J. Am. Chem. Soc. **2000,** *122,* 4815−4816

Cation−π Interaction Controlled Selective Geometric Photoisomerization of Diphenylcyclopropane

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Received January 11, 2000
Revised Manuscript Received March 10, 2000

Geometric isomerizations of alkenes and cyclopropanes have played a key role in the development of mechanistic organic photochemistry.[1] Although novel strategies toward obtaining cis geometric isomers have been developed for alkene photoisomerization[2] no method is currently available for selective geometric isomerization of *trans*-diarylcyclopropanes. We now present a strategy based on differential cation−π interaction that has enabled us to selectively convert *trans*-diphenylcyclopropane (DPC) to the corresponding cis isomer.

The ability of cations to interact with π-systems, especially phenyl rings, has been implicated in a number of important processes.[3] The enhanced stability resulting from binding of a potassium ion to more than one benzene ring has been quantified in the gas phase,[4] while crystal structures are available in which sodium ions form sandwich structures.[5] Hence the "bowl"-shaped *cis*-DPC with optimally poised phenyl rings may be expected to bind to a cation more strongly than the trans isomer (Figure 1). Ab initio calculations on alkali cation complexes with *cis*-DPC (vide infra) reveal that the binding energies are comparable to those of sandwich structures with free benzene ligands, and also are cation dependent. These insights have allowed us to selectively convert *trans*-DPC to the cis isomer. Since Y zeolite contains a large number of cations that are free to interact with the guest molecules, we have employed it as the medium for the above selective trans to cis photoisomerization.[6]

As reported in the literature, triplet sensitization of DPC in acetonitrile solution gave a photostationary mixture consisting of both cis and trans isomers (45% cis and 55% *trans*; *p*-methoxyacetophenone as sensitizer in acetonitrile).[1b,7] For zeolite irradiations, both triplet sensitizer (xanthone, *p*-methoxyacetophenone, and benzophenone) and DPC were included within alkali cation (Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$) exchanged Y zeolites.[8] All photostationary state measurements were made from both *trans*- and *cis*-DPC. The loading levels of the sensitizer and DPC were maintained at one molecule per 10 supercages. The above samples were dried on a vacuum line (10^{-4} Torr at 65 °C for 12 h), transferred to dry hexane (10 mL) and following bubbling with nitrogen irradiated as hexane slurries. The products were extracted with methylene chloride−diethyl ether and analyzed by GC. The geometric isomers accounted for over 90% of the extracted materials (GC, calibration method). The photoreaction was clean and the photostationary state was reached within 48 h. The photostationary state composition was cation dependent (percent cis at the photostationary state: Li$^+$Y, 91%; Na$^+$Y, 92%; K$^+$Y, 88%; Rb$^+$Y, 85% and Cs$^+$Y, 65%; the error limit was ±4% based on at least six independent runs).

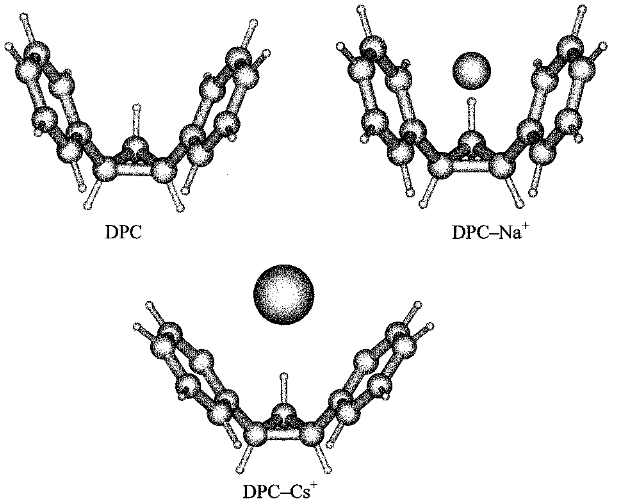

Figure 1. MP2 geometry optimized structures of *cis*-1,2-diphenylcyclopropane and its complex with Na$^+$ and Cs$^+$ ions.

A slightly modified conventional potential energy surface for the photoreaction helps one understand the unexpected selective isomerization observed in this study (Figure 1). The photostationary state composition is generally controlled by excitation and decay ratios. Since the diffuse reflectance spectra of the cation complexed and uncomplexed DPC remained the same, we assume the singlet and triplet energies of the cation complexed *cis*-DPC to be very close to that of free *cis*-DPC. Further, the triplet energies of the sensitizers used in this study are much higher than the accepted triplet energy of DPC (53 kcal mol^{-1}).[9] Alteration in excitation ratio within zeolites is therefore not likely to be responsible for the one-way isomerization. To probe whether the decay ratio to cis and trans isomers from the intermediate twisted 1,2-diradical state is altered within a zeolite, the singlet diradical was generated by decarboxylation of α,γ-diphenyl-γ-butyrolactone.[10] Upon photolysis of either *trans*- or *cis*-α,γ-diphenyl-γ-butyrolactone within NaY both isomers of DPC were obtained. Thus it is clear that if *cis*-DPC triplet reaches the twisted 1,2-diradical stage it will give both cis and trans isomers. The failure to reach this point is obviously what causes cis enrichment within a zeolite. The failure most likely results from the presence of a barrier between the vertically excited *cis*-DPC triplet and twisted 1,2-diradical states (Figure 1). The barrier, we suggest, results from π-interaction of the cation to the two phenyl rings of the *cis*-DPC.[3−5] The barrier must be quite substantial since irradiation at higher temperatures (up to 80 °C) did not decrease the cis content in the photostationary state.

Ab initio calculations on alkali cation−*cis*-DPC complexes provide insights into the above cation controlled selective isomerization process. The interaction energies computed at the

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(1) (a) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. *J. Am. Chem. Soc.* **1964**, *86*, 3197. (b) Hammond, G. S.; Wyatt, P.; DeBoer, C. D.; Turro, N. J. *J. Am. Chem. Soc.* **1964**, *86*, 2532.

(2) (a) Liu, R. S. H.; Asato, A. E. *Tetrahedron* **1984**, *40*, 1931. (b) Ramamurthy, V.; Liu, R. S. H. *J. Am. Chem. Soc.* **1976**, *98*, 2935.

(3) (a) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303. (b) Dougherty, D. A. *Science* **1996**, *271*, 163.

(4) Sunner, J.; Nishizawa, K.; Kebarle, P. *J. Phys. Chem.* **1981**, *85*, 1814.

(5) (a) Corbelin, S.; Kopf, J.; Lorenzen, N. P.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 825. (b) Bock, H.; Ruppert, K.; Havlas, Z.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1042. (c) Bock, H.; Ruppert, K.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1685.

(6) The type II cations present in supercages are free to interact with the guest molecules: Breck, D. W. *Zeolite Molecular Sieves*; Krieger Publishing Company: Malabar, FL, 1984.

(7) The photostationary state reported in the literature varies between 43 and 47% cis: (a) Ouannes, C.; Beugelmans, R.; Rossi, G. *J. Am. Chem. Soc.* **1973**, *95*, 8472. (b) Faljoni, A.; Zinner, K.; Weiss, R. G. *Tetrahedron Lett.* **1974**, 1127. (c) Karki, S. B.; Dinnocenzo, J. P.; Farid, S.; Gould, I. R.; Zona, T. A. *J. Am. Chem. Soc.* **1997**, *119*, 431.

(8) For experimental details, see the Supporting Information.

(9) Becker, R. S.; Edwards, L.; Bost, R.; Elam, M.; Griffinn, G. *J. Am. Chem. Soc.* **1972**, *94*, 6584.

(10) Givens, R. S.; Oettle, W. F. *J. Org. Chem.* **1972**, *37*, 4325.

10.1021/ja000138h CCC: $19.00

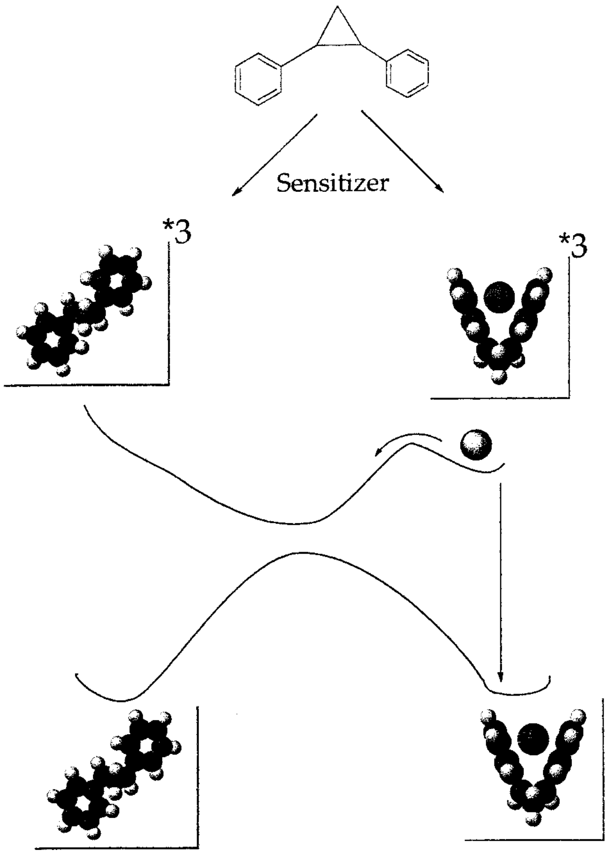

Figure 2. Proposed potential energy surface for the geometric isomerization of 1,2-diphenylcyclopropane. Upon cation complexation a barrier is visualized for the rotation of cis to trans isomer.

Table 1. Computed Interaction Energies (kcal·mol^{-1}) and Selected Geometric Parameters of Alkali Metal Cation Complexes[a,b]

metal ion M$^+$	(C_6H_6) M$^+$ (C_6H_6)	*cis*-DPC··M$^+$	*R*1 (Å)	*R*2 (Å)	*A*1 (deg)
Li$^+$	−81.1	−75.8	1.99	3.78	116.3
Na$^+$	−56.2	−53.9	2.46	4.28	118.8
K$^+$	−32.3	−32.6	3.10	4.61	120.9
Rb$^+$	−27.7	−28.2	3.10	4.76	122.0
Cs$^+$	−22.6	−22.7	3.46	4.90	123.1

[a] *R*1 is the distance between M and the center of the phenyl rings; *R*2 is the distance between the centers of the phenyl rings; *A*1 is the $C_iC_aC_b$ angle, where C_i is the ipso phenyl carbon and C_a and C_b are the substituted carbon atoms of the cyclopropyl ring. [b] The values of *R*2 and *A*1 for the *cis*-DPC system are 4.36 Å and 119.6°, respectively.

MP2 level using polarized basis sets (6-31G* for H, C, Li, and Na; Hay−Wadt effective core potentials for K, Rb, and Cs)[11] for alkali cations bound to *cis*-DPC are provided in Table 1. The energies for cation bound to two benzene molecules in sandwich geometries are also included for comparison. The most significant trend in the present context is the similarity of the complexation energies of the cations to *cis*-DPC compared to those with two free benzene units. The geometrical parameters optimized at the MP2 level reveal that coordination to Na$^+$ requires negligible distortion of DPC. The distance between the phenyl ring centers (*R*2) as well as the angle made by the phenyl rings to the cyclopropyl C−C bond (*A*1) are virtually unaltered on going to the complex. However, the DPC unit distorts considerably to accommodate the other cations as indicated by the optimized *R*2 and *A*1 values (Table 1; Figure 1). In particular, the large Cs$^+$ ion projects outside the bowl. Thus, at relatively little energetic cost, the DPC unit is predicted to accommodate the various cations. An additional point relates to the entropy of binding. While the experimental enthalpy of binding of two benzene molecules to K$^+$ is 35 kcal mol^{-1}, the free energy of binding is only 21 kcal mol^{-1}.[4] Since the host cavity of *cis*-DPC is predesigned to accept a cation, such a large reduction in binding free energy is not expected in this case. The large magnitude of the interaction computed for Li$^+$, Na$^+$, and K$^+$ must have a significant bearing on the observed photochemistry in the metal-exchanged zeolite. The effect of Cs$^+$ is predicted to be small. The differences in binding energies of cations to *cis*-DPC rationalize the differential influence on the photoisomerization process by small and large cations.

The hypothesis that cation−π interaction is responsible for the one way isomerization process is consistent with what is known concerning the binding of cations, in the presence of water, to benzene. On the basis of computational and experimental studies, Dougherty, Lisy and co-workers have suggested that in the presence of water, Li$^+$ and Na$^+$ ions would bind preferentially to water rather than to benzene, whereas K$^+$ ion would bind to benzene over water molecules.[12] This proposal implies that the cation-dependent one-way isomerization within "wet" zeolites should show a trend different from the one observed within "dry" zeolites. The expectation is indeed borne out by additional experiments. When triplet sensitizations were conducted under "wet" conditions, the K$^+$ ion exhibited the greatest effect; Li$^+$ and Na$^+$, unlike under dry conditions, had little effect on the photostationary state composition (percent cis at the photostationary state: Li$^+$Y, 49%; Na$^+$Y, 78%; K$^+$Y, 91%; Rb$^+$Y, 77% and Cs$^+$Y, 53%).[8]

We examined the possibility of modulating the cation−π interaction through substitution on the DPC phenyl ring. Previous studies[13] have shown that oxygen donors do not enhance cation−arene binding while nitrogen substituents cause a modest increase. However, a *significant reduction* can be achieved through a single acceptor. Consistently, we find that the MP2 binding energy of Na$^+$ with 1-(4-methoxyphenyl)-2-phenylcyclopropane (−53.7 kcal mol^{-1}) is virtually identical with that obtained for *cis*-DPC, while the corresponding value for the *p*-cyano derivative is *less* by 11 kcal mol^{-1}. Further, the structure of the latter complex is quite unsymmetrical, with the cation closer to the unsubstituted phenyl ring. The cation may therefore be expected to induce a lower barrier between the triplet of *cis*-1-(4-cyanophenyl)-2-phenylcyclopropane and the corresponding twisted 1,2-biradical. In complete accord with these predictions, the photostationary states observed within "dry" Na Y and acetonitrile for the cyano derivative are almost the same (55% cis in acetonitrile and 56% in Na Y).

In summary, preferential binding of alkali metal cations to ideally placed phenyl rings is proposed as a novel strategy to direct the course of photoisomerization in diarylcyclopropanes to occur unidirectionally. The use of metal-exchanged zeolite has enabled us to successfully exploit this approach. The use of cation−π interactions has considerable generality and can be brought into play in other suitably crafted substrates.

Acknowledgment. The authors at Tulane University thank the Division of Chemical Sciences, Office of Basic Sciences, US Department of Energy (DE-FGOR-96ER14635) for support of this program and J. P. Dinnocenzo, J. L. Goodman, A. Cuppolletti and L. Johnston for useful discussions. R.B.S. thanks CSIR, New Delhi for a research fellowship.

Supporting Information Available: Experimental details, table of MP2 energies, and geometries of DCP and its complexes with alkali metal cations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) (a) Hay, J. P.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (b) The Gaussian 94 suite of programs were used for all the calculations: Frisch, M. J. et al. Gaussian 94, Revision C.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(12) (a) Kumpf, R. A.; Dougherty, D. A. *Science* **1993**, *261*, 1708. (b) Cabarcos, O. M.; Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys*. **1998**, *108*, 5151.

(13) Mecozzi, S.; West, A. P., Jr.; Dougherty, D. A. *J. Am. Chem. Soc*. **1996**, *118*, 2307.