

## Supplementary Materials for

### Cation- $\pi$ Interaction Controlled One-Way Geometric Photoisomerization of Diphenylcyclopropane

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#### *Materials:*

4-Methoxyacetophenone, benzophenone and xanthone were purchased from Aldrich and recrystallised before use. The zeolite NaY (CBV-100) was purchased from PQ Corporation and used after activation at 500°C in an oven for 12 hours. HPLC grade hexane was used for all loading and irradiation purposes.

#### *Preparation of 1,2-diphenylcyclopropane:*

The diphenylcyclopropane was prepared following the procedure reported by Applequist et. al<sup>1</sup>. The typical procedure involved preparation of the hydrazone by refluxing chalcone and hydrazine hydrate under nitrogen for 45 minutes. The hydrazone was taken in diethylene glycol and the solution was refluxed for one hour. The glycol solution was diluted with equal amount of water and extracted with ether. The ether extracts were combined and concentrated to get the crude diphenylcyclopropane.

*Purification and separation of the cis and trans isomers:*

In the case of 1,2-diphenylcyclopropane, the isomers were separated by fractional distillation under reduced pressure. The distillates were column chromatographed on a silica gel column with petroleum ether: dichloromethane mixture as the eluant.

*Preparation of 1-(4-cyanophenyl)-2-phenyl-cyclopropane<sup>1</sup>:*

A mixture of 21 mmol of 1-(4-chlorophenyl)-2-phenylcyclopropane, 42.4 mmol of cuprous cyanide, and 25 mL of N-methyl-2-pyrrolidone under a positive nitrogen pressure was refluxed for 65 hours and then cooled to room temperature. The reaction mixture was poured into ether (350 ml) and the ether solution was washed with concentrated ammonium hydroxide (4 x 100 ml) followed by water. The ether solution was dried over anhydrous magnesium sulfate and chromatographed on silica gel with petroleum ether:dichloromethane to yield 95% pure trans isomer.

*Preparation of exchanged zeolites:*

The cation exchanged Y-zeolites were prepared by repeatedly (4 times) refluxing 30 g of NaY zeolite with 300 ml of 10% solution of the alkali metal nitrate in deionized water for 12 hours. The zeolite was then washed with 4 liters of deionized water after each exchange. After the final exchange the zeolite was filtered, washed with 4 litres of deionized water, air-dried and stored in glass containers.

*Solution irradiation:*

*Irradiation of 1-(4-cyanophenyl)-2-phenylcyclopropane sensitized by xanthone in acetonitrile:*

In the case of solution irradiation, 2 ml of acetonitrile containing 0.06 mmol of 1-(4-cyanophenyl)-2-phenylcyclopropane and 0.01 mmol of xanthone was bubbled with nitrogen for 10 minutes, sealed with a rubber septa and irradiated for 115 hours using a 450W Hg vapor lamp, water-cooled by a Pyrex jacket. A uranyl sleeve was used to avoid any direct light absorption by the substrate. The photostationary state contained 55% cis isomer and 44% trans isomer.

***Triplet sensitized isomerization of 1,2-diphenylcyclopropane in acetonitrile:***

In this case, 2 ml of acetonitrile containing 0.06 mmol of 1,2-diphenylcyclopropane and 0.01 mmol of the sensitizer (para-methoxyacetophenone, xanthone and benzophenone), was bubbled with nitrogen for 10 minutes, sealed with a rubber septa and irradiated for 55 hours using a 450W Hg vapor lamp, water-cooled by a Pyrex jacket. The isomer ratio was monitored using GC. The photostationary state approached from both pure cis and trans isomers contained 70% cis isomer and 30% trans isomer.

***Zeolite irradiation:***

***Irradiation of 1,2-diphenylcyclopropane sensitized by 4-methoxyacetophenone in different alkali metal cation exchanged Y-Zeolites:***

Standard solutions of *trans*-1,2-diphenylcyclopropane and 4-methoxyacetophenone in hexane (3mg/ml or 1 in 10 supercages) were used in this study. 1 ml of each one of these standard solutions was pipetted out into a test-tube and diluted to 10 ml using hexane. To this solution, 300 mg of the zeolite activated in the oven at 500°C for 12 hours was added. This zeolite slurry was magnetically stirred for 12 hours. The zeolite was then filtered and washed with hexane (3 x

10 ml). The resulting zeolite-cyclopropane-sensitizer complex was dried under  $10^{-4}$  torr for 12 hours at  $65^{\circ}\text{C}$ . This zeolite complex was taken in 10ml of dry hexane (handled in a dry-box with nitrogen atmosphere), sealed and irradiated for 12 hours under same conditions described above. After irradiation, the solid was filtered off and extracted for 12 hours using ether by magnetically stirring the zeolite complex with 15 ml of ether in a test tube. The ether extract was then filtered and concentrated. To this concentrate, 1ml of a standard solution of pentadecane in hexane ( $1\mu\text{l/ml}$ ) was added for calibration purposes and analyzed using a SE-30 column as the stationary phase in a Shimadzu GC-17A. The isomer ratio was also confirmed by determining the ratio between the benzylic protons of the two isomers in a  $^1\text{H-NMR}$  using a 400MHz GE instrument.

*Irradiation under wet conditions:*

In the case of wet irradiation, the procedure was same as described above except for the fact that the dried zeolite was exposed to atmospheric humidity for an hour before irradiation.

***Irradiation of 1-(4-cyanophenyl)-2-phenylcyclopropane in NaY with xanthone as the sensitizer:***

For all these studies a standard solution of 1-(4-cyanophenyl)-2-phenylcyclopropane in hexane (3 mg/ml) were used. Also a standard solution of xanthone in 1:1 hexane:dichloromethane mixture (3 mg/ml) was used. The procedure is as follows. 1ml each of the standard solutions of the 1-(4-cyanophenyl)-2-phenylcyclopropane and xanthone were pipetted out into a test tube and diluted to 10ml using hexane. To this 300 mg of NaY activated at  $500^{\circ}\text{C}$  for 12 hours was added and stirred for 12 hours to ensure complete loading (checked by GC analysis of the supernatant hexane). The resulting zeolite-cyclopropane-xanthone complex was then filtered and washed

with hexane (4 x 10 ml). After washing the zeolite complex was taken in 10 ml of hexane, bubbled with nitrogen for 5 minutes, sealed using a rubber septa and irradiated for 48 hours using a 450W medium pressure Hg lamp through an uranyl sleeve (to avoid direct irradiation of some of 1-(4-cyanophenyl)-2-phenylcyclopropane). After irradiation, the zeolite was filtered and extracted for 12 hours by stirring with 15 ml of ether. The ether extract was concentrated; calibration compound added and analyzed using a SE-30 column on a Shimadzu GC-17A. (GC – Conditions: Column : SE-30, initial temperature : 120°C, initial time: 1 minute, rate: 5°C/minute, final temperature : 250°C, final time : 10 minutes, Carrier gas / flow rate: Nitrogen /40 ml per minute).

*References:*

1. Applequist, D. E.; Gdanski, R. D. *J. Org. Chem.* **1981**, *46*, 2502.

**Tables of MP2 Energies and Geometries**

Diphenylcyclopropane (DPC)

MP2=-578.05974

-----			
Coordinates (Angstroms)			
	X	Y	Z
-----			
C	-2.681405	0.407232	0.000000
C	-1.884376	-0.612169	0.764493
C	-1.884376	-0.612169	-0.764493
H	-3.764251	0.325653	0.000000
H	-2.314772	1.428190	0.000000
H	-2.458689	-1.420145	1.216991
H	-2.458689	-1.420145	-1.216991
C	1.744847	0.366477	2.860378
C	1.744847	0.366477	-2.860378
C	0.779342	1.352744	2.654888
C	1.515164	-0.931293	-2.395193
C	-0.405314	1.047744	1.980081
C	0.335926	-1.230460	-1.714622
C	-0.640732	-0.245546	1.498761
C	-0.640732	-0.245546	-1.498761
C	0.335926	-1.230460	1.714622
C	-0.405314	1.047744	-1.980081
C	1.515164	-0.931293	2.395193
C	0.779342	1.352744	-2.654888
H	2.666695	0.604078	3.385879
H	2.666695	0.604078	-3.385879
H	0.945826	2.362904	3.022427
H	2.261331	-1.706923	-2.552815
H	-1.160498	1.818468	1.845581
H	0.159923	-2.241983	-1.352093
H	2.261331	-1.706923	2.552815
H	0.945826	2.362904	-3.022427
H	0.159923	-2.241983	1.352093
H	-1.160498	1.818468	-1.845581

Li(+)..Diphenylcyclopropane

MP2=-585.41610

-----			
Coordinates (Angstroms)			
	X	Y	Z
-----			
C	-2.819191	0.599459	0.000000
C	-2.080853	-0.452654	0.774374
C	-2.080853	-0.452654	-0.774374
H	-3.903479	0.552943	0.000000
H	-2.432210	1.612888	0.000000
H	-2.678140	-1.238890	1.232042
H	-2.678140	-1.238890	-1.232042
C	1.880807	0.218101	2.343154
C	1.880807	0.218101	-2.343154
C	1.027841	1.311681	2.131217
C	1.393442	-1.084762	-2.144795
C	-0.287218	1.108034	1.683231
C	0.082550	-1.281492	-1.691061
C	-0.774201	-0.189062	1.433009
C	-0.774201	-0.189062	-1.433009
C	0.082550	-1.281492	1.691061
C	-0.287218	1.108034	-1.683231
C	1.393442	-1.084762	2.144795
C	1.027841	1.311681	-2.131217
H	2.896357	0.375702	2.697375
H	2.896357	0.375702	-2.697375
H	1.381684	2.322090	2.322133
H	2.033970	-1.941729	-2.339403
H	-0.936065	1.967352	1.536192
H	-0.281829	-2.293679	-1.523412
H	2.033970	-1.941729	2.339403
H	1.381684	2.322090	-2.322133
H	-0.281829	-2.293679	1.523412
H	-0.936065	1.967352	-1.536192
Li	1.170153	0.099191	0.000000

Na(+)..Diphenylcyclopropane

MP2=-739.80487

-----			
Coordinates (Angstroms)			
	X	Y	Z
-----			
C	2.838811	-0.593611	0.000000
C	2.113412	0.471278	0.769628
C	2.113412	0.471278	-0.769628
H	3.923783	-0.571530	0.000000
H	2.425682	-1.596936	0.000000
H	2.728754	1.247164	1.221787
H	2.728754	1.247164	-1.221787
C	-1.644185	-0.190119	2.796948
C	-1.644185	-0.190119	-2.796948
C	-0.815545	-1.281605	2.500585
C	-1.227129	1.105711	-2.452691
C	0.413890	-1.082158	1.853327
C	-0.003442	1.298085	-1.799460
C	0.835734	0.208467	1.486114
C	0.835734	0.208467	-1.486114
C	-0.003442	1.298085	1.799460
C	0.413890	-1.082158	-1.853327
C	-1.227129	1.105711	2.452691
C	-0.815545	-1.281605	-2.500585
H	-2.578741	-0.341181	3.331949
H	-2.578741	-0.341181	-3.331949
H	-1.106249	-2.284087	2.806980
H	-1.841334	1.964062	-2.715860
H	1.064580	-1.934637	1.675422
H	0.322339	2.307561	-1.553054
H	-1.841334	1.964062	2.715860
H	-1.106249	-2.284087	-2.806980
H	0.322339	2.307561	1.553054
H	1.064580	-1.934637	-1.675422
Na	-1.512168	-0.231232	0.000000

K(+)..Diphenylcyclopropane

MP2=-605.88667

-----			
Coordinates (Angstroms)			
	X	Y	Z
-----			
C	2.862600	-0.698641	0.000000
C	2.218022	0.421937	0.764711
C	2.218022	0.421937	-0.764711
H	3.945335	-0.770653	0.000000
H	2.359408	-1.660657	0.000000
H	2.896711	1.145096	1.214679
H	2.896711	1.145096	-1.214679
C	-1.391125	-0.024309	3.083721
C	-1.391125	-0.024309	-3.083721
C	-0.581497	-1.139306	2.838238
C	-1.028249	1.221848	-2.554782
C	0.579893	-1.011809	2.065002
C	0.126198	1.343352	-1.775473
C	0.953557	0.231090	1.528703
C	0.953557	0.231090	-1.528703
C	0.126198	1.343352	1.775473
C	0.579893	-1.011809	-2.065002
C	-1.028249	1.221848	2.554782
C	-0.581497	-1.139306	-2.838238
H	-2.268272	-0.114238	3.720318
H	-2.268272	-0.114238	-3.720318
H	-0.830452	-2.100739	3.282404
H	-1.630579	2.101605	-2.771174
H	1.231805	-1.871984	1.931978
H	0.422672	2.320412	-1.397471
H	-1.630579	2.101605	2.771174
H	-0.830452	-2.100739	-3.282404
H	0.422672	2.320412	1.397471
H	1.231805	-1.871984	-1.931978
K	-1.770825	-0.465831	0.000000

Rb(+)..Diphenylcyclopropane

MP2=-601.57714

-----			
Coordinates (Angstroms)			
	X	Y	Z
-----			
C	0.000000	3.004480	-0.971453
C	0.763344	2.517826	0.227837
C	-0.763344	2.517826	0.227837
H	0.000000	4.066079	-1.196343
H	0.000000	2.367804	-1.851415
H	1.208936	3.291764	0.851582
H	-1.208936	3.291764	0.851582
C	3.209255	-1.032096	0.246149
C	-3.209255	-1.032096	0.246149
C	2.991494	-0.343281	-0.952225
C	-2.597014	-0.580840	1.422887
C	2.167883	0.789345	-0.974509
C	-1.770054	0.545852	1.395420
C	1.552100	1.253599	0.198696
C	-1.552100	1.253599	0.198696
C	1.770054	0.545852	1.395420
C	-2.167883	0.789345	-0.974509
C	2.597014	-0.580840	1.422887
C	-2.991494	-0.343281	-0.952225
H	3.885103	-1.883893	0.272977
H	-3.885103	-1.883893	0.272977
H	3.497929	-0.659833	-1.861740
H	-2.789768	-1.087960	2.366023
H	2.053896	1.352694	-1.897995
H	-1.331601	0.917141	2.320119
H	2.789768	-1.087960	2.366023
H	-3.497929	-0.659833	-1.861740
H	1.331601	0.917141	2.320119
H	-2.053896	1.352694	-1.897995
Rb	0.000000	-1.787175	-0.378284

Cs(+)..Diphenylcyclopropane

MP2=-596.73089

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Coordinates (Angstroms)			
	X	Y	Z
-----			
C	3.134211	-1.235618	0.000000
C	2.810003	0.018985	0.762169
C	2.810003	0.018985	-0.762169
H	4.155134	-1.603610	0.000000
H	2.381232	-2.018912	0.000000
H	3.663208	0.533797	1.202809
H	3.663208	0.533797	-1.202809
C	-0.621456	0.472368	3.326941
C	-0.621456	0.472368	-3.326941
C	-0.054478	-0.791982	3.136906
C	-0.099767	1.573770	-2.637207
C	1.029365	-0.953398	2.265946
C	0.980333	1.408444	-1.766039
C	1.566994	0.144421	1.575985
C	1.566994	0.144421	-1.575985
C	0.980333	1.408444	1.766039
C	1.029365	-0.953398	-2.265946
C	-0.099767	1.573770	2.637207
C	-0.054478	-0.791982	-3.136906
H	-1.434365	0.606812	4.037180
H	-1.434365	0.606812	-4.037180
H	-0.426517	-1.645885	3.699572
H	-0.512856	2.566452	-2.804466
H	1.501947	-1.928506	2.168286
H	1.412788	2.275802	-1.270689
H	-0.512856	2.566452	2.804466
H	-0.426517	-1.645885	-3.699572
H	1.412788	2.275802	1.270689
H	1.501947	-1.928506	-2.168286
Cs	-1.837854	-0.295491	0.000000
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