Photophysical and Electrochemical Characterization of a Helical Viologen, N, N'-Dimethyl-5,10-diaza[5]helicene.

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SUPPORTING INFORMATION

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Experimental

General. Trimethyloxonium tetrafluoroborate and ferrocene were obtained from Aldrich and used without purification. Anthracene was obtained from Aldrich and sublimed before use. 9,10-Diphenylanthracene from Aldrich was twice recrystallized from xylene. Tetrabutylammonium perchlorate from Fluka was twice recrystallized from absolute ethanol. LUDOX AS-30 colloidal silica was used for fluorescence lifetime measurements as received from Aldrich. Dichloromethane from Fisher was purified following a literature procedure.[1] HPLC grade acetonitrile from Aldrich was used as received for cyclic voltammetry. Spectroscopy grade acetonitrile from Acros was used as received for all spectroscopy experiments. Cyclohexane from Aldrich was purified for fluorescence following a literature procedure.[2] Absolute ethanol from Decon was used as received for phosphorescence spectra. UV-Visible spectra were collected with an Agilent 8453 UV-visible spectrophotometer. Fluorescence lifetimes were determined on an Optical Building Blocks Co. Easylife X instrument. Phosphorescence and fluorescence spectra were recorded on a Cary Eclipse Fluorescence spectrophotometer. Cyclic Voltammograms were collected with a CH Instruments CHI600C Electrochemical Analyzer. ^{1}H NMR and ^{13}C NMR were obtained on Bruker Advance 400 and 600 MHz NMR.

Synthesis of N,N'-Dimethyl-5,10-diaza[5]helicene($\mathbf{1^{2+}}$). 40 mg , (0.14 mmol) of 5,10-Diaza[5]helicene was dissolved in 30 mL of dichloromethane saturated with dry N_2 gas. 55 mg, (0.37 mmol) of Trimethyloxonium tetrafluoroborate was then added. The mixture was stirred in nitrogen atmosphere for 24 hours. The solvent was then removed under vacuum. The yellow crude product was triturated in warm 95% ethanol. It was then dried under vacuum for 12 hours. 50 mg of yellow product was recovered (yield 73%). ^{1}H NMR(400 MHz, CD_3CN): δ 10.07(d, 2H, J=2.2Hz), 8.75(d, 2H, J=8.3Hz), 8.71 (d, 2H, J=1.7Hz), 8.61(d, 2H, J=8.8Hz), 8.27(ddd, 2H,

J=8.6, 7.1, 1.2Hz), 7.89(ddd, 2H, J=8.3, 7.1, 0.9Hz), 4.86(s, 6H)ppm. ^{13}C NMR (600 MHz, DMSO-d6): δ 154.9, 135.3, 133.6, 131.5, 130.9, 129.3, 128.6, 127.9, 125.6, 119.7 and 46.1ppm. Calculated for $C_{22}H_{18}N_2B_2F_8$: 54.59% C, 3.75% H, 5.79% N. Found for $C_{22}H_{18}N_2B_2F_8$: 54.35% C, 3.74% H, 5.82% N. It decomposes with a gradual color change starting at 200^0 C to finally form a black solid without ever clearly melting within the temperature range of our melting point apparatus. MALDI MS Found: 310 as Calcd. for $C_{22}H_{18}N_2^{+\cdot}$.

Synthesis of N-Methyl-5,10-diaza[5]helicene(3^+). 30 mg, (0.07 mmol) of N,N'-Dimethyl-5,10-diaza[5]helicene was added to 10 mL of deionized water and refluxed for 5 min. After the solution was cooled to room temperature the solid was removed by filtration. The solvent was then removed under vacuum. The residue was recrystallized from ethanol and dried in vacuum. 5 mg of Yellow solid was collected.(yield 22 % with around 10% impurity). ^{1}H NMR(400 MHz, CD_3CN,): δ=9.90(s, 1H), 9.68(s, 1H), 8.95(d, 1H, J=8.5Hz), 8.55(d, 1H, J=8.3Hz), 8.52(d, 1H, J=8.7Hz), 8.51(d, 1H, J=8.4Hz), 8.49(d, 1H, J=8.3Hz), 8.37(dd, 1H, J=8.3, 1.2Hz), 8.18(ddd, 1H, J=8.6, 7.2, 1.3Hz), 7.93(ddd, 1H, J=8.3, 7.0, 1.3Hz), 7.84(ddd, 1H, J=8.3, 7.1, 1.1Hz), 7.59(ddd, 1H, J=8.4, 7.0, 1.4Hz), 4.77(s, 3H)ppm.

Fluorescence Spectra. Fluorescence spectra of 5,10-diaza[5]helicene and N,N'-dimethyl-5,10-diaza[5]helicene were recorded in acetonitrile with a concentration of 21.6 μM and 8.1 μM, respectively. The sample solution was then introduced into a square 10 mm path length quartz cell clear on all four faces. Excitation wavelengths were 375 nm and 441 nm for 5,10-diaza[5]helicene and N,N'-dimethyl-5,10-diaza[5]helicene, respectively. Excitation and emission slit widths were both 5 nm.

Fluorescence Quantum Yield. 9,10-Diphenylanthracence was selected as standard (φ_F=0.90).[3] It was cross-checked with another well-known standard anthracene (φ_F=0.27) in order to demonstrate the accuracy of our method.[4] The fluorescence quantum yield of anthracene obtained using 9,10-diphenylanthracene as the standard was 0.28, acceptably close to the literature value. We used acetonitrile for determination of the fluorescence quantum yield of both 5,10-diaza[5]helicene and N,N'-dimethyl-5,10-diaza[5]helicene. Cyclohexane and absolute ethanol were used as solvents for 9,10-diphenylanthracene and anthracene, respectively. The excitation wavelengths used in the experiment for 5,10-diaza[5]helicene, N,N'-dimethyl-5,10-diaza[5]helicene, 9,10-diphenylanthrancence and anthracene were 375, 375, 375 and 355nm, respectively. The fluorescence quantum yield protocol used is as follows:

1. The UV-Vis absorbance spectra of 5,10-diaza[5]helicene, N,N'-dimethyl-5,10-diaza[5]helicene, 9,10-diphenylanthrancence and the standard were measured. These UV-Vis measurements were collected at five different concentrations to verify that the absorbance at the excitation wavelengths were ~ 0.02, 0.04, 0.06, 0.08 and 0.1. These low concentrations were chosen in order to minimize any re-absorption effects.[5]

2. Fluorescence spectra were recorded using these identical solutions with identical instrument settings (i.e. excitation and emission slits widths of 5 nm). The areas under the emission bands were then determined by integration.
3. Graphs of integrated fluorescence intensity vs absorbance were plotted for the two samples and the standard. The quantum yields of 5,10-diaza[5]helicene and N,N'-dimethyl-5,10-diaza[5]helicene were calculated as follow:

$$\Phi_X = \Phi_{ST} \times \frac{S_X}{S_{ST}} \times \frac{\eta_X^2}{\eta_{ST}^2}$$

Where the subscripts ST and X denote standard and sample respectively, φ is the fluorescence quantum yield, S is the slope from the plot, and η is the refractive index (sodium D line) of the solvent.

Fluorescence Lifetimes. Fluorescence lifetimes were collected with 21.8 μM and 8.1 μM acetonitrile solutions of 5,10-diaza[5]helicene and N,N'-dimethyl-5,10-diaza[5]helicene, respectively. The light source used was a 340 nm LED lamp. A 400 nm cutoff filter was used for the sample. The instrument response function (IRF) was collected on a dilute colloidal silica solution.

Phosphorescence Spectra and Phosphorescence Lifetimes. Spectra and lifetimes were determined using a 0.54 mM and a saturated ethanol solution of 5,10-diaza[5]helicene and N, N'-dimethyl-5,10-diaza[5]helicene, respectively. The saturated ethanol solution of N,N'-dimethyl-5,10-diaza[5]helicene was used due to its very limited solubility. The sample tube was introduced into a glass dewar containing liquid nitrogen. Phosphorescence spectra were then recorded at -196^{o}C. The excitation wavelength was 375 nm for both samples. The excitation and emission slit widths were both set to 20 nm in order to maximize signal to noise. Phosphorescence lifetimes were collected on the same samples under the same conditions as described above at emission wavelengths of 530 nm and 626 nm for 5,10-diaza[5]helicene and N,N'-dimethyl-5,10-diaza[5]helicene, respectively.

Cyclic Voltammetry. All CV were collected using a three electrode system consisting of a glassy carbon working electrode, a platinum wire counter electrode and a silver/silver nitrate(0.01 M in acetonitrile) reference electrode. Tetrabutylammonium perchlorate (Bu_4NClO_4) was used as supporting electrolyte. 9.7 mg of N,N'-Dimethyl-5,10-diaza[5]helicene was dissolved in 10 ml of 0.1 M Bu_4NClO_4 in CH_3CN. The concentration of N,N'-dimethyl-5,10-diaza[5]helicene was 2 mM. Ferrocene (4 mg) was added as an internal standard (2.15 mM). The solution was saturated with argon before collecting data and the working electrode was polished after every 3rd scan.

1. C. Puchot, O. Samuel, E. Dunach, S. Zhao, C. Agami, H. B. Kagan, *J. Am. Chem. Soc.,* 1986, **108**, 2353.
2. W. Armaego and C. Chai, *Purification of Laboratory Chemicals*, *6 Edition*, Page 213, 2009, Elsevier.
3. S. Hamai and F. Hirayama, *J. Phys. Chem*., 1983, **87**, 83.
4. W. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229.
5. S. Dhami, A. J. de Mello, G. Rumbles, S. M. Bishop, D. Phillips and A. Beeby, *Photochem. Photobiol.,* 1995, **61**, 341.

X-ray Crystallography Data for 5,10-Dimethyl-5,10-diaza[5]helicene

Crystallographic data. The X-ray diffraction data were measured at 150 K on a Bruker SMART APEX II CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube operated at 1.5 kW power (50 kV, 30 mA). A yellow rectangular prism of PhIm of approximate dimensions 0.27 × 0.33 × 0.48 mm^3 was glued to a glass fiber using Paratone N oil. The detector was placed at a distance of 5.13 cm from the crystal during the data collection.

A series of narrow frames of data were collected with a scan width of 0.5˚ in ω or ϕ and an exposure time of 10 s per frame. The frames were integrated with the Bruker SAINT Software package[1] using a narrow-frame integration algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 20227 reflections in the θ range of 1.84 to 33.73˚ of which 4046 were independent with $I \geq 2\sigma(I)$ (R_{int} = 0.0253). The data were corrected for absorption effects by the multi-scan method (SADABS). Crystallographic data collection parameters and refinement data are collected below in Table 1.

The structure was solved by the direct methods using the Bruker SHELXTL (V. 6.14) Software Package.[1] The crystal belongs to the centro symmetric orthorhombic space group, *Pbcn*, and is achiral. All non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. The asymmetric unit consists of a half of the helicene dication and one tetrafluoroborate anion. All

of the non-hydrogen atoms are located on general positions and refined anisotropically. The hydrogen atoms were also located in the Fourier maps, and were refined. The final refinement parameters are $R_1 = 0.0426$ and $wR_2 = 0.1182$ for data with $F > 4\sigma(F)$ giving the data to parameter ratio of 21. The refinement data for all data are $R_1 = 0.0521$ and $wR_2 = 0.1269$.

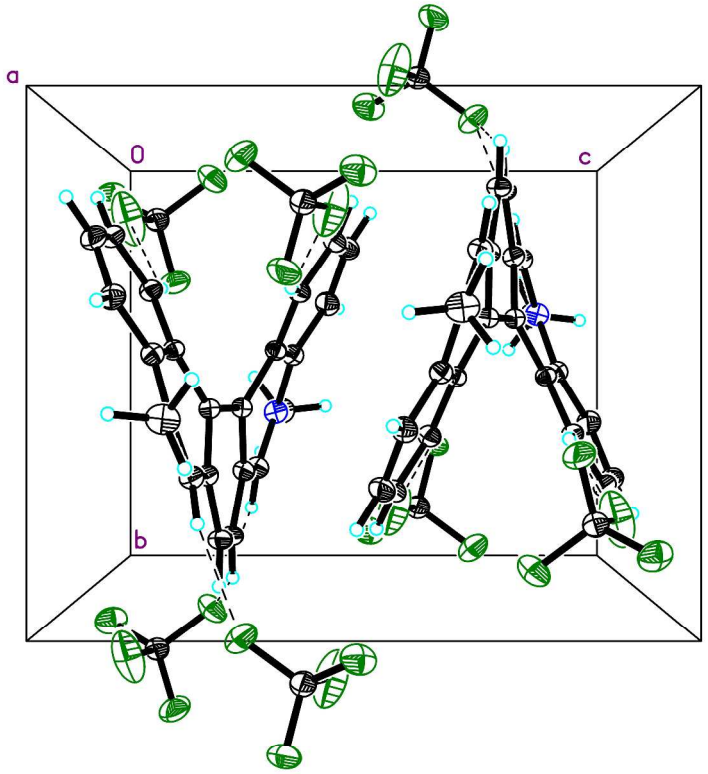
The pentacyclic helicene dication (Fig. 1) is non-planar and assumes a helical structure. As the dication is situated on a two-fold symmetry axis, a half of is the symmetry equivalent of the other. The central ring (A) is dissected by the axis. The pyridinium ring adjacent to the central ring (B) and the terminal phenyl ring (C) are more planar than ring A. Specifically the four unique bonds of ring A at 1.3616(17), 1.4047(11), 1.4245(11) and 1.4372(16) Å are significantly unequal, and the ring is the most non-planar of the three. The helicity of the dication is reflected in the torsion angle of 60.86(10)° for the central C42-C52-C52A-C42A linkage. The dihedral angle between the mean planes passing through the two symmetrically equivalent BC rings is 45.01(1)°. The BF_4^- anions are well separated from the dication and are not involved in hydrogen bonding interaction.

Acknowledgment. Financial support by the NSF (CHE 0619920) for the purchase of the Bruker Apex II Diffractometer is gratefully acknowledged.

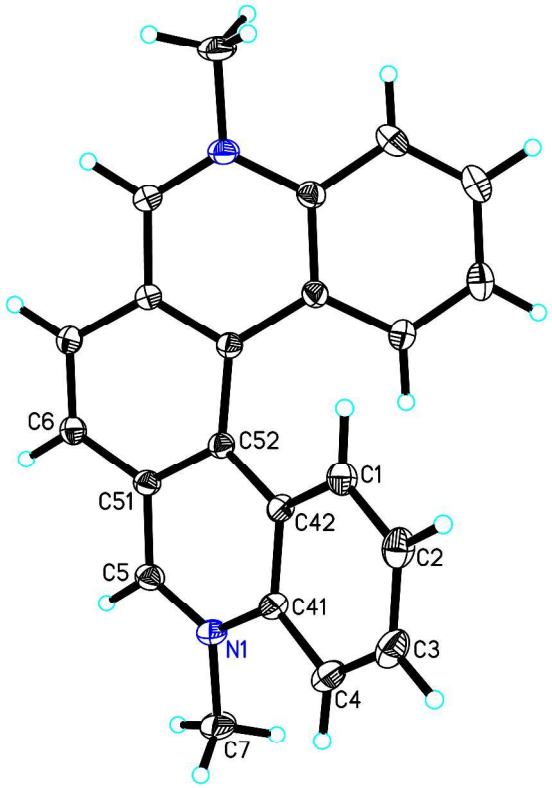
References

1. APEX2 Software Suite V. 2.2, Bruker AXS Inc.: Madison, WI, 2008.

Packing in the crystal of $\mathbf{1}^{2+}$.



Crystal structure of $\mathbf{1}^{2+}$ with thermal paramters drawn at 50% probability and the symmetric equivalent atoms unlabeled.



Computational Studies. The geometry optimizations were conducted using Gaussian 03 or Gaussian 09 using the B3LYP functional in conjunction with the 6-311+G(2d,p) basis set.[1a,b] Frequency calculations were done to verify the nature of the located stationary points for all helicene optimized geometries and for all helicene transition states. All the structures in Table S1 were characterized by zero negative frequencies establishing these as energy minima on the potential energy surfaces (PES). Selected structural parameters for six helicenes are given in Table S1 and their Cartesian coordinates, Mulliken charges, zero-point energy corrections and total energies are given in the pages following this table. The default FineGrid option was used for all DFT calculations. No counterion or solvent was used in any of the geometry optimization calculations of charged helicenes. Nevertheless, we believe that these calculated structures can be used for comparison to the X-ray structures since BF_4^- is a weakly coordinating counterion.[2] This viewpoint is supported by the observation that the shortest B-N distance is 3.45Å.

Transition states were located using the synchronous transit-guided quasi-Newton method in conjunction with the B3LYP/6-311+G(2d,p) computation model. Frequency calculations were used to demonstrate that all transitions states had a single negative frequency that was associated with movement along the racemization potential energy surface. A solvent was not included in these calculations since we were interested in using the results as intrinsic barriers (i.e. barriers that can be compared to experimental barriers that require counterion and solvent movement).

TD-DFT calculations did include acetonitrile as a solvent using the polarizable continuum model and polarizable conductor calculations as implemented in the Gaussian computational package.

1. a. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
   b. Gaussian 03, Revision D.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K.

Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

2. Krossing, I. and I. Raabe (2004) Noncoordinating Anions-Fact or Fiction? A Survey of Likely Candidates. *Angew Chem, Int. Ed.,* **43,** 2066-2090.

Computational Results

Helicenes

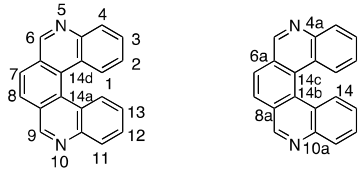
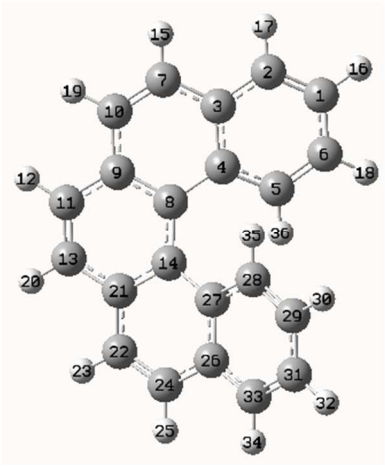


Table S1. B3LYP/6-311+G(2d,p) Structural Parameters Helicenes						
	a	b	c	d	e	f
$d_{1,14}$	2.963Å	2.997Å	2.998Å	3.009Å	3.012Å	3.058Å
$d_{1H,14H}$	2.630Å	2.486Å	2.548Å	2.573Å	2.633Å	2.730Å
$d_{1,2}$	1.376Å	1.376Å	1.374Å	1.375Å	1.379Å	1.387Å
$d_{2,3}$	1.405Å	1.405Å	1.402Å	1.403Å	1.396Å	1.390Å
$d_{3,4}$	1.373Å	1.374Å	1.376Å	1.376Å	1.381Å	1.387Å
$d_{4,4a}$	1.413Å	1.410Å	1.405Å	1.404Å	1.403Å	1.403Å
$d_{4a,14d}$	1.426Å	1.425Å	1.423Å	1.428Å	1.420Å	1.421Å
$d_{4a,5}$	1.426Å	1.375Å	1.397Å	1.397Å	1.398Å	1.393Å
$d_{6a,14c}$	1.417Å	1.412Å	1.422Å	1.416Å	1.436Å	1.462Å
$d_{8a,14b}$	1.417Å	1.413Å	1.416Å	1.416Å	1.436Å	1.462Å
$d_{5,6}$	1.356Å	1.296Å	1.323Å	1.317Å	1.348Å	1.386Å
$d_{7,8}$	1.360Å	1.360Å	1.358Å	1.357Å	1.350Å	1.344Å
$d_{9,10}$	1.356Å	1.296Å	1.295Å	1.317Å	1.348Å	1.386Å
$d_{10,10a}$	1.426Å	1.376Å	1.372Å	1.397Å	1.398Å	1.393Å
$d_{14b,14c}$	1.447Å	1.445Å	1.439Å	1.449Å	1.411Å	1.381Å
$>_{14a, 14b, 14c, 14d}$	30.22^0	27.89^0	28.04^0	29.80^0	25.89^0	23.90^0
$>_{1, 14d, 14c, 14b}$	18.06^0	16.96^0	17.38^0	17.01^0	20.57^0	23.59^0
$>_{14, 14a, 14b, 14c}$	18.21^0	16.91^0	18.04^0	17.06^0	20.68^0	23.95^0

a. [5]helicene [E_{RB3LYP} = -847.02880944 a.u.] ; b. 5,10-diaza[5]helicene [E_{RB3LYP} = -879.11738914 a. u.]; c. N-Methyl-5,10-diaza[5]helicene (R = CH_3) [E_{RB3LYP} = -918.82043811 a. u.] ; d. N, N'-Dimethyl-5,10-diaza[5]helicene [E_{RB3LYP} = -958.42791577 a. u.]; e. N, N'-Dimethyl-5,10-diaza[5]helicene radical cation [E_{UB3LYP} = -958.74558126 a. u.]; f. neutral N, N'-Dimethyl-5,10-diaza[5]helicene [E_{RB3LYP} = -958.92495879 a. u.] . g. d-distance in Å. h. > angle in degrees



[5]helicene B3LYP/6-311+G(2d,p)

C	3.113584	-2.817657	-0.751278	C	3.682417	-1.738138	-0.121258	C	2.941756	-0.558737	0.118409
C	1.556340	-0.511092	-0.215581	C	1.025941	-1.615930	-0.922766	C	1.779922	-2.736091	-1.186197
C	3.593094	0.613632	0.603038	C	0.797684	0.703236	0.051486	C	1.544452	1.880771	0.306438
C	2.933360	1.797711	0.628111	C	0.927027	3.155359	0.202579	H	1.529544	4.040298	0.372541
C	-0.374907	3.260692	-0.176318	C	-0.643271	0.820408	-0.016608	H	4.641212	0.555647	0.873791
H	3.695946	-3.710776	-0.943644	H	4.726525	-1.760741	0.170769	H	1.342105	-3.556546	-1.742275
H	3.450705	2.712024	0.896335	H	-0.826654	4.230851	-0.348813	C	-1.189938	2.101983	-0.276782
C	-2.574002	2.242650	-0.599637	H	-2.936719	3.227233	-0.872677	C	-3.416277	1.180660	-0.570198
H	-4.459877	1.291294	-0.841976	C	-2.962962	-0.079065	-0.078983	C	-1.588196	-0.253841	0.256576
C	-1.243588	-1.424641	0.972429	C	-2.168682	-2.406415	1.242315	H	-1.869475	-3.282507	1.805364
C	-3.497517	-2.274981	0.804868	H	-4.216434	-3.061200	1.001902	C	-3.884175	-1.122273	0.166262
H	-4.917919	-0.978521	-0.128112	H	-0.234020	-1.546015	1.335150	H	0.009328	-1.575170	-1.283718

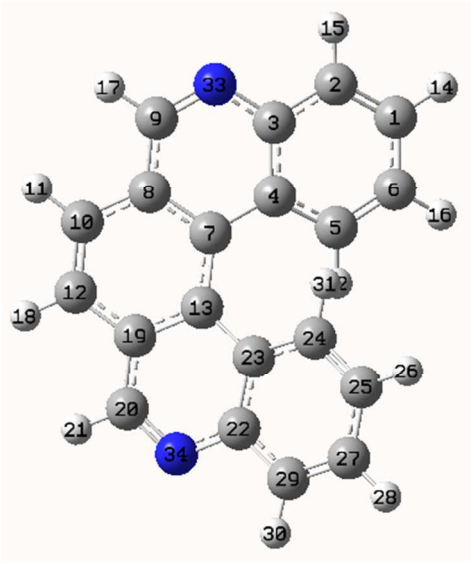
Zero-point correction= 0.286776 (Hartree/Particle)
Thermal correction to Energy= 0.301464
Thermal correction to Enthalpy= 0.302408

Thermal correction to Gibbs Free Energy= 0.245633
Sum of electronic and zero-point Energies= -846.742033
Sum of electronic and thermal Energies= -846.727346
Sum of electronic and thermal Enthalpies= -846.726401
Sum of electronic and thermal Free Energies= -846.783176

Atomic charges with hydrogens summed into heavy atoms:

1 C -0.181671	2 C 0.036368	3 C 0.412918	4 C 0.159128	5 C -0.286866	6 C -0.046695
7 C -0.295907	8 C 0.055389	9 C 0.646664	10 C -0.170590	11 C -0.327158	12 H 0.000000
13 C -0.329277	14 C 0.053224	15 H 0.000000	16 H 0.000000	17 H 0.000000	18 H 0.000000
19 H 0.000000	20 H 0.000000	21 C 0.647702	22 C -0.170846	23 H 0.000000	24 C -0.295718
25 H 0.000000	26 C 0.412474	27 C 0.162738	28 C -0.288622	29 C -0.047862	30 H 0.000000
31 C -0.180202	32 H 0.000000	33 C 0.034809	34 H 0.000000	35 H 0.000000	36 H 0.000000

Sum of Mulliken charges= 0.00000



5,10-Diaza[5]helicene B3LYP/6-311+G(2d,p)

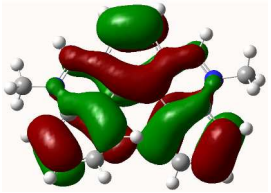
C	-4.471562	1.527751	0.029372	C	-3.942150	2.653812	0.611174	C	-4.740270	3.796217	0.828627
C	-6.133658	3.760527	0.531427	C	-6.627300	2.607923	-0.121316	C	-5.819126	1.522063	-0.369047

C	-6.918019	4.954699	0.786003	C	-6.175795	6.135631	1.010039	C	-4.776269	6.030377	1.292235
C	-6.780851	7.415367	0.931310	H	-6.167692	8.295474	1.086806	C	-8.095621	7.521726	0.595524
C	-8.357831	5.071683	0.749825	H	-3.847774	0.660848	-0.152260	H	-2.896150	2.718647	0.882700
H	-6.226191	0.660735	-0.885039	H	-4.240980	6.939151	1.562111	H	-8.558656	8.488830	0.437127
C	-8.899508	6.356129	0.521097	C	-10.298004	6.477107	0.239747	H	-10.679429	7.459077	-0.034908
C	-10.694430	4.280642	0.715504	C	-9.324543	4.021111	1.010847	C	-9.022708	2.807223	1.669403
C	-9.995831	1.868553	1.925399	H	-9.732653	0.955639	2.446161	C	-11.325688	2.090651	1.529335
H	-12.081436	1.337600	1.717502	C	-11.666754	3.284116	0.940994	H	-12.689036	3.516047	0.670455
H	-8.013266	2.618742	2.003144	H	-7.653366	2.584206	-0.456578	N	-4.094930	4.928417	1.269757
N	-11.148668	5.500073	0.268699								

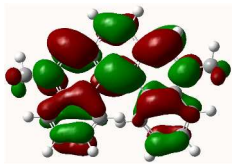
Zero-point correction= 0.263361 (Hartree/Particle)
Thermal correction to Energy= 0.277730
Thermal correction to Enthalpy= 0.278674
Thermal correction to Gibbs Free Energy= 0.222318
Sum of electronic and zero-point Energies= -878.854028
Sum of electronic and thermal Energies= -878.839659
Sum of electronic and thermal Enthalpies= -878.838715
Sum of electronic and thermal Free Energies= -878.895072

Mulliken charges with hydrogens summed into heavy atoms:

1	C	-0.013375	2 C	-0.206801	3 C	0.016572	4 C	0.406252	5 C	-0.390594	6 C	-0.044631
7	C	0.333271	8 C	0.728914	9 C	0.018096	10 C	-0.539010	12 C	-0.539645	13 C	0.331602
19	C	0.728386	20 C	0.020565	22 C	0.017265	23 C	0.404973	24 C	-0.389366	25 C	-0.046023
27	C	-0.013375	29 C	-0.207530	33 N	-0.307692	34 N	-0.307855				



HOMO
-0.47339



LUMO
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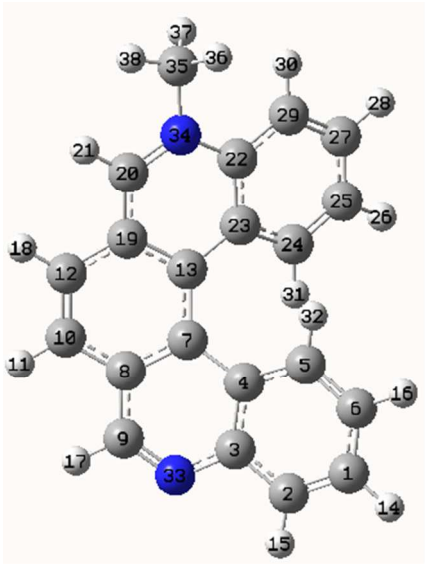


N-Methyl-5,10-diaza[5]helicene B3LYP/6-311+G(2d,p)

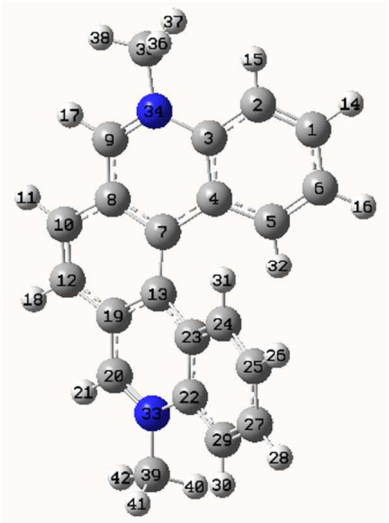
C	-1.225633	-0.977804	0.029580	C	-0.688307	0.141975	0.615854	C	-1.483703	1.284435	0.839497
C	-2.879155	1.255419	0.542519	C	-3.381256	0.109154	-0.111115	C	-2.574465	-0.976984	-0.365412
C	-3.646424	2.455434	0.809882	C	-2.901243	3.635533	1.051797	C	-1.500538	3.521686	1.325640
C	-3.497149	4.922557	0.995292	H	-2.872596	5.793868	1.150627	C	-4.810774	5.053389	0.675001
C	-5.079514	2.584962	0.807347	H	-0.606859	-1.845743	-0.160299	H	0.358492	0.201597	0.883699
H	-2.981945	-1.834066	-0.887288	H	-0.953390	4.420858	1.599078	H	-5.262418	6.025762	0.522906
C	-5.618144	3.884612	0.603152	C	-6.984350	4.017250	0.324917	H	-7.390149	4.981022	0.047358
C	-7.422360	1.753458	0.822519	C	-6.042704	1.541956	1.099256	C	-5.705180	0.344619	1.768249
C	-6.648501	-0.613362	2.052897	H	-6.358123	-1.512271	2.581437	C	-7.983692	-0.428664	1.667911
H	-8.720411	-1.195366	1.870338	C	-8.371641	0.747260	1.068266	H	-9.411575	0.897547	0.821026
H	-4.684218	0.189320	2.079557	H	-4.406580	0.086695	-0.450997	N	-0.837317	2.409717	1.285599
N	-7.834365	3.004107	0.354461	C	-9.240209	3.232531	-0.031043	H	-9.522167	2.532365	-0.815394
H	-9.890411	3.103331	0.832934	H	-9.336105	4.247065	-0.405995				

Zero-point correction= 0.304897 (Hartree/Particle)
Thermal correction to Energy= 0.320982
Thermal correction to Enthalpy= 0.321927
Thermal correction to Gibbs Free Energy= 0.262078

Sum of electronic and zero-point Energies= -918.515541
Sum of electronic and thermal Energies= -918.499456
Sum of electronic and thermal Enthalpies= -918.498512
Sum of electronic and thermal Free Energies= -918.558360

Mulliken charges with hydrogens summed into heavy atoms:

1 C 0.016043	2 C -0.196307	3 C 0.052934	4 C 0.450765	5 C -0.399346	6 C -0.009129
7 C 0.313687	8 C 0.697049	9 C 0.109862	10 C -0.477807	12 C -0.453254	13 C 0.203681
19 C 0.543292	20 C 0.294252	22 C 0.323681	23 C 0.313431	24 C -0.367032	25 C -0.075515
27 C -0.169927	29 C -0.261487	33 N -0.265435	34 N 0.133098	35 C 0.223464	



N, N'-Dimethyl-5,10-diaza[5]helicene B3LYP/6-311+G(2d,p)

C	3.197998	-2.798509	-0.722260	C	3.749293	-1.698399	-0.106718	C	2.965996	-0.553218	0.109326
C	1.576353	-0.542167	-0.217164	C	1.073730	-1.673098	-0.896733	C	1.863011	-2.769340	-1.152312
C	0.793994	0.646251	0.044352	C	1.518628	1.836773	0.293168	C	2.888427	1.748386	0.617544
C	0.922714	3.126533	0.202649	H	1.526367	4.007883	0.379310	C	-0.375573	3.231630	-0.176272
C	-0.648884	0.763475	-0.011373	H	3.809096	-3.673216	-0.904218	H	4.791372	-1.716371	0.173866
H	1.454527	-3.611704	-1.695859	H	3.433306	2.633206	0.919066	H	-0.829157	4.198522	-0.354495

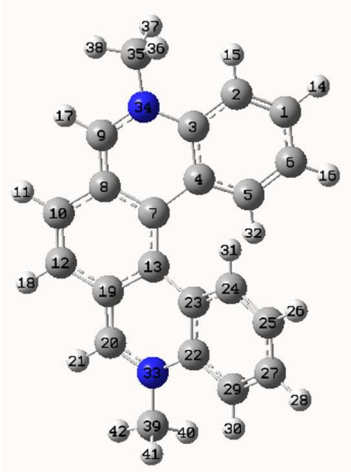
C	-1.171739	2.054498	-0.264240	C	-2.537954	2.186884	-0.589086	H	-2.932601	3.146686	-0.895151
C	-2.986417	-0.069386	-0.069428	C	-1.612805	-0.281584	0.256393	C	-1.298830	-1.474383	0.943419
C	-2.254903	-2.426374	1.207224	H	-1.987482	-3.319933	1.756733	C	-3.577579	-2.241789	0.777903
H	-4.322044	-3.004626	0.966399	C	-3.944373	-1.071255	0.154540	H	-4.976178	-0.922795	-0.125222
H	-0.291969	-1.632159	1.297855	H	0.054752	-1.667890	-1.251468	N	-3.381704	1.176270	-0.564158
N	3.557800	0.614723	0.597416	C	4.977941	0.612821	1.025621	H	5.115732	-0.128559	1.810257
H	5.617462	0.384687	0.174620	H	5.223604	1.597353	1.411495	C	-4.783102	1.401454	-0.994923
H	-5.037765	0.688205	-1.776388	H	-5.451950	1.283523	-0.144094	H	-4.866337	2.410784	-1.385886

Zero-point correction= 0.346369 (Hartree/Particle)
Thermal correction to Energy= 0.364087
Thermal correction to Enthalpy= 0.365031
Thermal correction to Gibbs Free Energy= 0.301920
Sum of electronic and zero-point Energies= -958.081546
Sum of electronic and thermal Energies= -958.063829
Sum of electronic and thermal Enthalpies= -958.062885
Sum of electronic and thermal Free Energies= -958.125996

Atomic charges with hydrogens summed into heavy atoms:

1 C -0.125221	2 C -0.272180	3 C 0.335778	4 C 0.372818	5 C -0.356908	6 C -0.040942
7 C 0.274556	8 C 0.621367	9 C 0.196192	10 C -0.432552	11 H 0.000000	12 C -0.433117
13 C 0.272362	14 H 0.000000	15 H 0.000000	16 H 0.000000	17 H 0.000000	18 H 0.000000
19 C 0.619525	20 C 0.197098	21 H 0.000000	22 C 0.336611	23 C 0.370793	24 C -0.355160
25 C -0.042339	26 H 0.000000	27 C -0.125269	28 H 0.000000	29 C -0.272236	30 H 0.000000
31 H 0.000000	32 H 0.000000	33 N 0.145806	34 N 0.147130	35 C 0.282994	36 H 0.000000
37 H 0.000000	38 H 0.000000	39 C 0.282894	40 H 0.000000	41 H 0.000000	42 H 0.000000

Sum of Mulliken charges= 2.00000



N, N'-Dimethyl-5,10-diaza[5]helicene Radical Cation B3LYP/6-311+G(2d,p)

C	0.612966	3.349564	0.011756	C	1.173419	4.447367	0.632856	C	0.413522	5.609401	0.835786
C	-0.963357	5.640186	0.488689	C	-1.471712	4.525098	-0.201933	C	-0.707105	3.401922	-0.440254
C	-1.752272	6.847881	0.739730	C	-0.981809	8.041292	0.951952	C	0.360416	7.942385	1.271039
C	-1.596002	9.333007	0.870497	H	-0.981920	10.215697	1.000976	C	-2.911756	9.439553	0.587979
C	-3.159052	6.962328	0.727601	H	1.212604	2.463137	-0.151212	H	2.210318	4.412852	0.931869
H	-1.131125	2.565449	-0.980755	H	0.932240	8.824446	1.523215	H	-3.375441	10.409474	0.455358
C	-3.726432	8.263546	0.509844	C	-5.066906	8.381106	0.189675	H	-5.488330	9.342672	-0.067757
C	-5.496622	6.089653	0.636977	C	-4.132783	5.899481	0.985095	C	-3.811352	4.721960	1.684219
C	-4.747308	3.738659	1.929072	H	-4.464056	2.848541	2.475982	C	-6.058241	3.896988	1.475318
H	-6.793134	3.120018	1.643099	C	-6.434027	5.066714	0.846181	H	-7.462959	5.197347	0.546242
H	-2.803978	4.588146	2.048620	H	-2.488025	4.553413	-0.564845	N	-5.910164	7.329977	0.142873
N	1.022735	6.769145	1.322991	C	2.422688	6.754024	1.757861	H	2.562062	6.015503	2.546960
H	3.085606	6.522761	0.922792	H	2.675349	7.735241	2.149826	C	-7.293847	7.538979	-0.294170
H	-7.549725	6.829714	-1.080920	H	-7.986010	7.420423	0.540761	H	-7.385041	8.546650	-0.689824

Zero-point correction= 0.344201 (Hartree/Particle)
Thermal correction to Energy= 0.362262
Thermal correction to Enthalpy= 0.363206
Thermal correction to Gibbs Free Energy= 0.298689
Sum of electronic and zero-point Energies= -958.401381

Sum of electronic and thermal Energies= -958.383319
Sum of electronic and thermal Enthalpies= -958.382375
Sum of electronic and thermal Free Energies= -958.446892

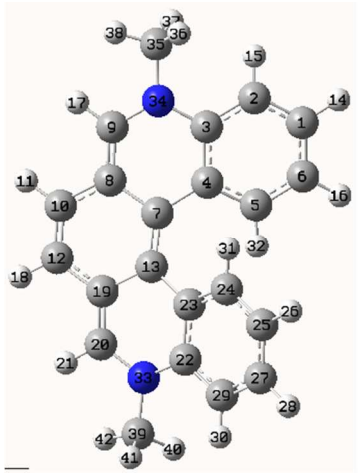
Atomic charges with hydrogens summed into heavy atoms:

1 C -0.193165	2 C -0.295035	3 C 0.346060	4 C 0.385476	5 C -0.375773	6 C -0.114801
7 C 0.266158	8 C 0.515150	9 C 0.181602	10 C -0.487211	11 H 0.000000	12 C -0.487413
13 C 0.265217	14 H 0.000000	15 H 0.000000	16 H 0.000000	17 H 0.000000	18 H 0.000000
19 C 0.514493	20 C 0.182249	21 H 0.000000	22 C 0.346701	23 C 0.385438	24 C -0.376126
25 C -0.115596	26 H 0.000000	27 C -0.193116	28 H 0.000000	29 C -0.296137	30 H 0.000000
31 H 0.000000	32 H 0.000000	33 N 0.077903	34 N 0.079173	35 C 0.194441	36 H 0.000000
37 H 0.000000	38 H 0.000000	39 C 0.194313	40 H 0.000000	41 H 0.000000	42 H 0.000000

Mulliken atomic spin densities:

1 C -0.001577	2 C 0.038385	3 C -0.031557	4 C 0.035999	5 C 0.006833	6 C 0.033222
7 C 0.077805	8 C 0.021305	9 C 0.141508	10 C 0.039785	11 H -0.000300	12 C 0.040083
13 C 0.077943	14 H -0.000206	15 H -0.001684	16 H -0.002257	17 H -0.010587	18 H -0.000303
19 C 0.021105	20 C 0.141895	21 H -0.010603	22 C -0.031646	23 C 0.035891	24 C 0.006791
25 C 0.033238	26 H -0.002257	27 C -0.001622	28 H -0.000203	29 C 0.038435	30 H -0.001687
31 H 0.000274	32 H 0.000270	33 N 0.153797	34 N 0.153720	35 C -0.017965	36 H 0.006920
37 H 0.009718	38 H 0.000428	39 C -0.017950	40 H 0.006933	41 H 0.009702	42 H 0.000420

Sum of Mulliken spin densities= 1.00000



Neutral N,N'-Dimethyl-5,10-diaza[5]helicene B3LYP/6-311+G(2d,p)

C	3.112890	-2.830671	-0.716436	C	3.676137	-1.740179	-0.071359	C	2.931173	-0.569942	0.141337
C	1.563030	-0.522155	-0.238007	C	1.059129	-1.615162	-0.953285	C	1.807089	-2.758855	-1.188523
C	0.764834	0.698088	0.012042	C	1.576393	1.899413	0.198327	C	2.886137	1.786042	0.535266
C	0.941307	3.195203	0.115516	H	1.559899	4.081316	0.208309	C	-0.383496	3.302619	-0.082389
C	-0.611698	0.810118	0.026294	H	3.707090	-3.722921	-0.874071	H	4.707838	-1.791789	0.245509
H	1.373121	-3.586022	-1.736481	H	3.487200	2.657952	0.753918	H	-0.851537	4.276774	-0.174720
C	-1.218708	2.125751	-0.165905	C	-2.528317	2.223072	-0.507996	H	-2.980531	3.179410	-0.731891
C	-2.953476	-0.092866	-0.103940	C	-1.596971	-0.263471	0.281737	C	-1.278651	-1.416740	1.008736
C	-2.201834	-2.423362	1.248081	H	-1.909084	-3.304811	1.805002	C	-3.499825	-2.288365	0.768372
H	-4.230344	-3.072417	0.928546	C	-3.877568	-1.126664	0.112193	H	-4.902571	-1.014611	-0.210617
H	-0.272090	-1.527790	1.386015	H	0.045599	-1.565927	-1.324818	N	-3.360524	1.123409	-0.648124
N	3.531780	0.567926	0.675720	C	4.932025	0.556389	1.055615	H	5.125737	-0.223263	1.795065
H	5.592855	0.393084	0.195707	H	5.179345	1.515571	1.505860	C	-4.743955	1.336700	-1.030317
H	-5.061939	0.593341	-1.764138	H	-5.422784	1.289808	-0.170130	H	-4.831947	2.319789	-1.488312

Zero-point correction= 0.341300 (Hartree/Particle)
Thermal correction to Energy= 0.359816
Thermal correction to Enthalpy= 0.360760
Thermal correction to Gibbs Free Energy= 0.295737

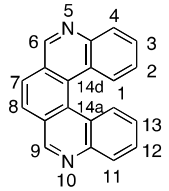
Sum of electronic and zero-point Energies= -958.583659
Sum of electronic and thermal Energies= -958.565142
Sum of electronic and thermal Enthalpies= -958.564198
Sum of electronic and thermal Free Energies= -958.629222

Atomic charges with hydrogens summed into heavy atoms:

1 C -0.253458	2 C -0.291059	3 C 0.397743	4 C 0.383712	5 C -0.382012	6 C -0.176039
7 C 0.246769	8 C 0.384056	9 C 0.094910	10 C -0.504628	11 H 0.000000	12 C -0.505531
13 C 0.246563	14 H 0.000000	15 H 0.000000	16 H 0.000000	17 H 0.000000	18 H 0.000000
19 C 0.386575	20 C 0.089974	21 H 0.000000	22 C 0.397401	23 C 0.386587	24 C -0.383648
25 C -0.175633	26 H 0.000000	27 C -0.251970	28 H 0.000000	29 C -0.293112	30 H 0.000000
31 H 0.000000	32 H 0.000000	33 N -0.002120	34 N 0.000372	35 C 0.102465	36 H 0.000000
37 H 0.000000	38 H 0.000000	39 C 0.102083	40 H 0.000000	41 H 0.000000	42 H 0.000000

Sum of Mulliken charges= 0.00000

Computational Results
Helicene Racemization Transition States



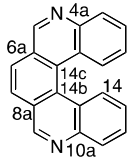
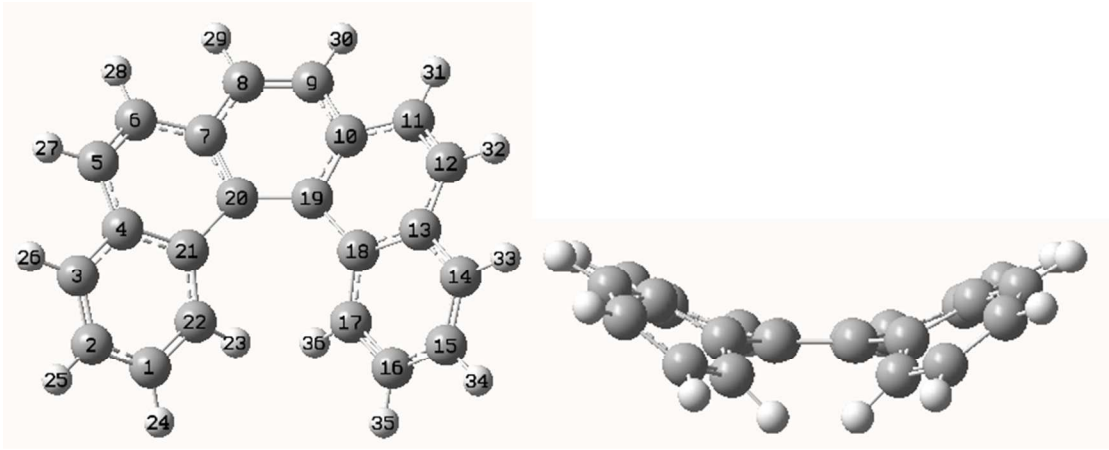


Table. B3LYP/6-311+G(2d,p) Structural Parameters Helicene Racemization Transition States						
	a	b	c	d	e	f
$d_{1,14}$	3.042Å	3.109Å	3.081Å	3.083Å	3.102Å	3.169Å
$d_{1H,14H}$	1.550Å	1.520Å	1.548Å	1.545Å	1.585Å	1.652Å
$d_{1,2}$	1.381Å	1.380Å	1.378Å	1.379Å	1.384Å	1.390Å
$d_{2,3}$	1.397Å	1.398Å	1.394Å	1.396Å	1.390Å	1.386Å
$d_{3,4}$	1.374Å	1.373Å	1.376Å	1.376Å	1.381Å	1.386Å
$d_{4,4a}$	1.410Å	1.409Å	1.403Å	1.403Å	1.402Å	1.402Å
$d_{4a,14d}$	1.434Å	1.435Å	1.432Å	1.437Å	1.430Å	1.429Å
$d_{4a,5}$	1.424Å	1.374Å	1.396Å	1.395Å	1.395Å	1.391Å
$d_{6a,14c}$	1.429Å	1.425Å	1.432Å	1.427Å	1.448Å	1.474Å
$d_{8a,14b}$	1.429Å	1.425Å	1.430Å	1.427Å	1.448Å	1.474Å
$d_{5,6}$	1.349Å	1.290Å	1.317Å	1.310Å	1.343Å	1.383Å
$d_{7,8}$	1.354Å	1.354Å	1.352Å	1.352Å	1.345Å	1.339Å
$d_{9,10}$	1.349Å	1.290Å	1.291Å	1.310Å	1.343Å	1.383Å
$d_{10,10a}$	1.424Å	1.374Å	1.370Å	1.395Å	1.395Å	1.391Å
$d_{14b,14c}$	1.473Å	1.474Å	1.461Å	1.472Å	1.425Å	1.384Å
$>_{14a, 14b, 14c, 14d}$	0.01^0	0.003^0	-2.41^0	-0.006^0	0.002^0	0.012^0
$>_{1, 14b, 14c, 14b}$	-39.22^0	-33.32^0	-33.64^0	-35.18^0	38.57^0	41.74^0
$>_{14, 14a, 14b, 14c}$	39.24^0	33.29^0	37.24^0	35.18^0	-38.57^0	-41.75^0

a. [5]helicene [E_{RB3LYP} = -846.99146645 a.u.]; b. 5,10-diaza[5]helicene [E_{RB3LYP} = -879.08571253 a. u.]; c. N-Methyl-5,10-diaza[5]helicene (R = CH_3) [E_{RB3LYP} = -918.78853979 a. u.]; d. N, N'-Dimethyl-5,10-diaza[5]helicene [E_{RB3LYP} = -958.39411726 a. u.]; e. N, N'-Dimethyl-5,10-diaza[5]helicene radical cation [E_{UB3LYP} = -958.7155701 a.u.]; f. neutral N, N'-Dimethyl-5,10-diaza[5]helicene [-958.90255458 a.u.]. g. d-distance in Å. h. > angle in degrees



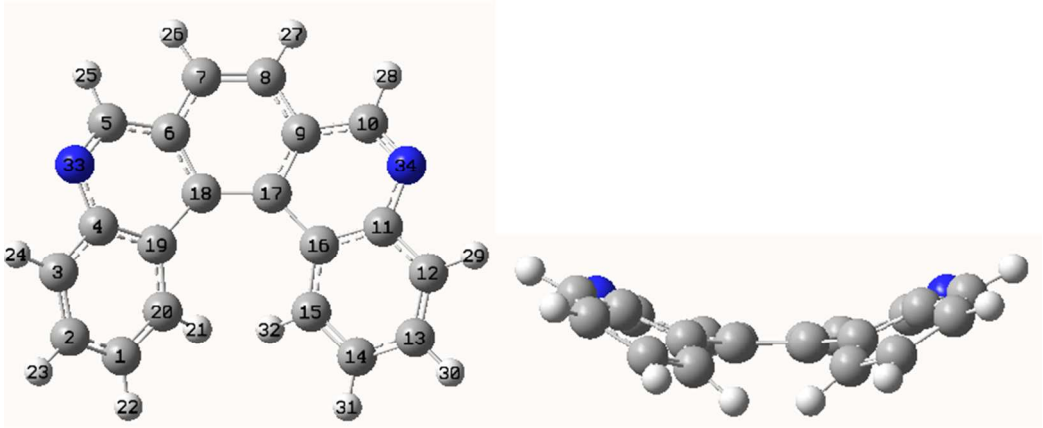
[5]helicene racemization transition state B3LYP/6-311+G(2d,p)

C	-2.375175	-2.747153	-0.497055	C	-3.470001	-2.573796	0.353451	C	-3.750075	-1.303780	0.797870
C	-2.918539	-0.210268	0.478292	C	-3.413632	1.107850	0.691865	C	-2.720982	2.157312	0.203102
C	-1.379745	2.002904	-0.268577	C	-0.676899	3.205010	-0.511734	C	0.676906	3.204936	-0.511583
C	1.379626	2.002752	-0.268371	C	2.720773	2.157000	0.203656	C	3.413326	1.107405	0.692271
C	2.918275	-0.210643	0.478173	C	3.750017	-1.304195	0.797066	C	3.470134	-2.574011	0.351937
C	2.375203	-2.747080	-0.498466	C	1.520853	-1.695483	-0.764873	C	1.669864	-0.412554	-0.198765
C	0.736387	0.728054	-0.336252	C	-0.736609	0.728131	-0.336278	C	-1.670161	-0.412374	-0.198624
C	-1.521082	-1.695549	-0.764186	H	-0.775214	-1.857552	-1.512104	H	-2.202214	-3.703563	-0.976091
H	-4.122813	-3.403651	0.595400	H	-4.656173	-1.107029	1.360071	H	-4.380217	1.238070	1.164338
H	-3.123603	3.162143	0.255353	H	-1.236200	4.130516	-0.582571	H	1.236294	4.130391	-0.582321
H	3.123437	3.161799	0.256159	H	4.379847	1.237472	1.164915	H	4.656149	-1.107603	1.359269
H	4.123190	-3.403855	0.593266	H	2.202240	-3.703270	-0.977942	H	0.774811	-1.857333	-1.512658

Zero-point correction= 0.286154 (Hartree/Particle)
Thermal correction to Energy= 0.300261
Thermal correction to Enthalpy= 0.301205
Thermal correction to Gibbs Free Energy= 0.245761
Sum of electronic and zero-point Energies= -846.705312
Sum of electronic and thermal Energies= -846.691206
Sum of electronic and thermal Enthalpies= -846.690262
Sum of electronic and thermal Free Energies= -846.745706

Mulliken charges with hydrogens summed into heavy atoms:

1 C -0.067377	2 C -0.186699	3 C -0.047889	4 C 0.440127	5 C -0.333790	6 C -0.205317
7 C 0.650065	8 C -0.281333	9 C -0.281516	10 C 0.650073	11 C -0.205177	12 C -0.333493
13 C 0.440044	14 C -0.048095	15 C -0.186639	16 C -0.067292	17 C -0.334088	18 C 0.322422
19 C 0.043526	20 C 0.043609	21 C 0.322304	22 C -0.333464		



5, 10-Diaza[5]helicene racemization transition state B3LYP/6-31G+(2d,p)

C	-4.464639	8.194746	-0.143394	C	-5.612209	8.436825	0.617178	C	-5.870762	9.726730	1.011062
C	-4.976557	10.774540	0.716199	C	-4.725700	13.018271	0.550110	C	-3.361255	12.898269	0.131531
C	-2.667272	14.119018	-0.011550	C	-1.313433	14.116749	-0.006973	C	-0.624584	12.893655	0.140712
C	0.737520	13.008845	0.568162	C	0.979539	10.764275	0.735711	C	1.867953	9.713177	1.036364
C	1.607022	8.424190	0.641080	C	0.463383	8.186138	-0.126720	C	-0.443475	9.196941	-0.370281
C	-0.298104	10.505539	0.135922	C	-1.258017	11.621525	0.039876	C	-2.731544	11.623976	0.034939
C	-3.695963	10.511224	0.124602	C	-3.552372	9.202174	-0.380917	H	-2.756233	8.978518	-1.056555
H	-4.292631	7.215942	-0.574994	H	-6.313436	7.639801	0.832008	H	-6.793277	9.999712	1.507188
H	-5.139342	14.021384	0.633321	H	-3.231725	15.043776	-0.027437	H	-0.745817	15.039620	-0.019085
H	1.154107	14.010512	0.654124	H	2.788340	9.982687	1.538311	H	2.303910	7.624603	0.860475
H	0.290556	7.207831	-0.559115	H	-1.236107	8.976697	-1.051116	N	-5.467283	12.038224	0.941001
N	1.473227	12.026216	0.963688								

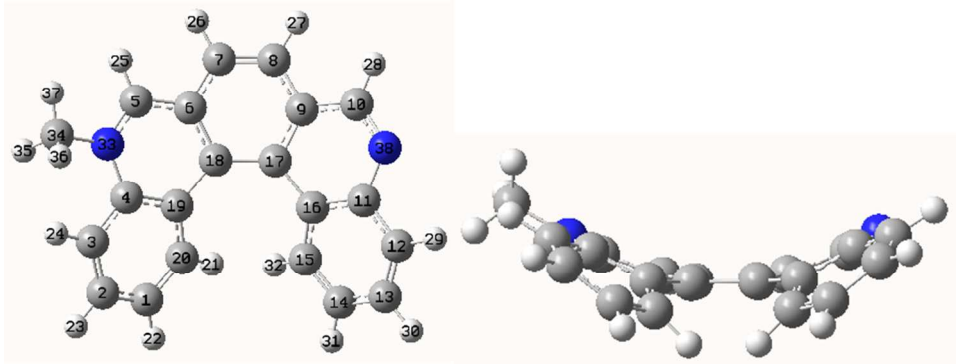
Zero-point correction= 0.262808 (Hartree/Particle)

Thermal correction to Energy= 0.276621
Thermal correction to Enthalpy= 0.277565
Thermal correction to Gibbs Free Energy= 0.222373
Sum of electronic and zero-point Energies= -878.822904
Sum of electronic and thermal Energies= -878.809091
Sum of electronic and thermal Enthalpies= -878.808147
Sum of electronic and thermal Free Energies= -878.863339

Mulliken charges with hydrogens summed into heavy atoms:

1	C	-0.088143	2	C	-0.014694	3	C	-0.323243	4	C	-0.053105
5	C	0.061826	6	C	0.594699	7	C	-0.420797	8	C	-0.420693
9	C	0.594804	10	C	0.061811	11	C	-0.053059	12	C	-0.323196
13	C	-0.014435	14	C	-0.088468	15	C	-0.377377	16	C	0.486992
17	C	0.398649	18	C	0.398746	19	C	0.487317	20	C	-0.377598
33	N	-0.264988	34	N	-0.265045						

Sum of Mulliken charges with hydrogens summed into heavy atoms = 0.00000



N-Methyl-5,10-diaza[5]helicene racemization transition state B3LYP/6-311+G(2dp)

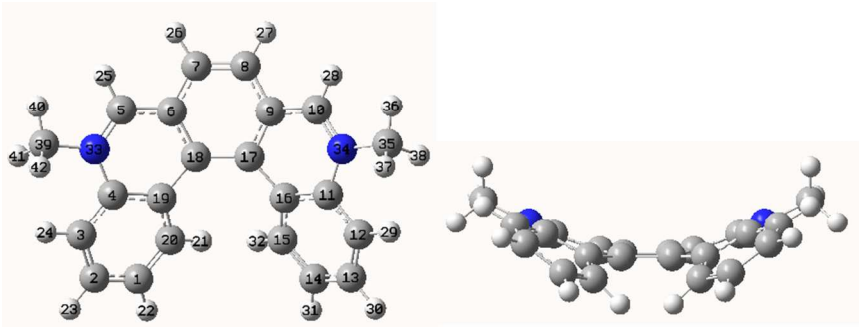
C	-3.851118	2.764565	3.387256	C	-4.966234	2.961137	4.200810	C	-5.253940	4.233322	4.640407
C	-4.398448	5.301377	4.332463	C	-4.109305	7.618324	4.161855	C	-2.808332	7.486141	3.662258
C	-2.121856	8.708762	3.449448	C	-0.770326	8.688433	3.418960	C	-0.086141	7.464592	3.600896
C	1.273922	7.580818	4.031636	C	1.485095	5.330295	4.269896	C	2.362392	4.284960	4.617703
C	2.113512	2.992636	4.223706	C	1.005613	2.750276	3.407271	C	0.101752	3.755369	3.119845
C	0.226997	5.062314	3.630831	C	-0.721182	6.185727	3.524177	C	-2.181848	6.201606	3.565715
C	-3.141176	5.093231	3.679685	C	-2.979172	3.803112	3.141020	H	-2.188503	3.633641	2.444941

H	-3.671152	1.799091	2.932140	H	-5.634551	2.142671	4.434426	H	-6.165323	4.407290	5.191411
H	-4.534139	8.604392	4.291585	H	-2.678174	9.637111	3.417047	H	-0.195784	9.604373	3.358496
H	1.709853	8.574966	4.088760	H	3.266704	4.559658	5.144765	H	2.801088	2.194774	4.473389
H	0.861624	1.771906	2.965576	H	-0.645293	3.527617	2.388335	N	-4.830726	6.603209	4.590578
C	-6.121199	6.860614	5.255936	H	-6.936252	6.446096	4.664783	H	-6.117880	6.413490	6.248651
H	-6.252214	7.934569	5.349291	N	1.976486	6.592872	4.474193				

Zero-point correction= 0.304450 (Hartree/Particle)
Thermal correction to Energy= 0.319903
Thermal correction to Enthalpy= 0.320847
Thermal correction to Gibbs Free Energy= 0.262445
Sum of electronic and zero-point Energies= -918.484090
Sum of electronic and thermal Energies= -918.468637
Sum of electronic and thermal Enthalpies= -918.467693
Sum of electronic and thermal Free Energies= -918.526094

Mulliken charges with hydrogens summed into heavy atoms:

1	C	-0.087265	2	C	-0.191806	3	C	-0.456976	4	C	0.317009
5	C	0.102598	6	C	0.418904	7	C	-0.380316	8	C	-0.384505
9	C	0.653759	10	C	0.146325	11	C	-0.106302	12	C	-0.316441
13	C	0.009667	14	C	-0.032244	15	C	-0.360753	16	C	0.526242
17	C	0.379030	18	C	0.443916	19	C	0.565172	20	C	-0.428672
33	N	0.172901	34	C	0.226834	38	N	-0.217077			



N, N'-Dimethyl-5,10-diaza[5]helicene transition state for racemization B3LYP/6-311+G(2d,p)

C	-2.423143	-2.743130	-0.489194	C	-3.532099	-2.542871	0.333960	C	-3.816418	-1.267635	0.764799

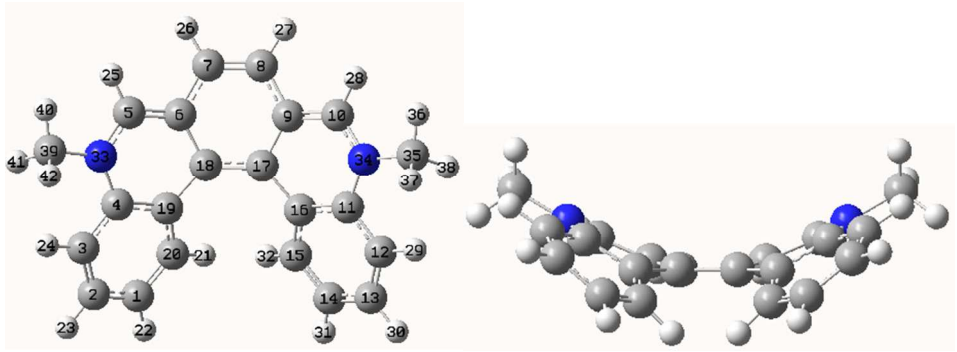
C	-2.958465	-0.204017	0.447484	C	-2.682305	2.111516	0.251721	C	-1.352242	1.973624	-0.200836
C	-0.669112	3.199674	-0.397686	C	0.682632	3.197419	-0.393939	C	1.360557	1.969100	-0.193263
C	2.688479	2.102569	0.266862	C	2.955746	-0.213850	0.464335	C	3.808314	-1.280293	0.786617
C	3.522183	-2.554616	0.354277	C	2.417284	-2.751247	-0.475183	C	1.541109	-1.716899	-0.729147
C	1.693084	-0.427173	-0.186650	C	0.738328	0.687748	-0.283898	C	-0.733808	0.690198	-0.288020
C	-1.692804	-0.421532	-0.196252	C	-1.542049	-1.711718	-0.737998	H	-0.771377	-1.891723	-1.454730
H	-2.258769	-3.706959	-0.953899	H	-4.201768	-3.359055	0.571672	H	-4.729933	-1.087612	1.310188
H	-3.115040	3.097694	0.350193	H	-1.229968	4.124037	-0.452236	H	1.246841	4.119912	-0.445410
H	3.123952	3.087297	0.367717	H	4.719325	-1.103259	1.337159	H	4.187743	-3.373013	0.595891
H	2.252334	-3.714572	-0.940728	H	0.773978	-1.894392	-1.450299	N	-3.402087	1.100078	0.670743
N	3.402431	1.088758	0.690100	C	4.720142	1.347831	1.318880	H	4.865226	2.421939	1.381243
H	4.731854	0.923139	2.320975	H	5.509147	0.906932	0.712578	C	-4.722541	1.363599	1.291874
H	-4.864458	2.438193	1.353148	H	-5.509476	0.925151	0.681123	H	-4.741451	0.939199	2.293988

Zero-point correction= 0.345918 (Hartree/Particle)
Thermal correction to Energy= 0.363000
Thermal correction to Enthalpy= 0.363944
Thermal correction to Gibbs Free Energy= 0.302285
Sum of electronic and zero-point Energies= -958.048199
Sum of electronic and thermal Energies= -958.031117
Sum of electronic and thermal Enthalpies= -958.030173
Sum of electronic and thermal Free Energies= -958.091833

Mulliken charges with hydrogens summed into heavy atoms:

1 C	-0.046282	2 C	-0.143565	3 C	-0.470291	4 C	0.276799	5 C	0.185277	6 C	0.512467
7 C	-0.376939	8 C	-0.376790	9 C	0.512334	10 C	0.185077	11 C	0.276630	12 C	-0.470038
13 C	-0.143595	14 C	-0.046392	15 C	-0.417307	16 C	0.595234	17 C	0.423915	18 C	0.424066
19 C	0.595367	20 C	-0.417491	33 N	0.190307	34 N	0.190313	35 C	0.270466	39 C	0.270439

Sum of Mulliken charges with hydrogens summed into heavy atoms = 2.00000



N, N'-Dimethyl-5,10-diaza[5]helicene radical cation racemization transition state UB3LYP/6-311+G(2d,p)

C	-2.427002	-2.727471	-0.567755	C	-3.506865	-2.535208	0.286722	C	-3.763340	-1.267569	0.768982
C	-2.910056	-0.199467	0.459403	C	-2.619124	2.130666	0.244214	C	-1.351951	1.990757	-0.287144
C	-0.651754	3.192680	-0.627012	C	0.693353	3.186658	-0.615718	C	1.376937	1.978576	-0.264118
C	2.636223	2.107183	0.288406	C	2.902509	-0.225442	0.508538	C	3.740849	-1.301105	0.832479
C	3.481145	-2.566481	0.346008	C	2.414217	-2.749149	-0.526645	C	1.551332	-1.700711	-0.790139
C	1.681193	-0.431165	-0.205756	C	0.719490	0.689788	-0.324901	C	-0.705193	0.696146	-0.336970
C	-1.678727	-0.416151	-0.234190	C	-1.550345	-1.686858	-0.816380	H	-0.786255	-1.849628	-1.546978
H	-2.273074	-3.683264	-1.051778	H	-4.179084	-3.349596	0.524325	H	-4.655079	-1.096885	1.352861
H	-3.062566	3.110954	0.347479	H	-1.211972	4.105633	-0.787628	H	1.264321	4.094539	-0.766911
H	3.086761	3.083437	0.398941	H	4.624221	-1.138209	1.431139	H	4.141902	-3.386845	0.594940
H	2.259990	-3.703565	-1.013284	H	0.798492	-1.856610	-1.533813	N	-3.320356	1.102127	0.748489
N	3.319570	1.072469	0.804426	C	4.569800	1.322095	1.527787	H	4.690701	2.394834	1.649829
H	4.532361	0.859962	2.514076	H	5.422101	0.927084	0.973504	C	-4.580127	1.362958	1.451053
H	-4.692861	2.436681	1.572272	H	-5.426742	0.976654	0.882101	H	-4.563614	0.899543	2.437303

Zero-point correction= 0.343795 (Hartree/Particle)
Thermal correction to Energy= 0.361149
Thermal correction to Enthalpy= 0.362093
Thermal correction to Gibbs Free Energy= 0.299385
Sum of electronic and zero-point Energies= -958.371762
Sum of electronic and thermal Energies= -958.354408
Sum of electronic and thermal Enthalpies= -958.353464
Sum of electronic and thermal Free Energies= -958.416172

Mulliken charges with hydrogens summed into heavy atoms:

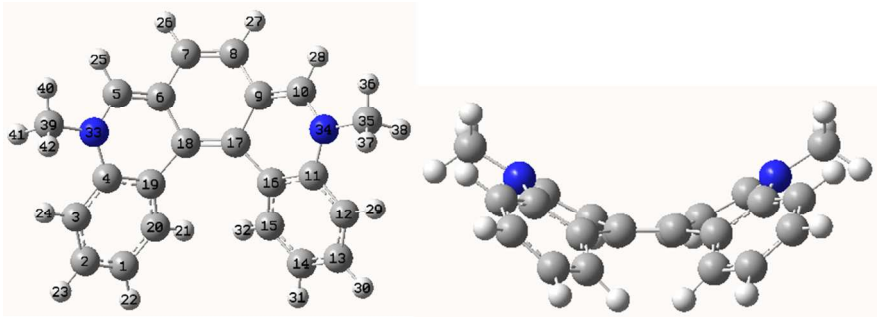
1 C -0.132027	2 C -0.218695	3 C -0.481569	4 C 0.378149	5 C 0.121270	6 C 0.497886
7 C -0.468698	8 C -0.468762	9 C 0.498470	10 C 0.121554	11 C 0.377894	12 C -0.481807
13 C -0.218616	14 C -0.132053	15 C -0.415466	16 C 0.573444	17 C 0.335488	18 C 0.334874
19 C 0.573125	20 C -0.415329	33 N 0.120958	34 N 0.120808	35 C 0.189565	39 C 0.189536

Sum of Mulliken charges with hydrogens summed into heavy atoms = 1.00000

Mulliken atomic spin densities:

1 C 0.051015	2 C -0.014159	3 C 0.054504	4 C -0.038902	5 C 0.134053	6 C 0.032514
7 C 0.037757	8 C 0.037859	9 C 0.032250	10 C 0.134163	11 C -0.038847	12 C 0.054523
13 C -0.014151	14 C 0.051011	15 C -0.006725	16 C 0.043692	17 C 0.069862	18 C 0.070031
19 C 0.043727	20 C -0.006733	21 H 0.001210	22 H -0.003351	23 H 0.000597	24 H -0.002664
25 H -0.009023	26 H -0.000662	27 H -0.000662	28 H -0.009024	29 H -0.002665	30 H 0.000597
31 H -0.003352	32 H 0.001208	33 N 0.150588	34 N 0.150585	35 C -0.016803	36 H 0.000248
37 H 0.007061	38 H 0.009080	39 C -0.016799	40 H 0.000250	41 H 0.009083	42 H 0.007054

Sum of Mulliken atomic spin densities = 1.00000



Neutral N, N'-Dimethyl-5,10-diaza[5]helicene racemization transition state B3LYP/6-311+G(2d,p)

C	-2.471529	-2.709553	-0.637453	C	-3.521317	-2.519254	0.247938	C	-3.732160	-1.263690	0.796985
C	-2.864917	-0.199496	0.512117	C	-2.544384	2.144360	0.280395	C	-1.353796	1.996867	-0.342506
C	-0.647607	3.149329	-0.873655	C	0.691726	3.143428	-0.862842	C	1.379092	1.984763	-0.320653
C	2.560936	2.121596	0.321035	C	2.856897	-0.225047	0.557294	C	3.709936	-1.297021	0.855591
C	3.496429	-2.550615	0.303052	C	2.459093	-2.731389	-0.598889	C	1.584765	-1.681497	-0.852891

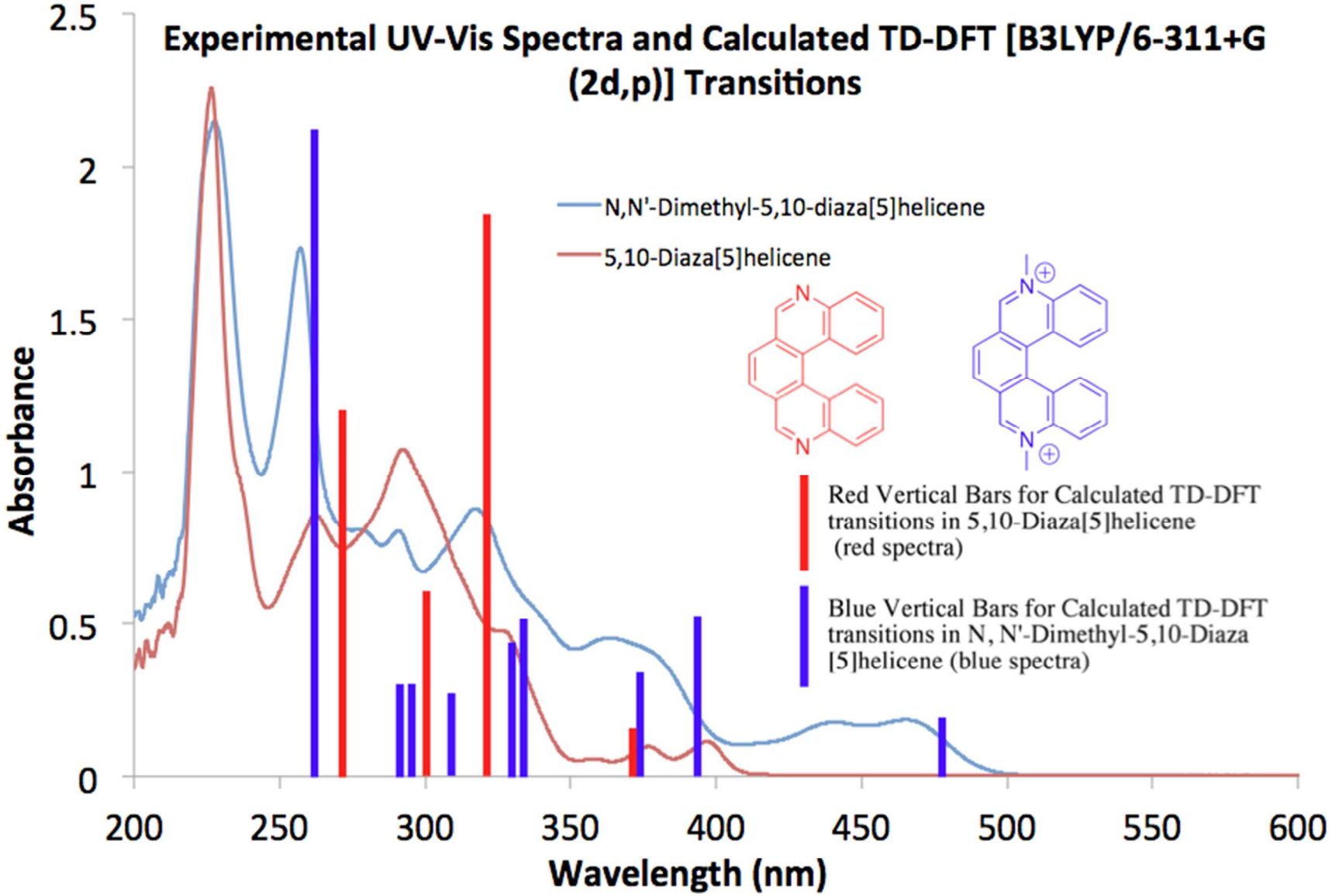
C	1.677178	-0.438034	-0.219994	C	0.698806	0.676904	-0.340243	C	-0.684972	0.683006	-0.351250
C	-1.674983	-0.423228	-0.246421	C	-1.583776	-1.667678	-0.877581	H	-0.819982	-1.819654	-1.615166
H	-2.338692	-3.657210	-1.144325	H	-4.207277	-3.326207	0.476557	H	-4.599092	-1.102024	1.421110
H	-3.023298	3.110425	0.366738	H	-1.210321	4.017318	-1.199043	H	1.267257	4.006439	-1.178958
H	3.046941	3.083372	0.415212	H	4.568437	-1.143158	1.493207	H	4.171397	-3.363735	0.542290
H	2.325795	-3.677767	-1.108024	H	0.831553	-1.826304	-1.602734	N	-3.194432	1.094331	0.902914
N	3.191859	1.065785	0.953353	C	4.406894	1.320606	1.705356	H	4.461220	2.383971	1.929029
H	4.397247	0.777086	2.652253	H	5.305248	1.032297	1.146962	C	-4.418650	1.360158	1.635975
H	-4.466459	2.423859	1.859556	H	-5.310827	1.080668	1.063365	H	-4.428856	0.816034	2.582501

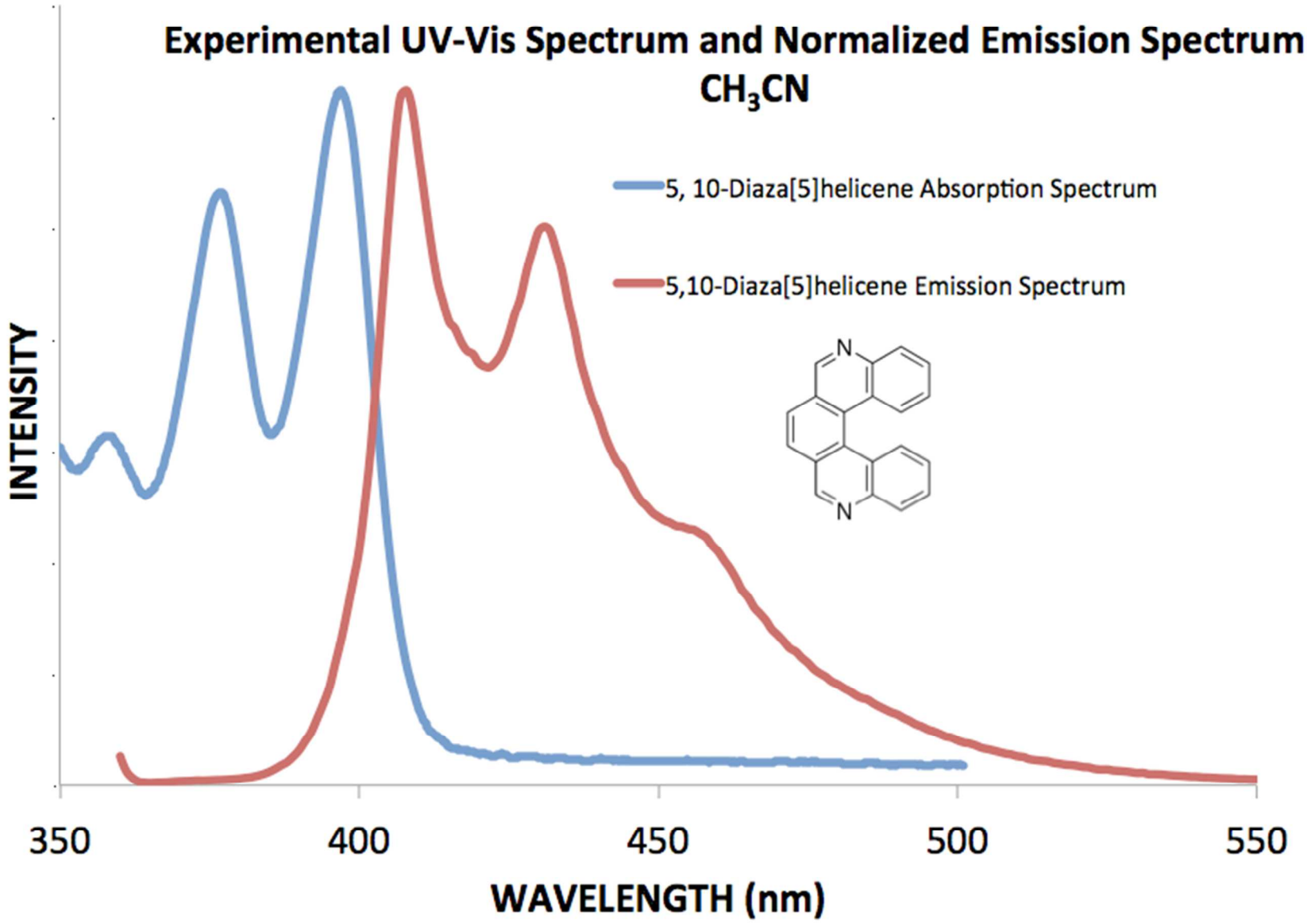
Zero-point correction= 0.340997 (Hartree/Particle)
Thermal correction to Energy= 0.358719
Thermal correction to Enthalpy= 0.359664
Thermal correction to Gibbs Free Energy= 0.296879
Sum of electronic and zero-point Energies= -958.561557
Sum of electronic and thermal Energies= -958.543835
Sum of electronic and thermal Enthalpies= -958.542891
Sum of electronic and thermal Free Energies= -958.605675

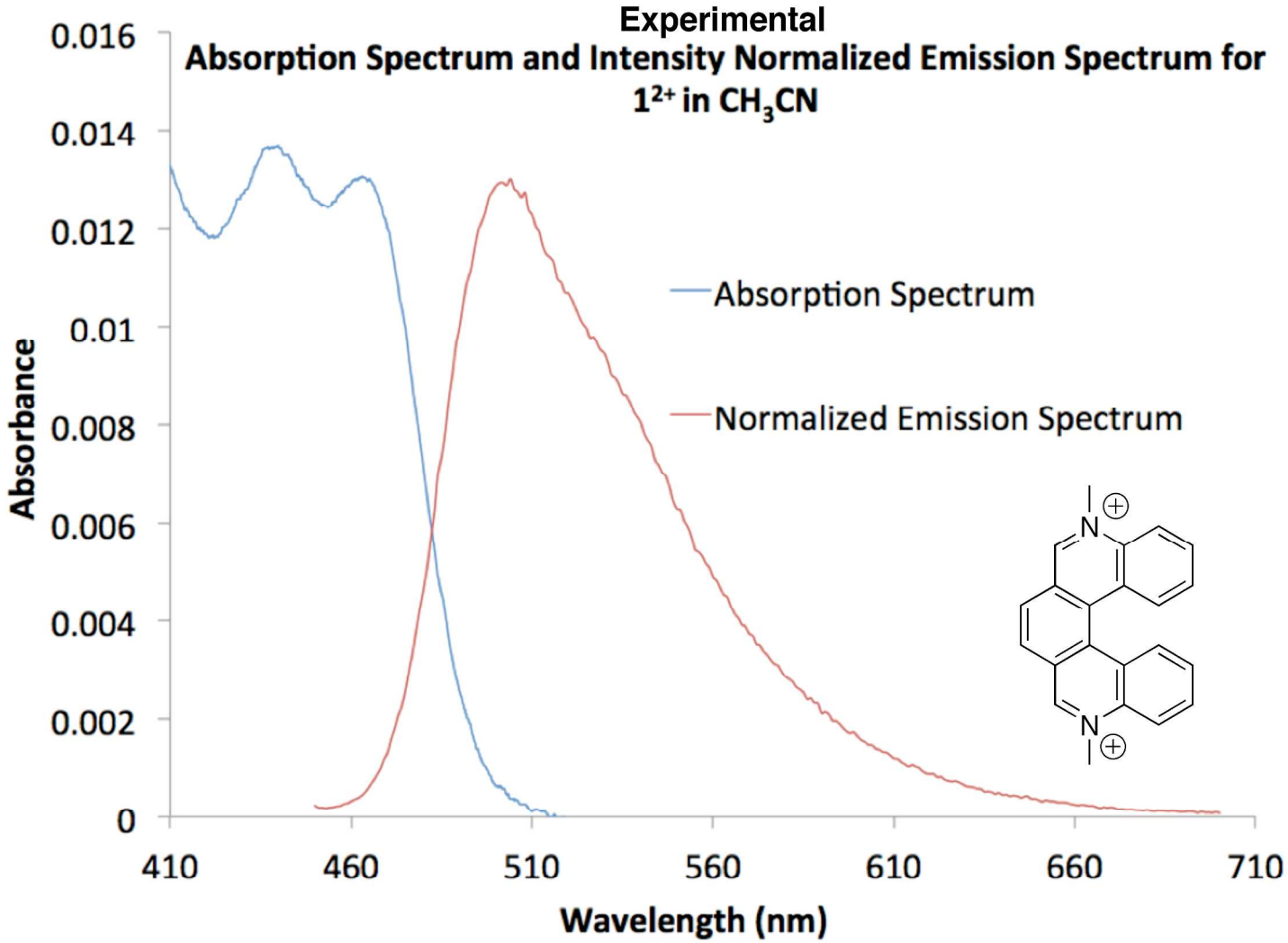
Mulliken charges with hydrogens summed into heavy atoms:

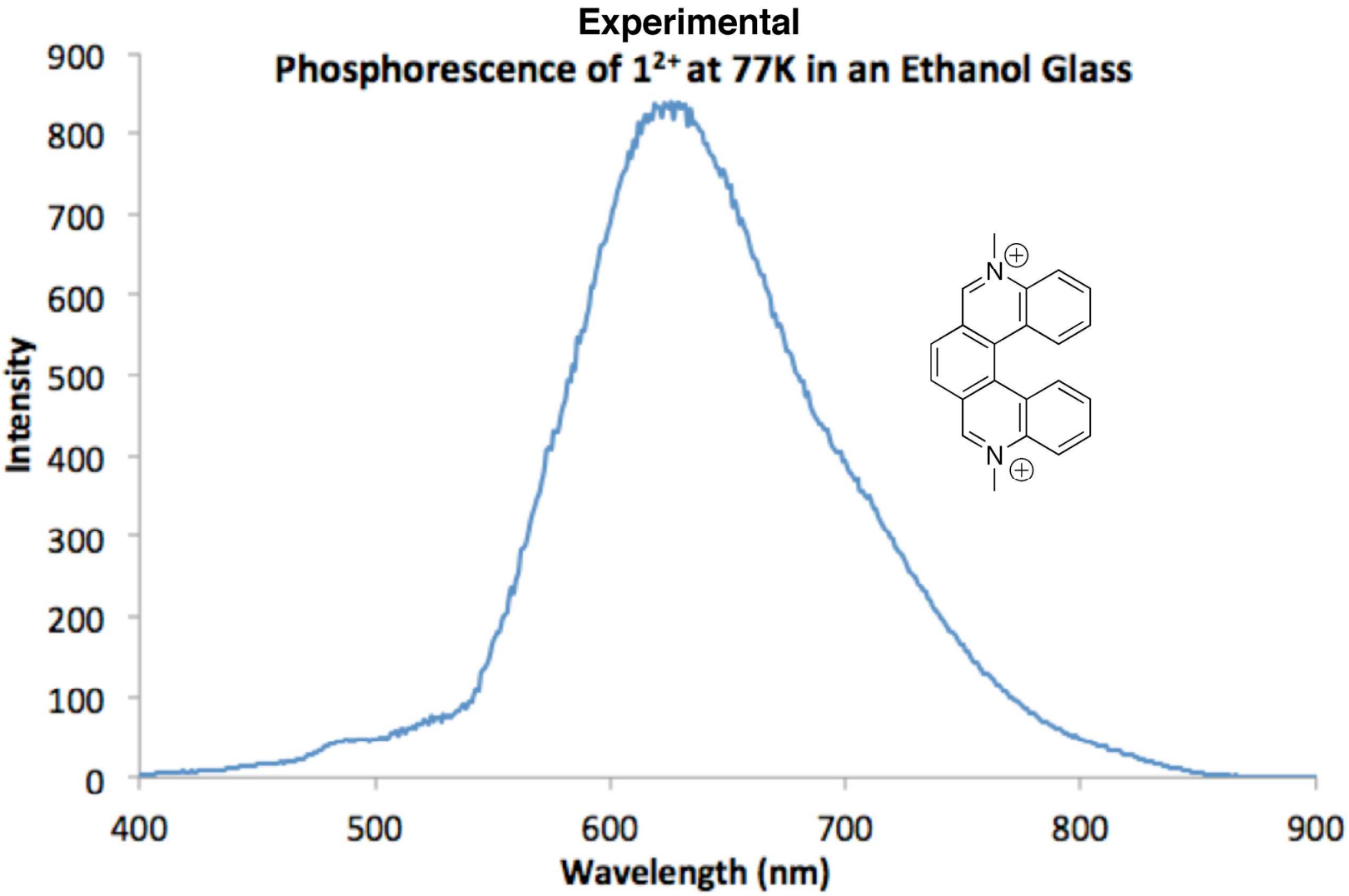
1 C -0.236312	2 C -0.256625	3 C -0.525132	4 C 0.479578	5 C 0.047812	6 C 0.406951
7 C -0.494636	8 C -0.494624	9 C 0.406778	10 C 0.047588	11 C 0.479214	12 C -0.526193
13 C -0.256643	14 C -0.236330	15 C -0.366614	16 C 0.521390	17 C 0.287396	18 C 0.287389
19 C 0.520569	20 C -0.366157	33 N 0.039997	34 N 0.040137	35 C 0.097235	39 C 0.097233

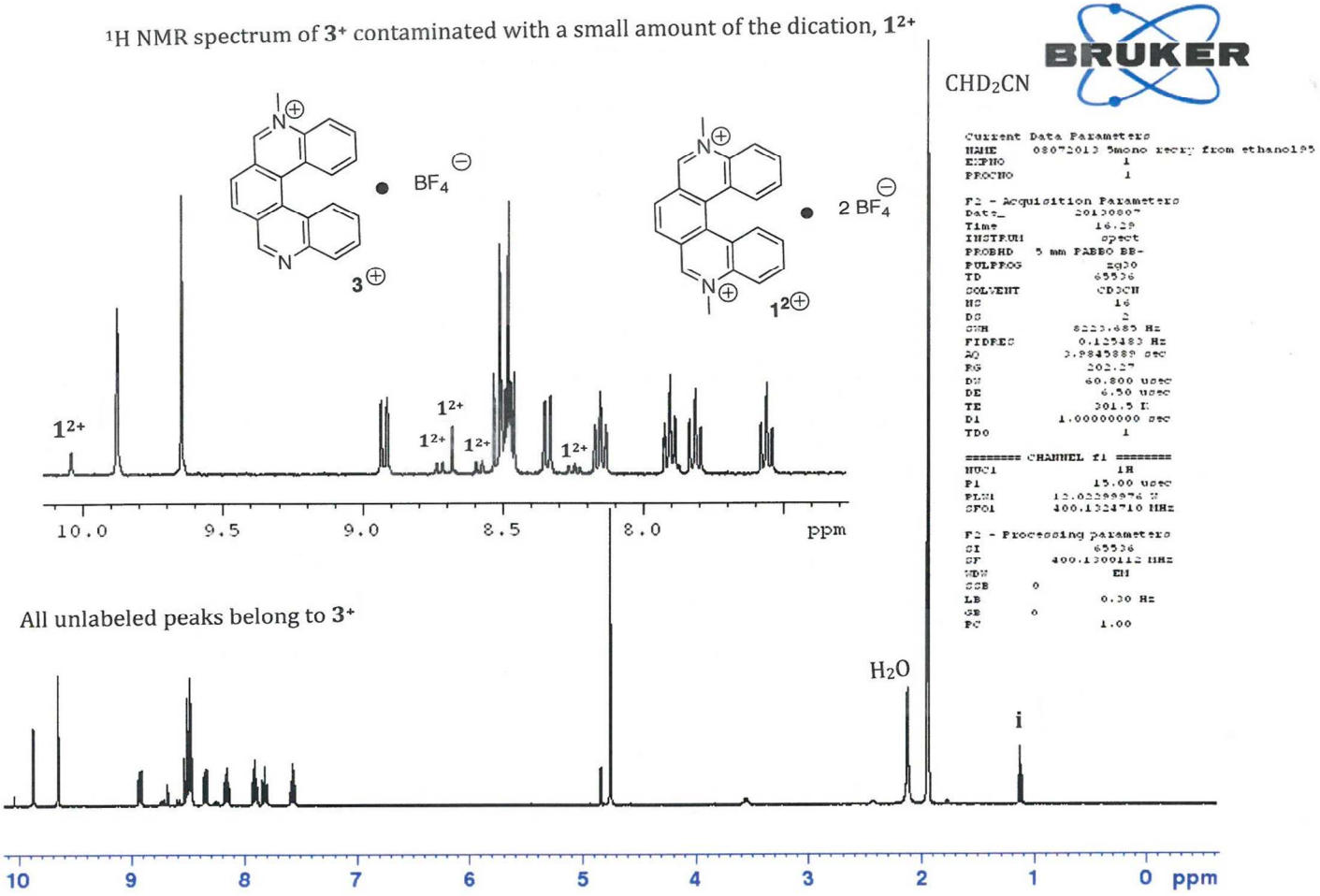
Sum of Mulliken charges with hydrogens summed into heavy atoms = 0.00000


Experimental UV-Vis Spectra and Calculated TD-DFT [B3LYP/6-311+G (2d,p)] Transitions
N,N'-Dimethyl-5,10-diaza[5]helicene
5,10-Diaza[5]helicene
Red Vertical Bars for Calculated TD-DFT transitions in 5,10-Diaza[5]helicene (red spectra)
Blue Vertical Bars for Calculated TD-DFT transitions in N, N'-Dimethyl-5,10-Diaza [5]helicene (blue spectra)
Absorbance
Wavelength (nm)
2.5
2
1.5
1
0.5
0
200
250
300
350
400
450
500
550
600

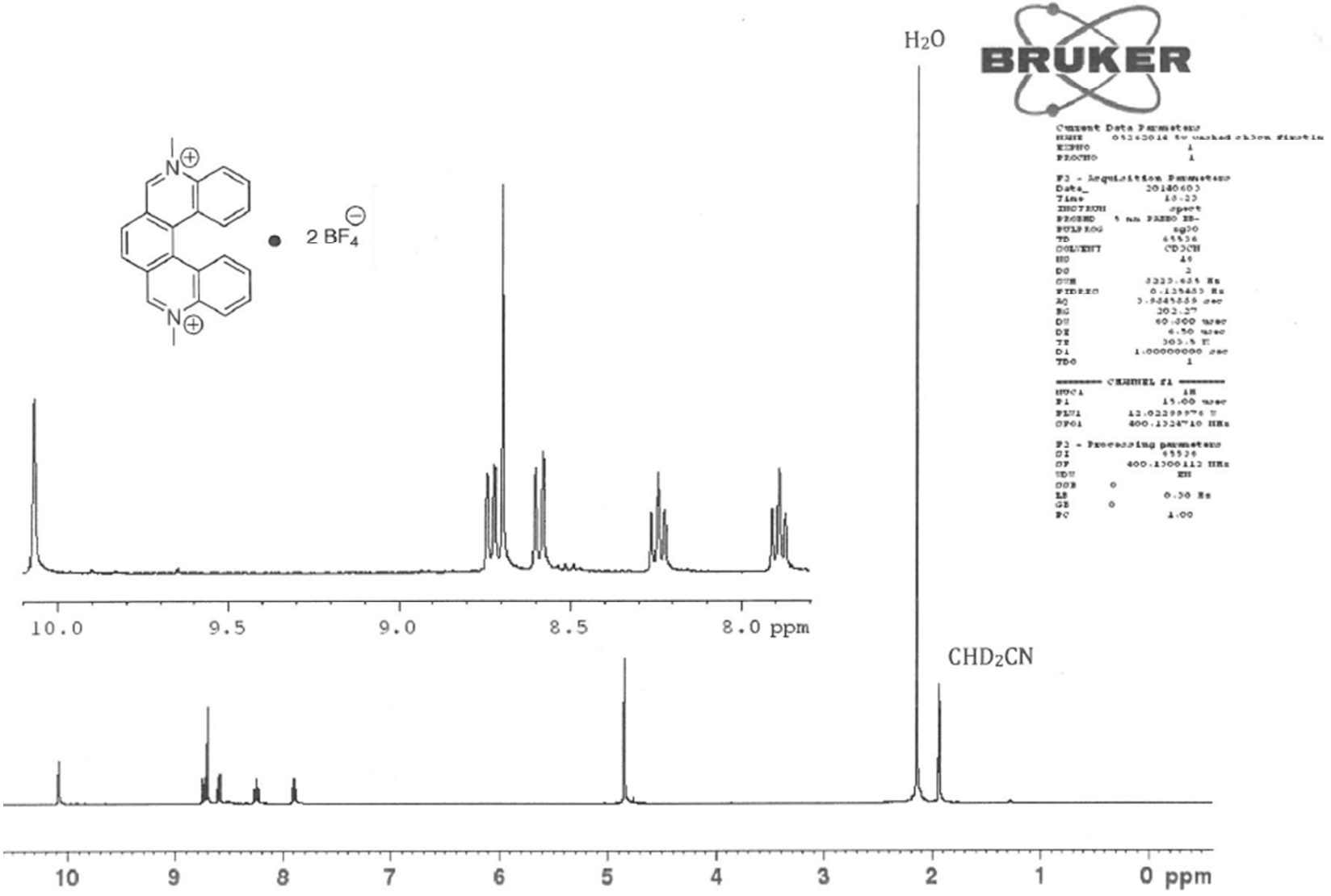

Experimental UV-Vis Spectrum and Normalized Emission Spectrum in CH_3CN
5, 10-Diaza[5]helicene Absorption Spectrum
5,10-Diaza[5]helicene Emission Spectrum
N
N
INTENSITY
350
400
450
500
550
WAVELENGTH (nm)

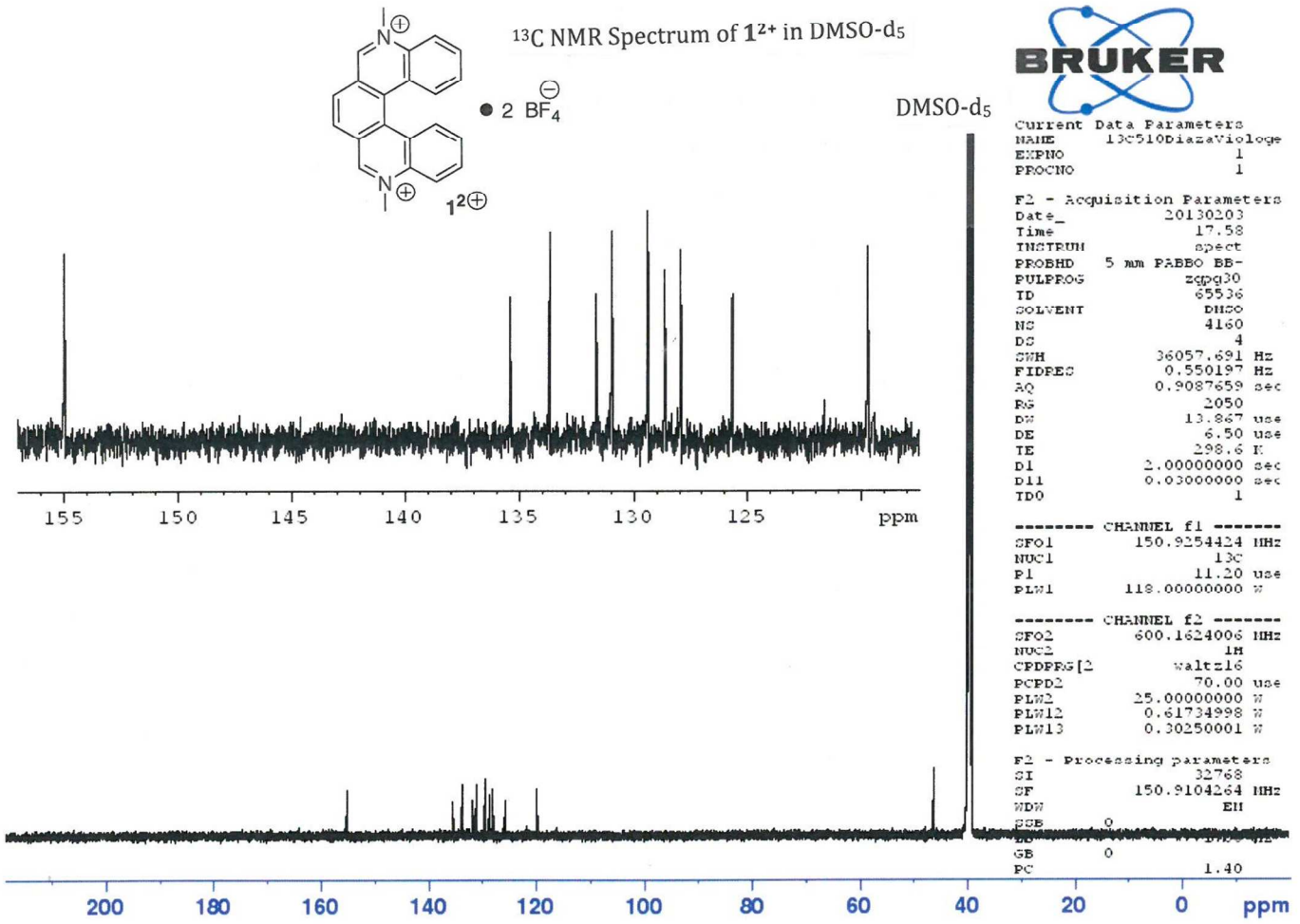

Experimental
Absorption Spectrum and Intensity Normalized Emission Spectrum for
1²⁺ in CH₃CN
Absorbance
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
410
460
510
560
610
660
710
Wavelength (nm)
Absorption Spectrum
Normalized Emission Spectrum
N
N

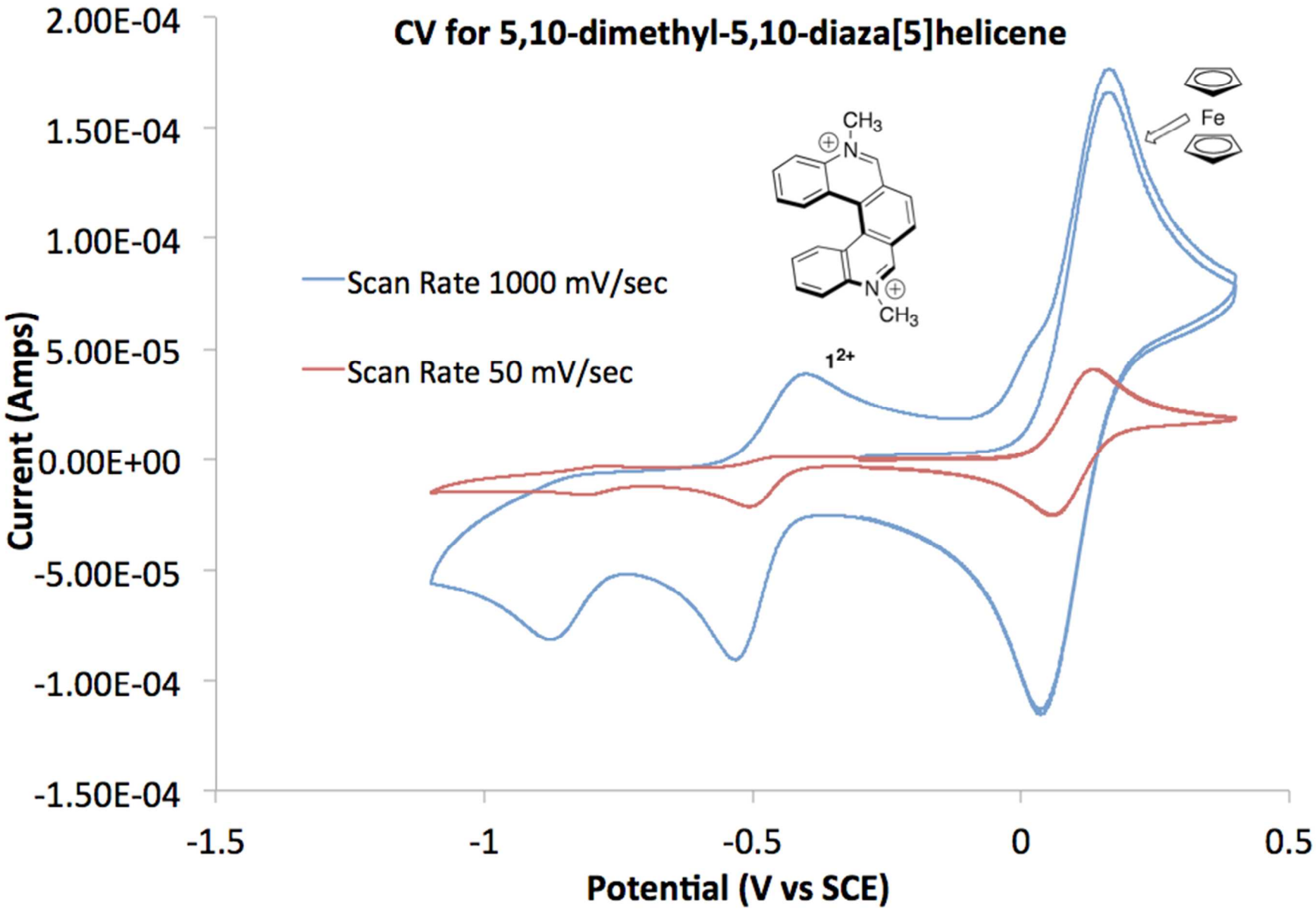

Experimental
Phosphorescence of 1²⁺ at 77K in an Ethanol Glass
Intensity
900
800
700
600
500
400
300
200
100
0
400
500
600
700
800
900
Wavelength (nm)
N
N

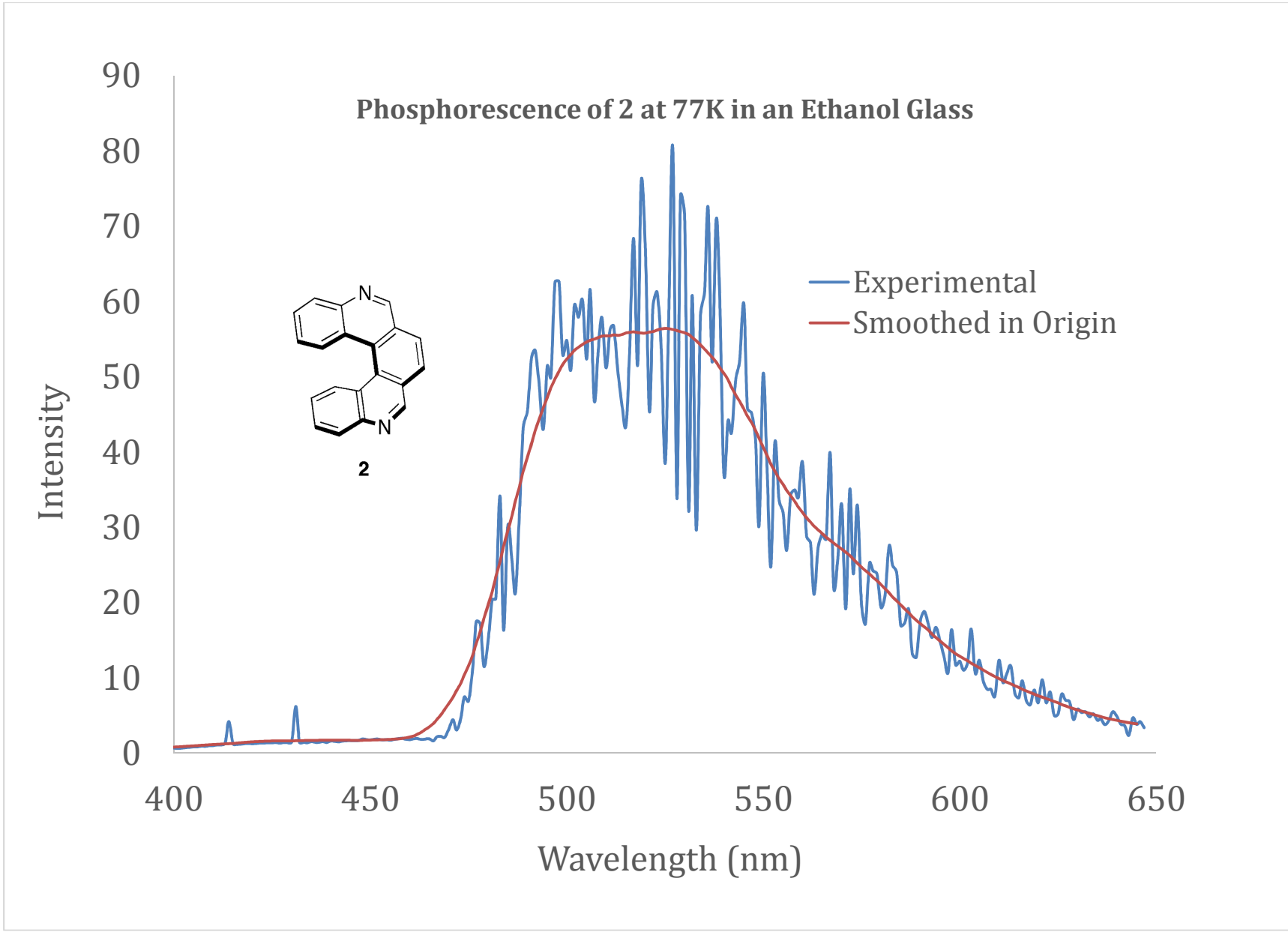

¹H NMR spectrum of 3⁺ contaminated with a small amount of the dication, 1²⁺
CHD₂CN
BRUKER
BF4
2 BF4
3⊕
1²⊕
1²⁺
10.0
9.5
9.0
8.5
8.0
ppm
All unlabeled peaks belong to 3⁺
H2O
i
10
9
8
7
6
5
4
3
2
1
0 ppm

Proton NMR Spectrum for N,N'-Dimethyl-5,10-diaza[5]helicene in acetonitrile




^{13}C NMR Spectrum of 1^{2+} in DMSO-d$_5$
2 BF_4^-
1^{2+}
DMSO-d$_5$
BRUKER
Current Data Parameters
NAME 13C510DiazaViologe
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130203
Time 17.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 4160
DS 4
SWH 36057.691 Hz
FIDRES 0.550197 Hz
AQ 0.9087659 sec
RG 2050
DW 13.867 use
DE 6.50 use
TE 298.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
SFO1 150.9254424 MHz
NUC1 13C
P1 11.20 use
PLW1 118.00000000 W
CHANNEL f2
SFO2 600.1624006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 use
PLW2 25.00000000 W
PLW12 0.61734998 W
PLW13 0.30250001 W
F2 - Processing parameters
SI 32768
SF 150.9104264 MHz
WDW EM
SSB 0
GB 0
PC 1.40
155 150 145 140 135 130 125 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm


CV for 5,10-dimethyl-5,10-diaza[5]helicene
2.00E-04
1.50E-04
1.00E-04
5.00E-05
0.00E+00
-5.00E-05
-1.00E-04
-1.50E-04
Current (Amps)
-1.5
-1
-0.5
0
0.5
Potential (V vs SCE)
Scan Rate 1000 mV/sec
Scan Rate 50 mV/sec
CH3
N
N
CH3
1 2+
Fe


Phosphorescence of 2 at 77K in an Ethanol Glass
Intensity
Wavelength (nm)
Experimental
Smoothed in Origin
2
90
80
70
60
50
40
30
20
10
0
400
450
500
550
600
650