Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

The Nature of Environmental Sensitivity about Symmetrical and Unsymmetrical Cyanine Dyes: Experimental and Theoretical Study

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1. Tests of functionals

2. Caculated the spectra and molecular orbitals of the free state and the bound state

3. Potential-energy curves of Cyanine Dyes

4. XYZ coordinates (angstrom)

1. Tests of functionals

A test with a large number of functionals was performed for photochemical properties for the TO-1. The results obtained with B97D, HFS, and HFB functionals are consisting with experimental data (502 nm). B97D, HFS, and HFB functionals were performed for photochemical properties for the Cy. The results obtained with HFB functional are nearly actual experiment. Therefore, we selected the HFB functional for our study.

Functional	**Calcd λ (nm)**	**Functional**	**calcd λ (nm)**	**Functional**	**calcd λ (nm)**
B3LYP	449.25	BHandH	398.93	X3LYP	446.05
B3P86	444.86	BHandHLYP	400.82	LC-wPBE	402.16
B3PW91	445.99	BMK	424.44	CAM-B3LYP	416.50
B1B95	439.35	M06	440.43	VSXC	484.67
mPW1PW91	437.06	M06HF	415.23	HCTH	484.74
mPW1LYP	441.05	M062X	427.67	HCTH93	485.59
mPW1PBE	437.06	tHCTHhyb	456.55	HCTH147	485.73
mPW3PBE	446.10	HSEh1PBE	442.06	HCTH407	484.74
B98	446.04	HSE2PBE	440.80	tHCTH	481.93
B971	448.14	PBEh1PBE	437.39	M06L	455.40
B972	443.01	wB97XD	416.03	**B97D**	**490.42**
PBE1PBE	437.51	wB97	402.03	**HFS**	**501.07**
B1LYP	440.91	wB97X	406.04	XAlpha	488.19
O3LYP	462.65	TPSSh	454.71	**HFB**	**513.09**

2. Caculated the spectra of the free state and the bound state

The absorption maxima for all four dyes shift to the red in 90% glycerol (a high viscosity solution) or upon binding to DNA. The absorption maxima for all four dyes shift slightly to the red upon binding to DNA/ in glycerol, indicative of the lower dielectric environment of the stacked base pairs/glycerol.[27] In addition, environment-induced conformational changes can also induce spectral shifts for all four dyes.

In water (low viscosity) solution, cyanine dyes are in free states and can rotate freely; however, in viscous or DNA microenvironment, rotation and twisting of molecules are restricted. So unrestraint for bonds, angles, or dihedral angles for free states were applied in the geometry optimization calculations. In contrast, we restricted the rotation of the methine chain on behalf of the bound states in the geometry optimization calculations. We calculated the absorption and emission spectra of the two states using the TD-DFT/HFB/TZVP method with COSMO solvation model, and compared them with the experimental data. The results in Table R1 show that computational absorption bands of all the dyes are well consistent with the experimental data. By computing the spectra of the two states, we found that the bound state spectrum is red shift compared to the free state.

The molecular orbitals involved in the $S_0 \rightarrow S_1$ transitions have been calculated for all the molecules in Figure R1, Compared with free states, the HOMO energy slightly increased or no change, yet the LUMO energy decreased in the bound state for cyanines, which leads to a decrease in the HOMO-LUMO gap, in agreement with the bathochromic shifts seen experimentally. Besides, the fact that viscosity has a relatively bigger influence on the LUMO energy indicates that the electronic excited state is more sensitive to viscosity. In conclusion, environment-induced conformational changes played an important role in red shifts of absorption/emission maximum for all four dyes.

Table S1 Absorption and emission maxima of different cyanine dyes for free state and bound state. Free state with no constrains for bonds, angles, or dihedral angles in the geometry optimization calculations. The bound state limited the rotation of the methine chain in the geometry optimization calculations.

Compound	free state λ (nm)		bound state λ (nm)	
	abs	flu	abs	flu
TO-1	513	543	525	569
TO-3	589	637	590	645
Cy1	478	549	480	557
Cy3	534	587	543	594
Cy5	591	636	593	641

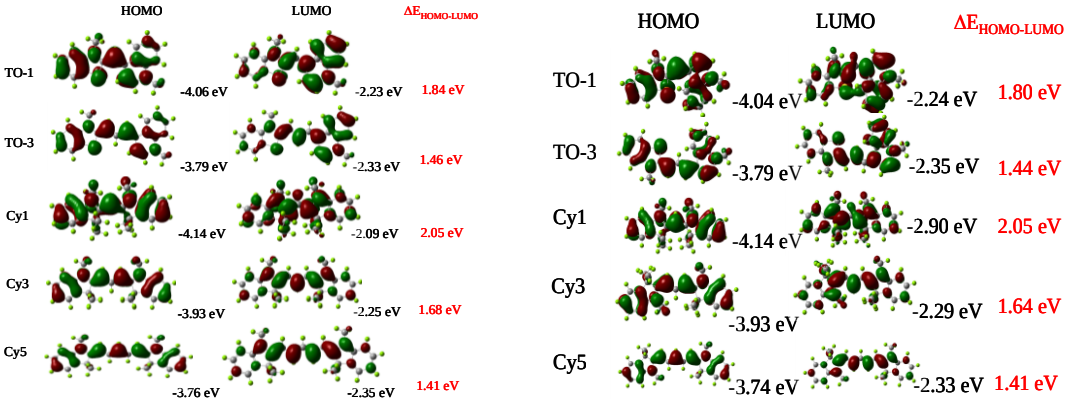

Figure S1 HOMO and LUMO for each of the cyanines in the free state(left) and in the bound state(right).

3. Potential-energy curves of Cyanine Dyes

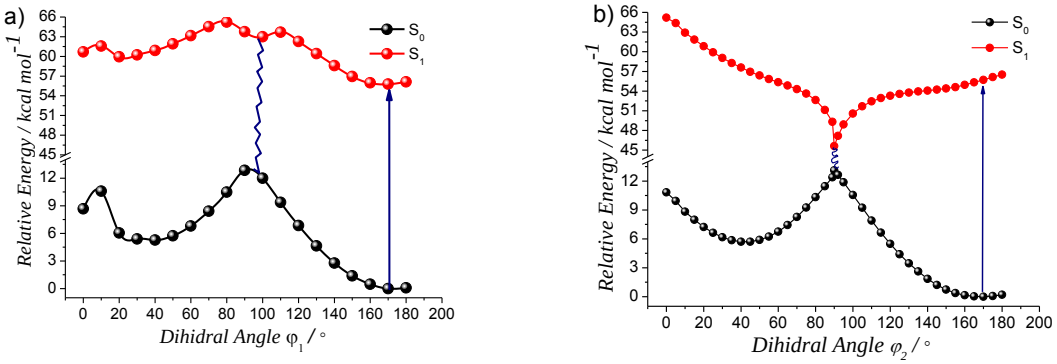

Figure S2 Potential-energy curves of the S_0 (black) and S_1 (red) states for TO-1 (a) φ_1 and (b) φ_2 as functions of the corresponding dihedral angles, calculated at the TD-DFT/HFB/TZVP level with COSMO solvation model.

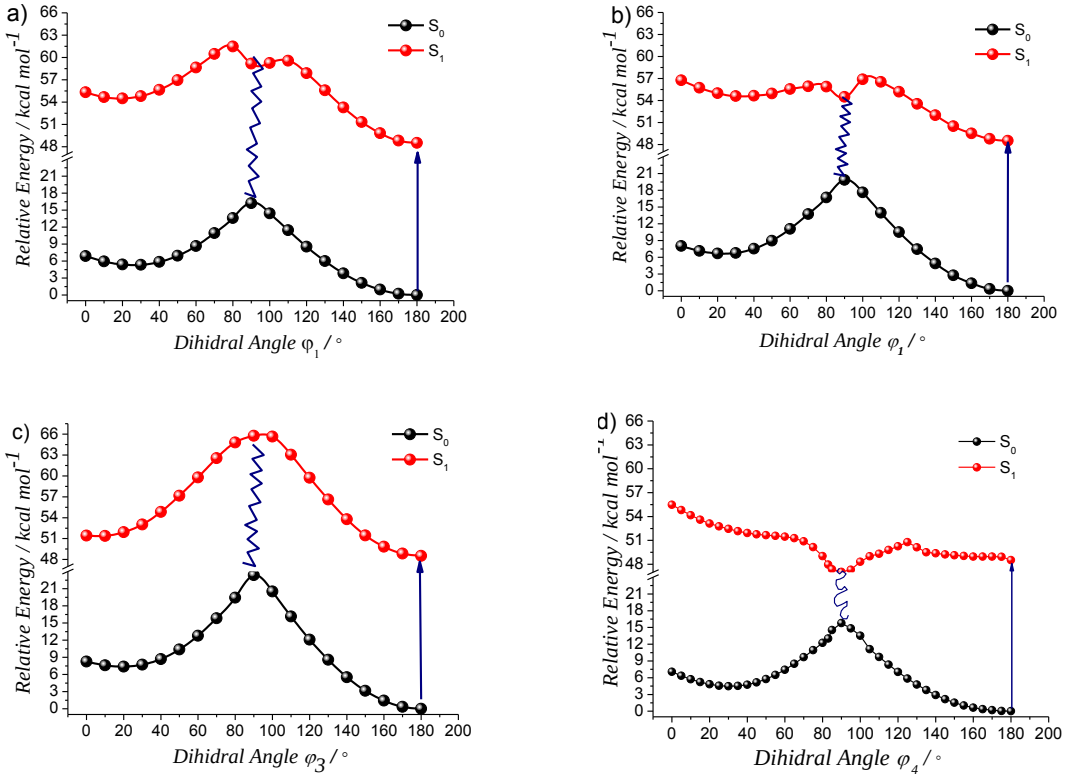

Figure S3 Potential-energy curves of the S_0 (black) and S_1 (red) states for TO-3 (a) φ_1 , (b) φ_2 (c) φ_3 and (d) φ_4 as functions of the corresponding dihedral angles, calculated at the TD-DFT/HFB/TZVP level with COSMO solvation model.

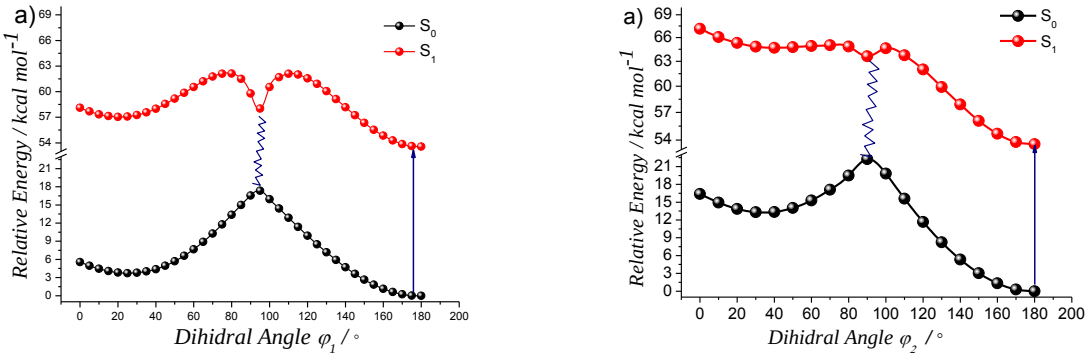

Figure S4 Potential-energy curves of the S_0 (black) and S_1 (red) states for Cy3 (a) φ_1 and (b) φ_2 as functions of the corresponding dihedral angles, calculated at the TD-DFT/HFB/TZVP level with COSMO solvation model.

Table S2 Activation energies of S_1 and energy gaps between the S_0 and S_1 States for Cy3 studied in this work for rotation around different dihedral angles (φ_1 and φ_2) in the S_0 and S_1 States

Cy3	φ_1	φ_2
E_a (kcal·mol^{-1})	8.54	11.05
E_{gap} (kcal·mol^{-1})	43.21	42.25

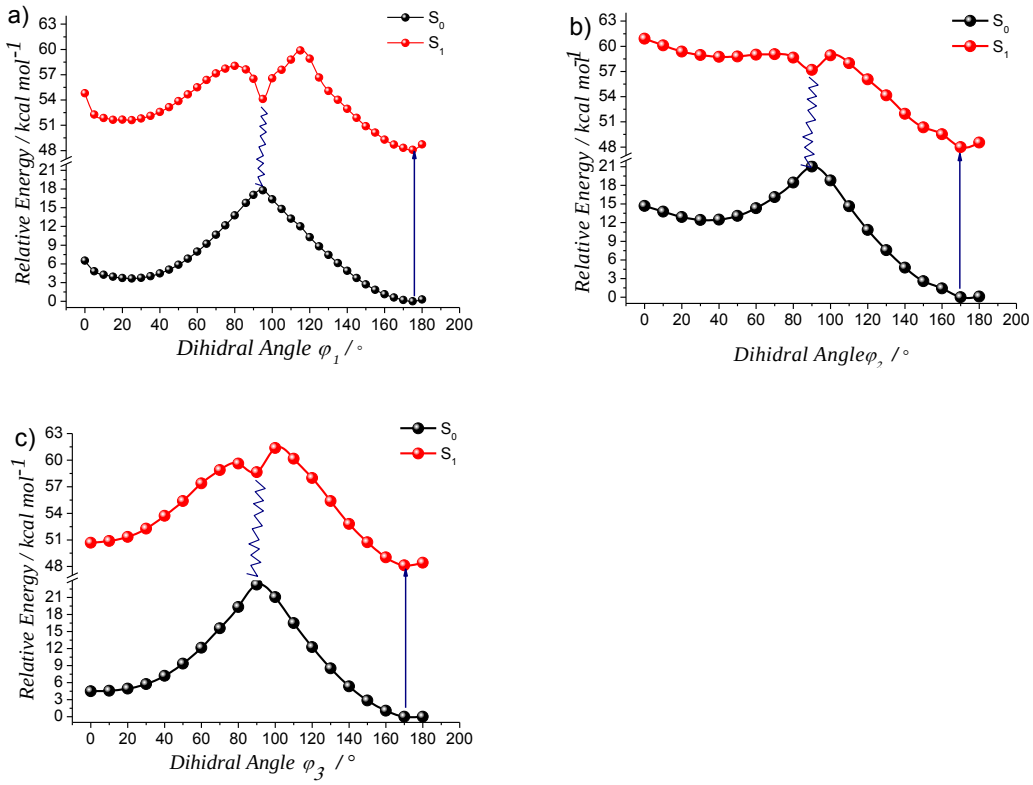

Figure S5 Potential-energy curves of the S_0 (black) and S_1 (red) states for Cy5 (a) φ_1 , (b) φ_2 and (c)φ_3 as functions of the corresponding dihedral angles, calculated at the TD-DFT/HFB/TZVP

level with COSMO solvation model.

Table S3 Activation energies of S_1 and energy gaps between the S_0 and S_1 States for TO-3 studied in this work for rotation around different dihedral angles (φ_1, φ_2 and φ_3) in the S_0 and S_1 States.

Cy5	φ_1	φ_2	φ_3
E_a (kcal·mol^{-1})	11.78	12.94	14..33
E_{gap} (kcal·mol^{-1})	36.31	36.16	35.39

4. XYZ coordinates (angstrom) and SCF Energies (a.u.)

Note: upper case letters before the atomic coordinates indicate the atomic symbol of the atoms involved in the calculations.

TO-1 in the S_0 state
Energy = -1236.2107

C	-4.75111900	-1.59863300	-0.41866800
C	-6.00460400	-0.93279800	-0.35907700
C	-6.06481700	0.46439100	-0.08228100
C	-4.88790100	1.22463900	0.14502000
C	-3.62554300	0.56156900	0.09599300
C	-3.57886100	-0.83624200	-0.19600700
N	-2.33006200	1.12960500	0.31112500
C	-1.24933900	0.25374600	0.13576900
S	-1.86570600	-1.42406900	-0.23312400
C	0.10504100	0.67069300	0.17243300
C	1.32907000	-0.09297300	0.14162600
C	2.64545700	0.59021400	-0.05189700
C	3.88431500	-0.18124900	-0.02160200
N	3.83187900	-1.59194000	0.17439700
C	2.61299200	-2.21023900	0.33741000
C	1.39970200	-1.51989000	0.32491600
C	2.76511800	2.00755900	-0.29073800
C	4.01130800	2.63491400	-0.46284900
C	5.21173200	1.86379600	-0.40702300
C	5.15111800	0.47520900	-0.19397800
C	-2.13271700	2.57876700	0.69042400
C	5.09417300	-2.43313300	0.21160800
H	-4.68958700	-2.67510700	-0.63721300
H	-6.93082200	-1.50193800	-0.53188800
H	-7.04093200	0.97233500	-0.04610800
H	-4.96294100	2.30093200	0.34805000
H	0.22007200	1.75728100	0.21633000
H	2.64299400	-3.29497500	0.49953800
H	0.50515800	-2.12007600	0.52061000
H	1.86264700	2.62786700	-0.35481600
H	4.05772800	3.71948100	-0.64580800
H	6.19091100	2.34984300	-0.53793000
H	6.08361100	-0.10045100	-0.16294700
H	-1.79591300	3.16316200	-0.18994900
H	-1.38327900	2.64595100	1.50060200
H	-3.08813800	2.98340400	1.06039500

H	4.79898900	-3.48248600	0.37994300
H	5.74712000	-2.09585100	1.03946100
H	5.63021500	-2.34994900	-0.75341900

TO-1 in the S_1 state
Energy = -1236.18910

C	-3.95218500	-0.62367300	-2.00429800
C	-5.32197700	-0.35738400	-1.78335000
C	-5.77987300	0.13916300	-0.51607600
C	-4.88799900	0.37921900	0.54680400
C	-3.49309100	0.11704200	0.34019500
C	-3.04465500	-0.38538900	-0.93934400
N	-2.44088800	0.28966400	1.26133400
C	-1.16214600	-0.06016200	0.76495000
S	-1.27113000	-0.64707300	-0.95681500
C	0.03705700	0.00705300	1.45879500
C	1.38084200	-0.41265300	0.89185000
C	2.28436900	0.54798500	0.25520700
C	3.59726400	0.09202600	-0.21329500
N	3.96091200	-1.28547700	-0.02975100
C	3.08834100	-2.17229800	0.63963100
C	1.83703100	-1.75385700	1.09393000
C	1.95898300	1.93933800	0.06417900
C	2.85933100	2.83947500	-0.55924700
C	4.12220000	2.38024000	-1.01277600
C	4.48887600	1.01408700	-0.83843600
C	-2.61996600	0.80657700	2.67500600
C	5.28791600	-1.80251500	-0.51613000
H	-3.59371400	-1.00543100	-2.97090600
H	-6.04645800	-0.53328300	-2.59230300
H	-6.85196500	0.33761500	-0.36970300
H	-5.26300000	0.75878500	1.50511400
H	0.00596500	0.36069900	2.50263100
H	3.45024300	-3.19849700	0.76425800
H	1.19932700	-2.49007000	1.60500700
H	0.98310100	2.31033900	0.40994900
H	2.57292700	3.89570200	-0.68716800
H	4.82910000	3.07065000	-1.49849600
H	5.47270000	0.68243500	-1.19277500
H	-2.04060700	1.74136800	2.79340500
H	-2.26491200	0.03873500	3.38768000
H	-3.68638000	1.00819700	2.85268600
H	5.34315600	-2.88281700	-0.29539600

H	6.12281200	-1.28407400	-0.00066500
H	5.38370900	-1.65213700	-1.61093500

TO-3 in the S_0 state
Energy = -1313.1510

C	-7.11326600	-1.26577900	-0.00001500
C	-7.30658900	0.14603400	0.00012800
C	-6.20583900	1.04290800	0.00016000
C	-4.88476000	0.50484200	0.00005500
C	-4.70464500	-0.91445600	-0.00010000
C	-5.80050200	-1.81037000	-0.00013200
N	-3.64418500	1.22172500	0.00006800
C	-2.49576600	0.42663900	-0.00008300
S	-2.94157000	-1.34209400	-0.00028000
C	-1.16456800	0.91534500	-0.00013700
C	-3.55286700	2.73036700	0.00047600
C	0.01393800	0.11075000	-0.00007200
C	1.32284500	0.64374900	-0.00014400
C	2.56056600	-0.10645700	-0.00003900
C	3.89175100	0.56732400	-0.00005400
C	5.11673700	-0.22913400	0.00005700
N	5.03246300	-1.65032400	0.00018100
C	3.79318200	-2.26135000	0.00017000
C	2.59617500	-1.54883700	0.00006200
C	4.04404600	2.00193700	-0.00019200
C	5.30693600	2.61979600	-0.00021500
C	6.49116800	1.82166300	-0.00010300
C	6.40005700	0.41820500	0.00002900
C	6.27705200	-2.51606100	0.00026900
H	-7.98177300	-1.94218100	-0.00003800
H	-8.32771300	0.55761200	0.00021100
H	-6.38546700	2.12623600	0.00026400
H	-5.63763100	-2.89842200	-0.00024600
H	-1.03480700	2.00752700	-0.00022700
H	-3.01650300	3.07048900	-0.90708900
H	-3.01639000	3.06996900	0.90817100
H	-4.56865100	3.15284400	0.00064300
H	-0.11573800	-0.98363800	0.00006100
H	1.39009400	1.74053700	-0.00027500
H	3.80205700	-3.35855600	0.00025000
H	1.67191200	-2.13961500	0.00004700
H	3.15421300	2.64360400	-0.00028600
H	5.37989700	3.71831700	-0.00032200

H	7.48293500	2.29989700	-0.00012300
H	7.32141400	-0.17595500	0.00010400
H	6.87886900	-2.31283300	0.90729400
H	6.87886200	-2.31302300	-0.90680400
H	5.95767100	-3.57178700	0.00038500

TO-3 in the S_1 state
Energy = -1313.1481

C	-7.12332100	-1.25233600	-0.00043600
C	-7.31218000	0.16648500	-0.00044900
C	-6.21620100	1.06037400	-0.00029500
C	-4.88675600	0.52156500	-0.00009300
C	-4.71276700	-0.91383000	-0.00016000
C	-5.81416300	-1.80225700	-0.00028800
N	-3.66750000	1.22830700	0.00011400
C	-2.49970600	0.41565500	0.00019700
S	-2.96407700	-1.35829400	0.00007600
C	-1.18024300	0.87849700	0.00033600
C	-3.55954400	2.73267500	0.00033200
C	0.02037000	0.04353700	0.00042000
C	1.30280200	0.59199400	0.00047500
C	2.59547200	-0.14136200	0.00048600
C	3.88560300	0.56405700	0.00021200
C	5.13831600	-0.21192100	-0.00011300
N	5.06943900	-1.63621800	-0.00000700
C	3.83870500	-2.28344200	0.00035000
C	2.63353900	-1.57866400	0.00054800
C	4.01665200	2.00589400	0.00021700
C	5.27735800	2.64305900	-0.00022800
C	6.47332600	1.87201500	-0.00072500
C	6.40491300	0.45513400	-0.00067400
C	6.32820500	-2.47461400	-0.00027400
H	-7.99576200	-1.92319900	-0.00053400
H	-8.33366300	0.57695400	-0.00059000
H	-6.39317400	2.14382200	-0.00029500
H	-5.65620400	-2.89089800	-0.00029100
H	-1.02633000	1.96795600	0.00039600
H	-3.01649600	3.06522100	-0.90697700
H	-3.01690800	3.06498700	0.90797400
H	-4.56943600	3.16927700	0.00015000
H	-0.11541300	-1.04897800	0.00042200
H	1.35750000	1.68996400	0.00042700
H	3.87139300	-3.37948000	0.00040800

H	1.71103700	-2.17299900	0.00076800
H	3.11756300	2.63447100	0.00057800
H	5.32930800	3.74345000	-0.00021400
H	7.45706400	2.36640700	-0.00116000
H	7.33729300	-0.12161700	-0.00105000
H	6.92866100	-2.25708200	0.90572300
H	6.92816400	-2.25726700	-0.90664700
H	6.03477500	-3.53799700	-0.00008600

Cy1 in the S_0 state

Energy = -995.95810191

C	-6.01449200	-0.61266300	0.40621500
C	-6.07503000	0.67435300	-0.19725800
C	-4.88770700	1.36438500	-0.57561300
C	-3.65000100	0.71703500	-0.32476300
C	-3.57092400	-0.56188200	0.28330700
C	-4.75578300	-1.24238900	0.64476900
N	-2.31226300	1.18708300	-0.59904900
C	-1.33964900	0.31064800	-0.12838200
C	-2.07988700	-0.99702000	0.39167100
C	0.00001200	0.80219700	0.00011000
C	1.33967000	0.31067300	0.12846400
C	-2.05210100	2.51287400	-1.25944800
N	2.31234600	1.18705100	0.59911700
C	3.65003600	0.71700400	0.32462600
C	3.57087000	-0.56188200	-0.28350300
C	2.07980500	-0.99703000	-0.39156200
C	4.88778000	1.36431400	0.57538200
C	6.07504800	0.67429600	0.19681500
C	6.01442000	-0.61267600	-0.40674000
C	4.75567000	-1.24237400	-0.64517500
C	2.05233800	2.51276700	1.25969500
C	-1.87524100	-2.25686700	-0.56039700
C	-1.69075700	-1.31366600	1.89498700
C	1.69042900	-1.31411200	-1.89465200
C	1.87537600	-2.25664900	0.56099600
H	-6.94459500	-1.12654200	0.69583800
H	-7.05160600	1.15240900	-0.37310700
H	-4.94725200	2.36145000	-1.03310400
H	-4.71754400	-2.23931600	1.11040200
H	-0.00002800	1.90054800	0.00019200
H	-1.13057300	2.44662700	-1.86512000
H	-1.94725000	3.31469600	-0.49833800

H	-2.90122200	2.74811000	-1.92478500
H	4.94739800	2.36136500	1.03289500
H	7.05164900	1.15232600	0.37259700
H	6.94447900	-1.12653800	-0.69653300
H	4.71735600	-2.23926300	-1.11088200
H	2.90152000	2.74783500	1.92502100
H	1.13085000	2.44654900	1.86542500
H	1.94753200	3.31470400	0.49869700
H	-0.83566600	-2.62183700	-0.54943800
H	-2.15357900	-2.00721100	-1.60488200
H	-2.53277700	-3.07772000	-0.20844800
H	-0.61449500	-1.54573800	1.99356500
H	-2.27197000	-2.18943200	2.24994500
H	-1.92461500	-0.44865200	2.54967400
H	2.27145800	-2.19008200	-2.24942400
H	1.92433100	-0.44936200	-2.54968000
H	0.61413000	-1.54606600	-1.99308900
H	2.53274300	-3.07763300	0.20904600
H	0.83576400	-2.62151200	0.55048800
H	2.15409000	-2.00666200	1.60529700

Cy1 in the S_1 state
Energy = -995.9324

C	-5.98234100	-0.27881400	0.49773600
C	-5.76952600	-1.18824800	-0.57484600
C	-4.47674600	-1.35551000	-1.15265100
C	-3.40910200	-0.57877200	-0.62400800
C	-3.60673700	0.34090800	0.44940800
C	-4.89429700	0.49290900	1.01276200
N	-2.03417400	-0.57130700	-1.01722800
C	-1.25865100	0.20947100	-0.10146300
C	-2.26313600	1.06928500	0.77266000
C	0.06715500	0.77322500	-0.57617100
C	1.33897200	0.36100800	-0.26225700
C	-1.52951800	-1.36950000	-2.17669700
N	2.49047500	1.06430800	-0.81399000
C	3.69115900	0.47908700	-0.40739700
C	3.41571300	-0.65215900	0.44554400
C	1.88724000	-0.82443600	0.62430300
C	5.03464700	0.87158100	-0.73696800
C	6.08513900	0.10701200	-0.19618800
C	5.81981300	-1.01951100	0.65142800
C	4.48439600	-1.40047600	0.97373400

C	2.39476700	2.26552500	-1.71461400
C	-1.92402200	1.04804600	2.31701800
C	-2.34230200	2.58924700	0.28337200
C	1.42053300	-2.24673600	0.08811300
C	1.49294400	-0.66632600	2.15612300
H	-6.98789900	-0.16667500	0.93352900
H	-6.61239700	-1.78014000	-0.96721400
H	-4.32273300	-2.06684100	-1.97697400
H	-5.06788100	1.19948800	1.84020600
H	-0.00922000	1.64190200	-1.25448300
H	-0.47724700	-1.10681900	-2.37629600
H	-2.13413000	-1.13765200	-3.07740900
H	-1.59757900	-2.45800700	-1.96579400
H	5.24703900	1.73121900	-1.38434400
H	7.12612900	0.37754400	-0.42704100
H	6.66230400	-1.59766300	1.05929800
H	4.30231500	-2.26680600	1.62600700
H	3.40784800	2.61373400	-1.96663000
H	1.84599500	3.07141800	-1.19088100
H	1.85852000	1.98528400	-2.64187800
H	-0.93823700	1.51922700	2.51113800
H	-1.90301600	0.01091000	2.71002600
H	-2.68951300	1.61950900	2.88422600
H	-1.38482900	3.11883700	0.47426400
H	-3.14402800	3.12255400	0.83627800
H	-2.56851300	2.65215200	-0.80212900
H	1.93112000	-3.04151900	0.66933300
H	1.67403200	-2.37474700	-0.98372500
H	0.32824600	-2.36593500	0.21796300
H	2.01229000	-1.44657100	2.74937900
H	0.40339800	-0.79601400	2.28273700
H	1.78727400	0.32970800	2.54528800

Cy3 in the S_0 state

Energy = -1072.9171

C	-6.95925200	-1.28465900	-0.08188600
C	-7.27312000	0.10035200	0.00247800
C	-6.24612700	1.08507900	0.06823400
C	-4.90093300	0.63136900	0.04642600
C	-4.57061300	-0.74930300	-0.04389400
C	-5.59903200	-1.71644300	-0.10572600
N	-3.67996600	1.40253000	0.10284300
C	-2.55554800	0.59074000	0.03092600
C	-3.02465400	-0.91540400	-0.05686800

C	-1.24413700	1.14109500	0.02671700
C	1.24413400	1.14110300	-0.02665500
C	0.00000300	0.44942400	0.00000500
C	2.55554800	0.59074400	-0.03090500
C	-3.64815300	2.90223800	0.22233200
N	3.67996300	1.40252900	-0.10284600
C	4.90093300	0.63136300	-0.04646000
C	4.57061200	-0.74930400	0.04389700
C	3.02465100	-0.91540300	0.05690600
C	6.24612400	1.08507500	-0.06835300
C	7.27312000	0.10035100	-0.00261400
C	6.95925300	-1.28465800	0.08180200
C	5.59903600	-1.71644300	0.10570400
C	-2.55389000	-1.60029300	-1.41290300
C	-2.54962200	-1.75599600	1.20756400
C	2.54960400	-1.75605000	-1.20747200
C	2.55390500	-1.60023100	1.41298600
C	3.64815500	2.90224200	-0.22229700
H	-7.76967300	-2.02880500	-0.13125400
H	-8.32579000	0.42430900	0.01693200
H	-6.50790500	2.15028100	0.13086000
H	-5.36239900	-2.78968700	-0.17336900
H	-1.17472800	2.23944700	0.04474900
H	1.17473000	2.23945600	-0.04462900
H	0.00001300	-0.64567500	-0.00003300
H	-3.01882600	3.19466600	1.08551000
H	-4.67248900	3.27293900	0.38557700
H	-3.24084000	3.35067600	-0.70662600
H	6.50789200	2.15027600	-0.13104000
H	8.32579000	0.42430500	-0.01712700
H	7.76967600	-2.02880400	0.13115400
H	5.36240500	-2.78968600	0.17337800
H	-1.45254100	-1.70501600	-1.45229800
H	-2.88435500	-1.00593000	-2.28988400
H	-3.00109600	-2.61284100	-1.48642700
H	-1.45004700	-1.88090200	1.22157300
H	-3.01133400	-2.76394400	1.17011000
H	-2.86218400	-1.26103200	2.15027500
H	3.01130200	-2.76400300	-1.16996600
H	2.86216700	-1.26114200	-2.15021200
H	1.45002800	-1.88095000	-1.22147900
H	3.00110800	-2.61277900	1.48654600
H	1.45255400	-1.70494300	1.45239400
H	2.88438600	-1.00582900	2.28993300

H	4.67251800	3.27295000	-0.38535800
H	3.24070400	3.35064500	0.70661600
H	3.01895500	3.19469300	-1.08556100

Cy3 in the S_1 state

Energy = -1072.9129

C	7.04839100	-1.15815600	0.00268000
C	7.30836000	0.24845300	-0.00037000
C	6.25253800	1.19157100	-0.00252700
C	4.90927800	0.68902300	-0.00152700
C	4.63768100	-0.72667600	0.00145000
C	5.70450800	-1.64621100	0.00361000
N	3.69291600	1.40006000	-0.00326400
C	2.56840600	0.51473100	-0.00119800
C	3.10219500	-0.96300800	0.00163500
C	1.24786100	1.01812800	-0.00110700
C	-1.24785800	1.01812300	0.00156700
C	0.00000200	0.30387700	0.00022800
C	-2.56840500	0.51472500	0.00151600
C	3.58541000	2.89564600	-0.00702000
N	-3.69290900	1.40005600	0.00338900
C	-4.90927600	0.68902400	0.00139900
C	-4.63768500	-0.72667400	-0.00151900
C	-3.10219900	-0.96301300	-0.00134300
C	-6.25253300	1.19157900	0.00205900
C	-7.30836000	0.24846600	-0.00040800
C	-7.04839500	-1.15814400	-0.00341900
C	-5.70451500	-1.64620500	-0.00398400
C	2.66271700	-1.75860600	1.31247200
C	2.66332200	-1.76320100	-1.30668800
C	-2.66361500	-1.76314000	1.30712100
C	-2.66244100	-1.75868300	-1.31204000
C	-3.58539400	2.89564300	0.00712900
H	7.88898200	-1.86935300	0.00433900
H	8.34927100	0.60849300	-0.00105200
H	6.47072100	2.26832600	-0.00482900
H	5.51581300	-2.73097100	0.00588600
H	1.14986700	2.11532100	-0.00201700
H	-1.14986800	2.11531600	0.00250900
H	0.00000500	-0.79087700	0.00014200
H	3.04026000	3.23386400	-0.91257500
H	4.59586200	3.33416700	-0.00962300
H	3.04288200	3.23880400	0.89826500
H	-6.47071300	2.26833500	0.00431500

H	-8.34926800	0.60851000	-0.00000600
H	-7.88899000	-1.86933700	-0.00532400
H	-5.51582400	-2.73096600	-0.00622700
H	1.56690700	-1.91567500	1.33681700
H	2.96239400	-1.20594500	2.22692800
H	3.15589800	-2.75256400	1.32400600
H	1.56751400	-1.92036300	-1.33101200
H	3.15655100	-2.75717700	-1.31452400
H	2.96342600	-1.21369800	-2.22290400
H	-3.15685800	-2.75711000	1.31490500
H	-2.96391000	-1.21358400	2.22324100
H	-1.56781500	-1.92031500	1.33169000
H	-3.15561500	-2.75264500	-1.32362200
H	-1.56662600	-1.91574700	-1.33614500
H	-2.96192800	-1.20607600	-2.22659200
H	-4.59584300	3.33417200	0.00947600
H	-3.04265200	3.23876900	-0.89803900
H	-3.04045000	3.23388000	0.91280200

Cy5 in the S_0 state

Energy = -1149.8536

C	8.10661800	-1.49116600	0.00661600
C	8.48760600	-0.12018900	-0.00393900
C	7.50844200	0.91423900	-0.01039200
C	6.14419100	0.52092700	-0.00565800
C	5.74583600	-0.84283200	0.00514100
C	6.72707900	-1.85980200	0.01119700
N	4.97196300	1.36110200	-0.01033300
C	3.80080800	0.60883700	-0.00238400
C	4.19371900	-0.92643000	0.00869000
C	2.50673300	1.19572800	-0.00337500
C	3.68596000	-1.65510500	1.32896100
C	3.68069800	-1.67672800	-1.29734500
C	5.10748800	2.85914700	-0.02177500
C	1.24935400	0.52904500	-0.00048500
C	-0.00288200	1.20427100	-0.00090400
C	-1.24950900	0.52209400	0.00041000
C	-2.51278100	1.18119300	0.00190600
C	-3.80293800	0.58804800	0.00221600
N	-4.96030900	1.35958900	0.01060800
C	-6.14816200	0.53922400	0.00498700
C	-5.76443300	-0.83125900	-0.00513300
C	-4.21275700	-0.93804500	-0.00774400
C	-7.51066200	0.93940100	0.00820200

C	-8.49858900	-0.08645600	0.00149800
C	-8.13111200	-1.46075800	-0.00799700
C	-6.75467700	-1.83926000	-0.01133900
C	-3.70820700	-1.69362900	1.29846200
C	-3.71180800	-1.67474400	-1.32607600
C	-4.98389500	2.86376200	0.02397600
H	8.88046700	-2.27485600	0.01144500
H	9.55494700	0.15206700	-0.00723900
H	7.81245000	1.97025900	-0.01848700
H	6.44062400	-2.92297000	0.01946200
H	2.45510200	2.29483100	-0.00761500
H	2.58100200	-1.71572100	1.36190000
H	4.03749400	-1.11897400	2.23480900
H	4.08991000	-2.68801300	1.35411600
H	2.57575700	-1.74021400	-1.32345500
H	4.08657100	-2.70913400	-1.30818800
H	4.02646900	-1.15424300	-2.21329700
H	4.11826300	3.33979900	-0.03084400
H	5.66969400	3.16555600	-0.92694900
H	5.66090000	3.18082000	0.88362600
H	1.21149500	-0.57025700	0.00151200
H	-0.00611200	2.30957100	-0.00224900
H	-1.20639900	-0.57750300	0.00120300
H	-2.47457700	2.28147000	0.00364200
H	-7.81271500	1.99588500	0.01562700
H	-9.56308900	0.19672500	0.00373200
H	-8.91164800	-2.23773300	-0.01298300
H	-6.47601300	-2.90454700	-0.01882300
H	-4.12218600	-2.72283900	1.30926300
H	-4.04963900	-1.16839100	2.21446600
H	-2.60358300	-1.76555100	1.32433400
H	-4.12307900	-2.70484700	-1.34894900
H	-2.60707000	-1.74305800	-1.35781400
H	-4.05869400	-1.13824600	-2.23348100
H	-6.02973400	3.20847500	0.04617600
H	-4.49153600	3.25834200	-0.88750600
H	-4.45936200	3.24139000	0.92436500

Cy5 in the S_1 state

Energy = -1149.8516

C	-8.30648100	-1.20204300	0.00045800
C	-8.56620400	0.20261300	-0.00042700
C	-7.50843600	1.14640300	-0.00092500

C	-6.16842400	0.64320400	-0.00053600
C	-5.89615600	-0.76833800	0.00040900
C	-6.96281700	-1.68954500	0.00090100
N	-4.94597700	1.35662800	-0.00093600
C	-3.82770700	0.47797700	-0.00027800
C	-4.35994400	-1.00228200	0.00067100
C	-2.50587700	0.97606600	-0.00046300
C	-3.91904100	-1.79759700	-1.30897700
C	-3.91916100	-1.79594200	1.31131800
C	-4.84075600	2.85335400	-0.00204600
C	-1.26498400	0.24894200	0.00010500
C	-0.00001400	0.90621600	0.00010000
C	1.26500200	0.24896800	0.00036500
C	2.50585600	0.97610100	0.00062500
C	3.82771800	0.47801500	0.00055800
N	4.94597000	1.35664500	0.00113000
C	6.16843500	0.64320600	0.00037500
C	5.89614900	-0.76832000	-0.00049500
C	4.35994200	-1.00225400	-0.00031300
C	7.50845000	1.14637700	0.00044500
C	8.56620300	0.20256800	-0.00049200
C	8.30646300	-1.20208400	-0.00139300
C	6.96279000	-1.68955500	-0.00137900
C	3.91882400	-1.79606100	-1.31077800
C	3.91939500	-1.79742500	1.30952800
C	4.84076800	2.85337700	0.00221500
H	-9.14669100	-1.91381100	0.00081700
H	-9.60674800	0.56385500	-0.00072700
H	-7.72675900	2.22320700	-0.00158900
H	-6.77301600	-2.77415800	0.00159700
H	-2.39759300	2.07231700	-0.00102300
H	-2.82280900	-1.95301600	-1.33392300
H	-4.21996400	-1.24646200	-2.22394300
H	-4.41086600	-2.79220100	-1.31933100
H	-2.82292500	-1.95129300	1.33656200
H	-4.41094700	-2.79055200	1.32286100
H	-4.22018800	-1.24369400	2.22558000
H	-4.29751900	3.19487200	0.90317100
H	-5.85206100	3.28978600	-0.00223600
H	-4.29773700	3.19353000	-0.90790000
H	-1.26554100	-0.85099500	0.00052600
H	-0.00002400	2.01251800	-0.00011800
H	1.26557100	-0.85096800	0.00039400
H	2.39756300	2.07235300	0.00085000

H	7.72681500	2.22317300	0.00110800
H	9.60675100	0.56380200	-0.00051300
H	9.14666100	-1.91386400	-0.00212100
H	6.77296200	-2.77416400	-0.00207900
H	4.41063200	-2.79065900	-1.32234900
H	4.21960700	-1.24389300	-2.22516900
H	2.82258800	-1.95143600	-1.33572000
H	4.41124100	-2.79201800	1.31985300
H	2.82317100	-1.95286400	1.33478600
H	4.22055300	-1.24619200	2.22435800
H	5.85207400	3.28980000	0.00318300
H	4.29710200	3.19350400	0.90769200
H	4.29819400	3.19496600	-0.90337900