopropane-1α-carboxylic acid. The goal is to identify the origin of differences in photobehavior between 1,2-diphenylcyclopropane and 2*β*,3*β*-diphenylcyclopropane-1α-carboxylic acid derivatives within zeolites and to show that chiral induction can be obtained with these systems within zeolites. In the context of chiral induction, we have utilized two approaches. In one, achiral zeolite MY was modified by including an optically pure organic molecule as an adsorbent (chiral inductor) within a zeolite.[11] In this case, achiral benzyl amide (**1c**) and the ethyl ester (**1f**) of 2*β*,3*β*-diphenylcyclopropane-1α-carboxylic acid were used as probe reactants. The derivatives **1c** and **1f** gave the corresponding trans isomers in ~20% enantiomeric excess (ee). In the second approach, the achiral zeolite MY was used as such, but the reactant was connected to a chiral perturber via a covalent bond (chiral auxiliary approach).[11] This chiral auxiliary approach with optically pure menthyl ester of 2*β*,3*β*-diphenylcyclopropane-1α-carboxylic acid **1g** gave the trans isomer in 55% diastereomeric excess. Admittedly, the enantiomeric excess (ee) and diastereomeric excess (de) obtained are at best moderate, but these are the highest among the *cis*-1,2-diphenylcyclopropane systems examined thus far in any media. Considering that the same systems in solution give zero % ee and very low de (<5%), the results presented here on achiral *cis*-1,2-diphenylcyclopropane and 2*β*,3*β*-diphenylcyclopropane-1α-carboxylic acid derivatives (amides and esters) and chiral esters of 2*β*,3*β*-diphenylcyclopropane-1α-carboxylic acid are significant. Further, our current goal is to show that while 1,2-diphenylcyclopropane failed to geometrically isomerize within a zeolite, isomerization and chiral induction of closely related systems can be achieved from the latter systems in this medium.

Results

The photochemistry of *cis*-1,2-diphenylcyclopropane **1a** and nine 2*β*,3*β*-diphenylcyclopropane-1α-carboxylic acid derivatives **1b**−**j** was investigated within MY zeolites (Scheme 2). Triplet sensitization was performed (450 W medium-pressure mercury lamp with Pyrex filter) with 4′-methoxyacetophenone as the sensitizer. Although the exact triplet energies of cis and trans isomers of **1** are unknown, they are expected to be lower than that of 4′-methoxyacetophenone (~71 kcal/mol).[12] As reported in the literature, triplet sensitization of 1,2-diphenylcyclopropane in acetonitrile solution gave a photostationary state mixture consisting of both cis and trans isomers

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TABLE 1. Cis/Trans Ratio at the Photostationary State upon Triplet Sensitization (4′-Methoxyacetophenone) of 1,2-Diphenylcyclopropane and 2,3-Diphenylcyclopropane Derivatives[a]

	diphenylcyclopropane derivatives[b]				
medium	**1a**	**1b**	**1c**	**1d**	**1e**
solution	45:55	48:52	50:50	35:65	39:61
LiY	95:5	12:88	11:89	10:90	45:55
NaY	92:8	40:60	35:65	21:79	39:61
KY	88:12	35:65	58:42	38:62	40:60
RbY	85:15	33:67	55:45	40:60	39:61
CsY	65:35	55:45	56:44	41:59	37:63

[a] The photostationary state ratios are based on starting from pure cis and pure trans isomers. Average of at least three independent runs from each isomer. [b] For structures, see Scheme 2.

TABLE 2. Enantiomeric Excess Obtained in Product 2 during the Triplet-Sensitized Photoisomerization of Achiral Derivatives of $2\beta,3\beta$-Diphenylcyclopropane-1α-carboxylic Acid (For Structures, See Scheme 2)

chiral inductor	**2b** % ee	**2c** % ee	**2d** % ee	**2f** % ee
ephedrine	8	20	2	0
pseudoephedrine	8	15	2	5
norephedrine	5	15	3	5
diethyl tartrate	-	-	-	12
cyclohexylethylamine	0	0	0	17

(45% cis and 55% trans; 4′-methoxyacetophenone as sensitizer in acetonitrile).[12] Almost similar photostationary state ratios were obtained with $2\beta,3\beta$-diphenylcyclopropane-1α-carboxylic acid derivatives **1b**−**e** (Table 1).

For zeolite irradiations, both triplet sensitizer (4′-methoxyacetophenone) and **1** were included within alkali cation (Li^+, Na^+, K^+, Rb^+, and Cs^+) exchanged Y zeolites. All photostationary state measurements were made from both pure *trans*- and *cis*-**1a**−**e**. The photostationary state compositions of **1a**−**e** included in MY zeolites are given in Table 1. Examination of Table 1 reveals two distinct trends: (a) In the case of **1a** the cis isomer is preferred inside the zeolite. The amount of the cis isomer at the photostationary state depends on the nature of the exchanged cation. (b) Amides and esters of $2\beta,3\beta$-diphenylcyclopropane-1α-carboxylic acid (**1b**−**e**) show a different behavior. In these cases, the cis isomer is no longer favored and the photostationary state ratio is much closer to that in solution.

The possibility of photoisomerization of the cis isomers of the amides and esters of $2\beta,3\beta$-diphenylcyclopropane-1α-carboxylic acid (**1b**−**e**) within zeolites provided an opportunity to examine the influence of chiral inductors during photoisomerization of achiral cyclopropanes **1c** and **1f**. Chiral induction during photoisomerization was monitored by either GC or HPLC by directly irradiating the cyclopropanes **1c** and **1f** within chirally modified NaY zeolite, and the results are presented in Table 2. Low but significant ee was obtained with several chiral inductors. The maximum ee obtained in the case of **1c** was with ephedrine (20%) and in the case of **1f** was with cyclohexylamine (17%). The opposite enantiomers were formed with equal ee when the optical antipode of the chiral inductor was used, indicating that the systems are well behaved. To examine the influence of the zeolite on a system with a chiral auxiliary, optically pure menthyl, neomenthyl, isomenthyl, and fenchyl esters of $2\beta,3\beta$-diphenylcyclopropane-1α-carboxylic acid (**1g**−**j**) were included within MY zeolites (1 molecule per 10 supercages) and irradiated. As expected, the trans isomer resulted and the de obtained in the product within NaY varied between 16 and 55% (Table 3).

TABLE 3. Diastereomeric Excess Obtained in Product 2g−j during the Triplet-Sensitized Photoisomerization of Chiral Derivatives of $2\beta,3\beta$-Diphenylcyclopropane-1α-carboxylic Acid 1g−j

MY-zeolite	**2g** % de	**2h** % de	**2i**[b] % de	**2j**[b] % de
LiY	50-B	25-A	12-A	7-B
NaY	55-B	40-A	32-B	16-A
KY	30-B	6-A	7-A	4-B
RbY	22-B	5-A	5-A	2-B
CsY	5-B	3-A	2-A	2-B
solution[a]	4-B	5-B	5-B	4-B

[a] Dichloromethane/hexane as solvent. [b] Loading in KY, RbY, and CsY were 50−70%.

To gain a better insight on the role of cations (present within zeolite supercages) on the observed photobehavior of *cis*-1,2-diphenylcyclopropane, density functional theory (DFT) calculations on cation binding to *cis*-1,2-diphenylcyclopropane were carried out.[13] The polarized 6-31G* basis set was used for C, H, Li, Na, and K. Interaction energies of cations were determined on the basis of gas-phase optimized geometries of metal ion complexes with *cis*-1,2-diphenylcyclopropane. Intuitively, binding of metal ions is expected to be higher with the substrate when it interacts simultaneously with two phenyl rings. Thus, we have chosen initial guess geometry for the *cis*-1,2-diphenylcyclopropane with the metal ion positioned between the two phenyl rings. During the calculation, the cations were free to move to find the most stable position. Calculations did not include any structural moiety from the zeolite. In the case of *cis*-1,2-diphenylcyclopropane a geometry-optimized structure obtained upon metal ion complexation is shown in Figure 2. Alkali metal ions are calculated to have a strong interaction with *cis*-1,2-diphenylcyclopropane. The computed values reveal a regular gradation from lithium to potassium ion. Interaction energies calculated for metal ion binding to two benzene molecules in the sandwich arrangement are closer for all alkali ions except Li^+ as in *cis*-1,2-diphenylcyclopropane complexes (interaction energy at MP2 level for sandwich arrangement: Li^+, −81.1; Na^+, −56.2; and K^+, 32.3 kcal/mol).[14] When comparing the binding energies of cations to two benzenes in a sandwich arrangement with that to *cis*-1,2-diphenylcyclopropane one should keep in mind that entropy also plays an important role in the overall free energy of binding of

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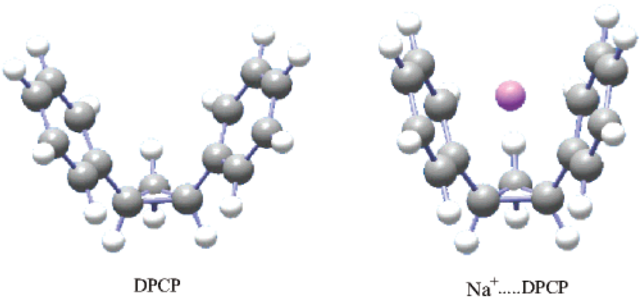

Binding Affinity (kcal/mol)

Cation	Structure
Li^+	66.83
Na^+	49.67
K^+	34.65

FIGURE 2. B3LYP/6-31G*-optimized geometry of *cis*-diphenylcyclopropane and its complex with Na^+ ion. Binding affinities with Li^+, Na^+, and K^+ are also included.

cations to substrates. For example, while the experimental enthalpy of binding of the two benzene molecules to K^+ is 35 kcal/mol, the free energy of binding is only 21 kcal/mol.[15] The large reduction in entropy makes binding of two benzene molecules quite unfavorable. On the other hand, since the host cavity of *cis*-1,2-diphenylcyclopropane is predesigned to accept a cation, such a large reduction in binding free energy is not expected. Therefore, one might anticipate that *cis*-1,2-diphenylcyclopropane to have a much larger free energy of binding than that of the two benzene molecules binding to a cation.

Computations on cation (Li^+, Na^+, and K^+) binding to the methyl amide of 2β,3β-diphenylcyclopropane-1α-carboxylic acid and the methyl ester of 2β,3β-diphenylcyclopropane-1α-carboxylic acid were performed at the RB3LYP/6-31G* level using the Gaussian 98 package.[13] In these cases, the structures of methyl amide of 2β,3β-diphenylcyclopropane-1α-carboxylic acid and the methyl ester of 2β,3β-diphenylcyclopropane-1α-carboxylic acid were optimized first. Using these structures, the interaction energies with cations were estimated by placing the cations at various positions near the structure. During the calculations, the cations were free to move. Interestingly, in these two cases, in addition to a structure corresponding to cation−*cis*-diphenyl binding (similar to Figure 2b), several others were found in which the cation is bound either solely to the amide or the ester or cooperatively to the amide/ester and a phenyl group. These structures are illustrated in Figures 3 and 4. More importantly, in each case at least one structure is equally stable than the one in which the cation is bound to the *cis*-diphenyl groups. Although we cannot be certain of the structure being preferred within a zeolite, it is clear that the presence of amide and ester groups offer additional choices for the alkali ion.

The above gas-phase computational data are very valuable in understanding the difference in the photobehavior between *cis*-1,2-diphenylcyclopropane and the amides and esters of 2β,3β-diphenylcyclopropane-1α-carboxylic acid. Within a zeolite, the cations are bound to oxygens on the framework. As a result, the metal ions are likely to interact less effectively than when they are free. Nevertheless, one should note that the cations present in the zeolites have been established to move from their original locations provided the binding with the guest molecules is stronger.[9,10] Given the large computed interaction energies, the cations moving from their original location to interact with diphenylcyclopropanes in the geometries shown in Figures 2−4 is likely. While one might question the validity of using gas-phase computational data to understand the chemistry that occurs within a more complex environment, we believe that this is a good starting point.

Discussion

The most important point we wish to address in this section is the difference in the photobehavior between *cis*-1,2-diphenylcyclopropane and the amides and esters of 2β,3β-diphenylcyclopropane-1α-carboxylic acid within a zeolite. In solution, *cis*-1,2-diphenylcyclopropane undergoes geometric isomerization from the excited singlet and triplet states. The photoisomerization from the excited singlet state is accompanied by other reactions, and therefore, prolonged irradiation results in the loss of 1,2-diphenylcyclopropane.[16] However, triplet sensitization is clean and establishes a photostationary state between the cis and trans isomers without any side reactions.[12] A similar behavior was observed with the amides and esters of 2β,3β-diphenylcyclopropane-1α-carboxylic acid **1b**−**e**. In solution, all systems investigated in this study (**1a**−**g**) underwent geometric isomerization upon direct excitation and triplet sensitization. The photostationary state (cis/trans ratio) in solution varied between 50:50 and 35:65 (Table 1). In contrast to the solution behavior, in LiY and NaY *cis*-1,2-diphenylcyclopropane (**1a**) failed to isomerize to the trans isomer both upon direct excitation and triplet sensitization. The photostationary state essentially contained only the cis isomer (Table 1). On the other hand, amides and esters of 2β,3β-diphenylcyclopropane-1α-carboxylic acid (**1b**−**g**) upon triplet sensitization in zeolites establish a photostationary state containing both cis and trans isomers. A minor point to note is that in LiY the photostationary state in the case of the amides **1b**−**d** is in favor of the trans isomer. Clearly, the cis isomers of the amides and esters of 2β,3β-diphenylcyclopropane-1α-carboxylic acid isomerize readily to the trans within MY zeolites, a behavior not expected on the basis of the chemistry of *cis*-1,2-diphenylcyclopropane.

We adopt the following model to understand the difference in the photobehavior between *cis*-1,2-diphenylcyclopropane and the amides and esters of 2β,3β-diphenylcyclopropane-1α-carboxylic acid. The triplet-sensitized geometric isomerization of 1,2-diphenylcyclopropanes is triggered by the cleavage of the PhC−CPh bond (β C−C bond with respect to the phenyl group) followed by rotation of one of the bonds substituted with

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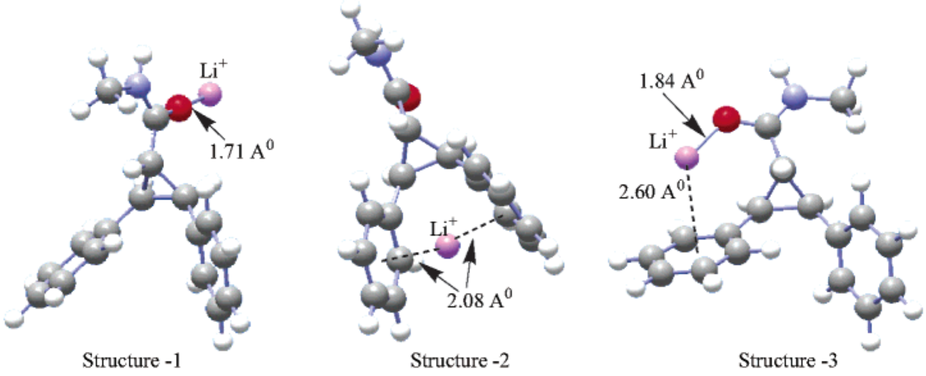

Structure -1 Structure -2 Structure -3

Binding Affinity (kcal/mol)

Cation	Structure -1	Structure -2	Structure -3
Li$^+$	64.13	64.82	67.96
Na$^+$	46.75	47.75	50.01
K$^+$	33.63	32.88	34.76

FIGURE 3. B3LYP/6-31G*-optimized geometries of complexes of Li$^+$ ion with methyl amide of 2β,3β-diphenylcyclopropane-1α-carboxylic acid. Binding affinities with Li$^+$, Na$^+$, and K$^+$ are also included. Note the difference in the location of cation in the two structures and the difference in binding affinities between them.

the phenyl group. As illustrated in Scheme 3, both cis and trans isomers would be expected to give the same diradical intermediate that would decay to the cis and trans isomers at a fixed ratio independent of its origin.[17] The photostationary state, in addition to the decay ratio (relative rates of ring closure of the diradical intermediate to the cis and trans isomers), will also be determined by the ease with which the diradical intermediate is formed from the two isomers. With sensitizers such as 4′-methoxyacetophenone having triplet energy above that of both isomers (under which conditions the excitation ratio is one), the photostationary state will be determined only by the decay ratio. The fact that the photostationary state in solution consists of both isomers suggests that there is no preferential decay of the diradical intermediate to any one isomer.

Enrichment of the cis isomer at the photostationary state during triplet sensitization of 1,2-diphenylcyclopropane within zeolites could be due to changes in any one (or all) of the following factors with respect to that in solution: (a) the decay ratio, (b) the excitation ratio, and (c) the relative rates of cleavage and isomerization with respect to other processes. Since there are no changes in the absorption spectra (diffuse reflectance mode) for the two isomers between solution and zeolite, we assume that the cation complexation will have no influence on the excited-state energies of the two isomers. We recognize that the absorption spectra provide information only about the excited singlet states. However, in the absence of any perturbation on the excited singlet state, the triplet energies are also likely to be the same both in solution and in zeolites. Based on this, we believe the excitation ratio within the zeolites to be more likely the same as in solution. To examine the influence of the zeolite on the decay ratio of the diradical intermediate, we generated the same diradical (singlet) intermediate by photolyzing γ-2,4-diphenyl butyrolactone included in NaY.[18] Photolysis of γ-2,4-diphenyl butyrolactone gave both *cis*- and *trans*-1,2-diphenylcyclopropane in equal amounts both in solution and in NaY zeolite suggesting that the diradical intermediate once generated decays to both cis and trans isomers. Such a rationalization leads us to believe that the enrichment of the cis isomer at the photostationary state in the case of 1,2-diphenylcyclopropane within zeolites is related to the presence of a barrier between the vertically excited *cis*-1,2-diphenylcyclopropane and the twisted diradical state (Figure 5). The barrier primarily arises from the cooperative interaction of alkali ion with the *cis*-phenyl groups. This model is supported by the computed structure for alkali ion bound *cis*-1,2-diphenylcyclopropane (Figure 2). Large interaction energies have been computed at the B3LYP level for binding of Li$^+$ and Na$^+$ to *cis*-1,2-diphenylcyclopropane (Figure 2). Any motion that would disrupt the cooperative interaction of the alkali ion to the *cis*-phenyl groups will have to surmount a barrier both in the ground and excited states. Since conversion from the cis geometry to the diradical intermediate involves such a disruption this process is expected to have a barrier in the excited state within a zeolite. Consistent with the postulate that cation is most important for the cis enrichment within zeolites, inclusion of water (a better coor-

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(17) Irradiations of pure diastereomers of the trans isomer of α-methylbenzyl amide of 2β,3β-diphenylcyclopropane-1α-carboxylic acid have shown that upon triplet sensitization a common intermediate results that leads to racemization while upon direct excitation leads to an intermediate where the diastereomers do not interconvert. Sivaguru, J.; Shichi, T.; Ramamurthy, V. *Org. Lett.* **2002**, *4*, 4221–4224.

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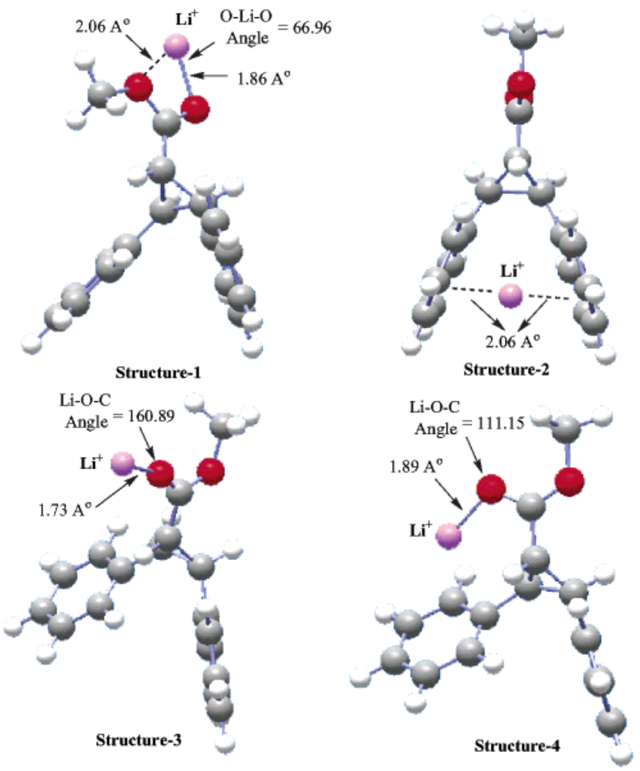

Binding affinity (kcal/mol)

cation	Structure -1	Structure -2	Structure -3	Structure -4
Li	62.70	64.69	56.64	59.29
Na	47.22	47.82	40.88	43.78
K	34.22	33.05	29.04	30.68

FIGURE 4. B3LYP/6-31G*-optimized geometries of complexes of Li^+ ion with methyl ester of 2β,3β-diphenylcyclopropane-1α-carboxylic acid. Binding affinities with Li^+, Na^+, and K^+ are also included. Note the difference in the location of cation in the two structures and the difference in binding affinities between them.

dinator to the cation) within LiY resulted in a photostationary state similar to that in solution (cis:trans, 49:51). Further, the cis: trans ratio in dry zeolites is dependent on the nature of cation. Cations such as Cs^+, which has a very small value of interaction energy, give much less cis (65%) in the photostationary state than Li^+ (95%). Consistent with the literature reports that alkali ions have smaller interaction energy with benzonitrile (compare benzene- - -Na^+, −27.1 kcal/mol, and benzonitrile- - -Na^+, −15.7 kcal/mol),[19] irradiation of 1-(4-cyanophenyl)-2-phenylcyclopropane included in NaY gave a photostationary state consisting of both cis (56%) and trans (44%) isomers. Our observations with 1,2-diphenylcyclopropane are along the lines reported for azobis(benzocrown ether) systems.[20] In these systems, the alkali ions suppress the thermal isomerization of the cis isomer to the trans form, and this phenomenon is attributed to the "tying effect" of alkali ions by coordinating to the benzocrown ether units present on the two phenyl groups of the azobenzene unit.

From the above discussion, one would expect that removal of the cation from the diphenyl "bowl" would prompt the diphenylcyclopropane systems to isomerize from cis to trans geometry. The photobehavior of the amides and esters of 2β,3β-diphenylcyclopropane-1α-carboxylic acid is consistent with this expectation. The difference in behavior between amides and esters of 2β,3β-diphenylcyclopropane-1α-carboxylic acid and 1,2-diphenylcyclopropane could be understood based on the computed geometries for Li^+-bound methyl amide and methyl ester of 2β,3β-diphenylcyclopropane-1α-carboxylic acid (Figures 3 and 4). Of the various computed structures two shown in Figures 3 and 4 suffice for the current discussion. In the case of the amide, the metal ion prefers to interact directly with the carbonyl oxygen (Figure 3) while in the case of the ester the cation prefers to bind to the ester oxygens (Figure 4). Strong dipolar interaction of the alkali ions with carbonyls has been established in the literature.[21] In esters, the O, O interaction of the type shown in Figure 4 is also known.[22] The interaction energies of Li^+ to the ester and amide groups are much larger than that of alkali ions to *cis*-diphenyl groups. In the case of Na^+ and K^+ the differences in energy between the two structures shown in Figures 3 and 4 are small. An important point to note is that when the alkali ion binds to the carbonyl chromophore the face of the alkali ion that is still free can interact with the zeolite wall. Such bindings (carbonyl- - -alkali ion- - -zeolite wall) are expected to be much more stable than the alkali ion interacting with two phenyl groups in a sandwich arrangement. This reasoning leads us to believe that within zeolites the cations interact with the amide and ester groups of 2β,3β-diphenylcyclopropane-1α-carboxylic acid derivatives rather than with the cis-diphenyl group. Such interactions would not impose a barrier for rotation of the *cis*-diphenyl to the diradical intermediate. The above rationalization is based on the assumption that within zeolites the photobehavior of the included diphenylcyclopropane is controlled by the cation−guest interaction. Such an interaction would require the cation to move from the original location (type II) and guest induced relocation of cations has been documented in the literature.[9,10] We recognize that our model will gain strength only if we provide experimental support for the proposed structures within zeolites. We hope to provide such data in the future.

The final aspect of this paper deals with the observed enantio- and diastereoselectivities within zeolites (Tables 2 and 3). The enantiomeric excess observed although low is consistent with our observations with most systems where 20−40% ee seemed to be the norm (highest ee we

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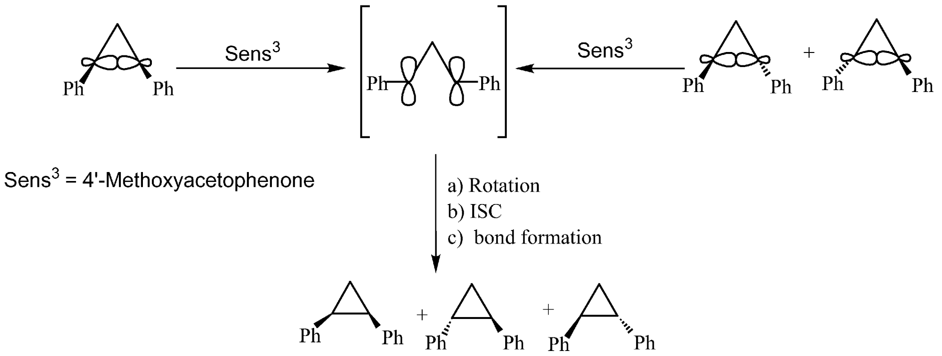
SCHEME 3



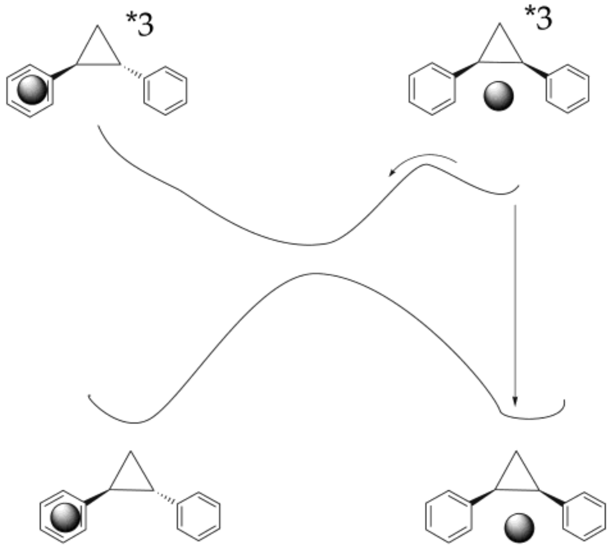


FIGURE 5. Proposed potential energy surface diagram for triplet-sensitized isomerization of 1,2-diphenylcyclopropane within cation-exchanged Y zeolite. Cation interaction with the cis isomer results in a barrier for rotation of the cis isomer in the excited state.

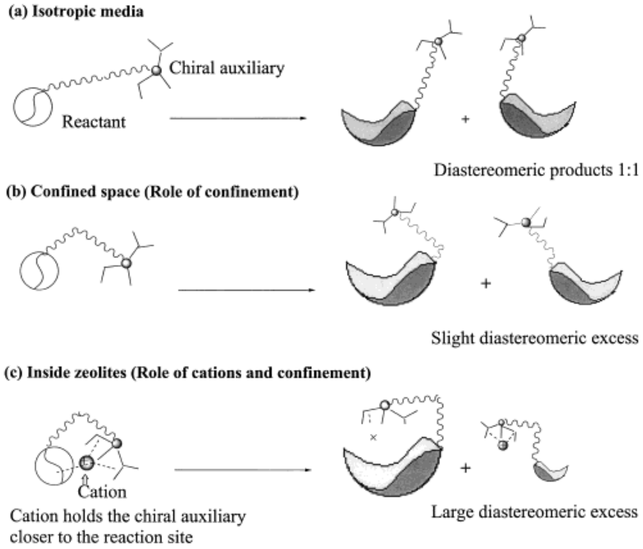


FIGURE 6. Schematic representation of the visualization of asymmetric induction in solution, confined media, and confined media with cations.

have observed is in the case of tropolone 2-phenyl ethyl ether, 78%).[23] An important point to note is that the two systems investigated here give the product as a racemic mixture in solution. It is obvious that the zeolite environment capable of forcing a stronger interaction between the chiral inductor and the reactant diphenylcyclopropane derivative. The diastereoselectivity observed with menthyl ester is moderate (the highest de we have observed is in tropolone systems, 88%).[24] The zeolite interior clearly is able to enhance the power of a chiral auxiliary. In doing so, both the confined space as well as the cation present in a zeolite are used effectively by the zeolite. The cation and confined space coerce the molecule to adopt a geometry resulting in a stronger interaction between the chiral center and the site of reaction present within a single molecule. Figure 6 is a schematic representation of the model we employ to visualize zeolite's ability to enhance the power of a chiral auxiliary. The very low diastereomeric excess (<5%) for most cases in solution suggests that the conformation of the reactant molecule is likely to be such that the chiral auxiliary and the reactive site of the molecule are far apart (Figure 6a). On the other hand, within the confined space of a zeolite the adoption of a folded conformation by the reactant brings its reactive site closer to the chiral auxiliary (Figure 6b). Cation presence within a zeolite besides restricting the conformational flexibility of the chiral auxiliary binds it closer to the reaction center (Figure

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6c). Weak interactions between chiral auxiliary, cation and reaction site play an important role in the overall asymmetric induction process within a zeolite.

Results presented in this paper suggest that one can influence the excited-state behavior of organic molecules through alkali ion binding.[25] In this context, zeolites with a reservoir of cations, only partially coordinated to the zeolite framework, can be very useful. Although we have no direct spectral evidence in favor of cation-guest interaction in the systems investigated here, existence of such interactions have been demonstrated previously in other systems.[7−10]

Experimental Section

Materials. NaY zeolite was obtained from Zeolyst International, The Netherlands. Monovalent cation-exchanged zeolites (LiY, KY, RbY, and CsY) were prepared by stirring 10 g of NaY with 100 mL of a 10% solution of the corresponding metal nitrate in water for 24 h with continuous refluxing. The zeolite was filtered and washed thoroughly with distilled water. This procedure was repeated three times. Subsequently, the zeolite was dried at 120 °C for about 3 h to obtain the cation-exchanged zeolite.

Synthesis of Amides and Esters of 2,3-Diphenylcyclopropane-1-carboxylic Acid. 2,3-Diphenylcyclopropane-1-carboxylic acid was synthesized following literature procedures[26] and converted to the ester or amide derivatives by coupling with the corresponding alcohol or amine using 1,3-dicyclohexylcarbodiimide/4-(dimethylamino)pyridine (DCC/DMAP).[27] The products were purified by silica gel column chromatography using hexanes−ethyl acetate as the eluent. Spectral data for esters and amides are provided as Supporting Information.

Measurement of Photostationary-State Composition. 4′-Methoxyacetophenone (20−25 mg) and compound **1a**−**e** (3−4 mg) were dissolved in 0.5 mL of dichloromethane followed by the addition of 15 mL of hexanes. MY (M = Li^+, Na^+, K^+, Rb^+, and Cs^+) zeolite (300 mg) activated at 500 °C was added with stirring. The slurry was stirred for 12 h on a water bath at 55 °C, filtered, and washed thoroughly with fresh hexanes (supernatant was analyzed for the absence of the reactant and the sensitizer). The zeolite was dried under vacuum (2×10^{-3} Torr) at 60 °C for 6−8 h. The sample was transferred into a test tube inside a drybox, fresh anhydrous hexanes was added, and the test tube was stoppered with a rubber septum and wrapped with Parafilm. The slurry was degassed with N_2 for 30 min, irradiated (unfiltered output from a 450 W medium-pressure mercury lamp) under positive N_2 pressure, filtered, and washed again with fresh hexanes (analysis of the supernatant showed the absence of reactant and products). The reactant and the photoproducts were extracted from the zeolite by stirring with acetonitrile. The extract was concentrated and analyzed on GC. The photostationary state was attained in all cases within 48 h. They were tested to be true photostationary states by continuing the irradiation for further 48 h. The extraction was carried out using dichloromethane or acetonitrile and the mass balance was checked by GC using tetradecane as the calibration compound. All the product recoveries had a mass balance of more than 90%.

Chiral Induction Studies within Zeolites. (a) The Chiral Inductor Approach: Enantioselectivity. Chiral inductor (20−25 mg) and compound (**1c** and **f**, 2−3 mg) were dissolved in 0.5 mL of dichloromethane followed by the addition of 15 mL of hexanes. NaY zeolite (300 mg) activated at 500 °C was added with stirring. The slurry was stirred for 12 h, filtered, and washed thoroughly with fresh hexanes (analysis of the supernatant showed absence of reactant and chiral inductor). The loading level of the cyclopropane was kept at one molecule for every 10 supercages ($\langle S \rangle = 0.1$). A higher ratio of the chiral inductor was employed to maximize the chances of every reactant molecule being adjacent to a chiral inductor within the supercage. The zeolite was dried under vacuum (2×10^{-3} Torr) at 60 °C for 6−8 h. The sample was transferred into a quartz test tube inside a drybox and fresh anhydrous hexanes was added, the test tube stoppered with a rubber septum and wrapped with Parafilm. The slurry was then irradiated (unfiltered output from a 450 W medium pressure mercury lamp), filtered, and washed again with fresh hexanes (analysis of the supernatant showed absence of reactants and products). The reactant and the photoproducts were extracted from the zeolite by stirring with acetonitrile. The extract was concentrated, and the reactant and its photoproducts were purified by a microcolumn with silica gel using hexane/ethyl acetate as eluent. The extract was then concentrated and analyzed on a chiral column (GC/HPLC). The authentic samples (photoproducts independently synthesized) were injected in the GC/HPLC and verified with the retention times of the photoproducts.

(b) The Chiral Auxiliary Approach: Diastereoselectivity. Compound **1g** (2−3 mg) was dissolved in 0.5 mL of dichloromethane followed by the addition of 15 mL of hexanes. MY (M = Li^+, Na^+, K^+, Rb^+ and Cs^+) zeolite (300 mg) activated at 500 °C was added with stirring. The slurry was stirred for 12 h, filtered, and washed thoroughly with fresh hexanes (analysis of the supernatant showed absence of the reactant). The zeolite was dried under vacuum (2×10^{-3} Torr) at 60 °C for 6−8 h. The sample was transferred into a quartz test tube inside a drybox, fresh anhydrous hexanes was added, and the test tube was stoppered with a rubber septum and wrapped with Parafilm. The slurry was then irradiated (unfiltered output from a 450 W medium pressure mercury lamp), filtered, and washed again with fresh hexanes (analysis of the supernatant showed absence of reactants and products). The reactant and the photoproducts were extracted from the zeolite by stirring with acetonitrile. The extract was concentrated and analyzed on GC. The authentic samples (photoproducts independently synthesized) were injected in the GC/HPLC and verified with the retention times of the photoproducts.

GC/HPLC Analysis Conditions. *n*-Butylamide of 2β,3β-diphenylcyclopropane-1α-carboxylic acid (**1b**): Chiralpak-AD; hexane/2-propanol = 90:10; flow = 0.4 mL/min; HP-5890 series II gas chromatograph; SE-30 column.

Benzylamide of 2β,3β-diphenylcyclopropane-1α-carboxylic acid (**1c**): Chiralpak-AD; hexane/2-propanol = 85:15; flow = 0.5 mL/min; HP-5890 series II gas chromatograph; SE-30 column.

3-Phenylethylamide of 2β,3β-diphenylcyclopropane-1α-carboxylic acid (**1d**): Chiralpak-AD-RH; hexane/2-propanol = 95:05; flow = 0.5 mL/min; HP-5890 series II gas chromatograph; SE-30 Column.

Methyl ester of 2β,3β-diphenylcyclopropane-1α-carboxylic acid (**1e**): Shimadzu 17-A gas chromatograph; SE-30 column.

Ethyl ester of 2β,3β-diphenylcyclopropane-1α-carboxylic acid (**1f**): HP-5980 series II gas chromatograph; column β-dex-350/OV170; Shimadzu 17-A gas chromatograph; SE-30 column.

(−) Menthyl ester of 2β,3β-diphenylcyclopropane-1α-carboxylic acid (**1g**): HP-5890 series II gas chromatograph; HP-5 column.

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Computational Methods Used. Full geometry optimizations were carried out primarily using the hybrid Hartree–Fock density functional theory (RB3LYP) with Becke three-parameter exchange functional in conjunction with correlation functional by Lee, Yang, and Parr (LYP). The 6-31G* basis set was used for C, H, O, N, Li, Na, and K. Stationary points have been characterized as true minima by frequency calculations. Binding affinities were computed using the "super system" approach without inclusion of basis set superposition error corrections. All the calculations were performed using Gaussian 98 A.6 suite of quantum chemical programs.

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Supporting Information Available: Spectral data for the cis and trans isomers of derivatives of 1,2-diphenylcyclopropane and 2β,3β-diphenylcyclopropane-1α-carboxylic acid **1** and **2** and Cartesian coordinates of all computed structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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