Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

A Simple Route to Phosphamethine Cyanines from *S,N*-Heterocyclic Carbenes

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Windsor, Ontario, Canada N9B 3P4

Computational Data:

Calculations were performed with the Gaussian 09 suite of programs[1] using Compute Canada's Shared Hierarchical Academic Research Computing Network (SharcNet). Model complexes were fully optimized with no symmetry constraints using the PBE1PBE density functional theory (DFT) method[2–4] in conjunction with the TZVP basis sets for all atoms.[5,6] Geometry optimizations were started using models in which the relevant phosphorus, nitrogen and carbon atoms were placed a the positions found experimentally using X-ray crystallography and the hydrogen atoms were placed in geometrically appropriate positions using Gaussview.[7] Frequency calculations were also performed at the same level of theory in order to confirm that the optimized structures were minima on the potential energy hypersurface and to determine thermochemical information. Natural bond orbital (NBO) analyses[8] to determine orbital contributions, Wiberg Bond Indicies and orbital energies were obtained using the routine included in the Gaussian distributions.[9] Atoms In Molecules (AIM) analysis was done using AIM2000.[10]

Olefin Dimer $(EtBTZ)_2$

1\1\GINC-ORC136\FOpt\RPBE1PBE\TZVP\C18H18N2S2\BINDERJ\18-Jul-2015\0\\#

PBE1PBE/TZVP scf=tight opt freq pop=(full,nboread) test\\Optimization

, frequency test and NBO analysis for (EtBTZ)2\\0,1\C,-1.8488680665,-1

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Zero-point correction= 0.321367 (Hartree/Particle)

Thermal correction to Energy= 0.341356

Thermal correction to Enthalpy= 0.342301

Thermal correction to Gibbs Free Energy= 0.272219

Sum of electronic and zero-point Energies= -1601.334867

Sum of electronic and thermal Energies= -1601.314878

Sum of electronic and thermal Enthalpies= -1601.313934

Sum of electronic and thermal Free Energies= -1601.384015

Phosphamethine Cyanine Model $[^{Et}TZ_2P]^+$

1\1\GINC-ORC302\FOpt\RPBE1PBE\TZVP\C14H22N2P1S2(1+)\BINDERJ\20-Jul-201

5\0\\# PBE1PBE/TZVP opt freq scf=tight pop=(full,nboread) test\\Optimi
zation, frequency and NBO for good_EtTZ2P\\1,1\P,5.7386777572,2.300467
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690485\S,5.8206115467,-0.5119882026,4.4835652508\C,5.7315734654,1.2068
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,8.0614036578\H,6.3395175858,2.0173687464,8.3026468215\H,5.6963494495,
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5587193,5.0268124622\C,5.7801268119,-1.7420684364,6.9957606611\H,4.885
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76,-0.0000007,-0.1753232,0.0000007\PG=C02 [C2(P1),X(C14H22N2S2)]\\@

Zero-point correction= 0.342167 (Hartree/Particle)
Thermal correction to Energy= 0.364873
Thermal correction to Enthalpy= 0.365817
Thermal correction to Gibbs Free Energy= 0.290035
Sum of electronic and zero-point Energies= -1792.467310
Sum of electronic and thermal Energies= -1792.444604
Sum of electronic and thermal Enthalpies= -1792.443660
Sum of electronic and thermal Free Energies= -1792.519441

NBO Results

1. (1.96908) BD (1) P 1 - C 3
(33.99%) 0.5830* P 1 s(17.17%)p 4.79(82.21%)d 0.04(0.62%)
0.0000 0.0000 0.4102 0.0587 -0.0008
0.0000 0.0437 -0.0014 0.0003 0.0000
0.7014 -0.0353 -0.0043 -0.0001 -0.5717
0.0088 -0.0030 0.0036 -0.0041 -0.0694
-0.0323 0.0169
(66.01%) 0.8125* C 3 s(39.46%)p 1.53(60.50%)d 0.00(0.04%)
0.0000 0.6281 0.0088 -0.0054 0.0000
-0.0369 -0.0007 0.0004 -0.6559 -0.0166
0.0105 0.4158 0.0143 -0.0067 0.0011

-0.0007 -0.0162 -0.0109 0.0047

2. (1.74718) BD (2) P   1 - C   3

(62.51%)   0.7906* P   1 s(0.00%)p 1.00(99.69%)d 0.00(0.31%)

0.0000 -0.0001 0.0001 -0.0003 0.0000

0.0009 0.9965 0.0052 0.0029 -0.0001

-0.0625 0.0020 0.0019 0.0000 -0.0004

0.0000 0.0003 0.0142 -0.0533 0.0025

0.0024 0.0007

(37.49%)   0.6123* C   3 s(0.00%)p 1.00(99.97%)d 0.00(0.03%)

0.0000 -0.0029 -0.0020 -0.0001 0.0001

0.9954 0.0074 0.0206 -0.0835 0.0003

0.0001 -0.0392 0.0004 0.0001 -0.0127

0.0098 -0.0012 -0.0017 -0.0003

3. (1.96909) BD (1) P   1 - C 23

(33.99%)   0.5830* P   1 s(17.17%)p 4.79(82.21%)d 0.04(0.62%)

0.0000 0.0000 0.4102 0.0587 -0.0008

0.0000 -0.0443 0.0014 -0.0003 0.0000

-0.7014 0.0353 0.0043 -0.0001 -0.5717

0.0088 -0.0030 0.0037 0.0042 0.0694

-0.0323 0.0169

(66.01%)   0.8125* C 23 s(39.46%)p 1.53(60.50%)d 0.00(0.04%)

0.0000 0.6281 0.0088 -0.0054 0.0000

0.0423 0.0006 -0.0003 0.6554 0.0166

-0.0105 0.4160 0.0143 -0.0067 0.0010

0.0008 0.0161 -0.0109 0.0048

78. (1.92530) LP (1) P   1   s(66.23%)p 0.51(33.74%)d 0.00(0.03%)

0.0000 -0.0006 0.8135 -0.0231 0.0003

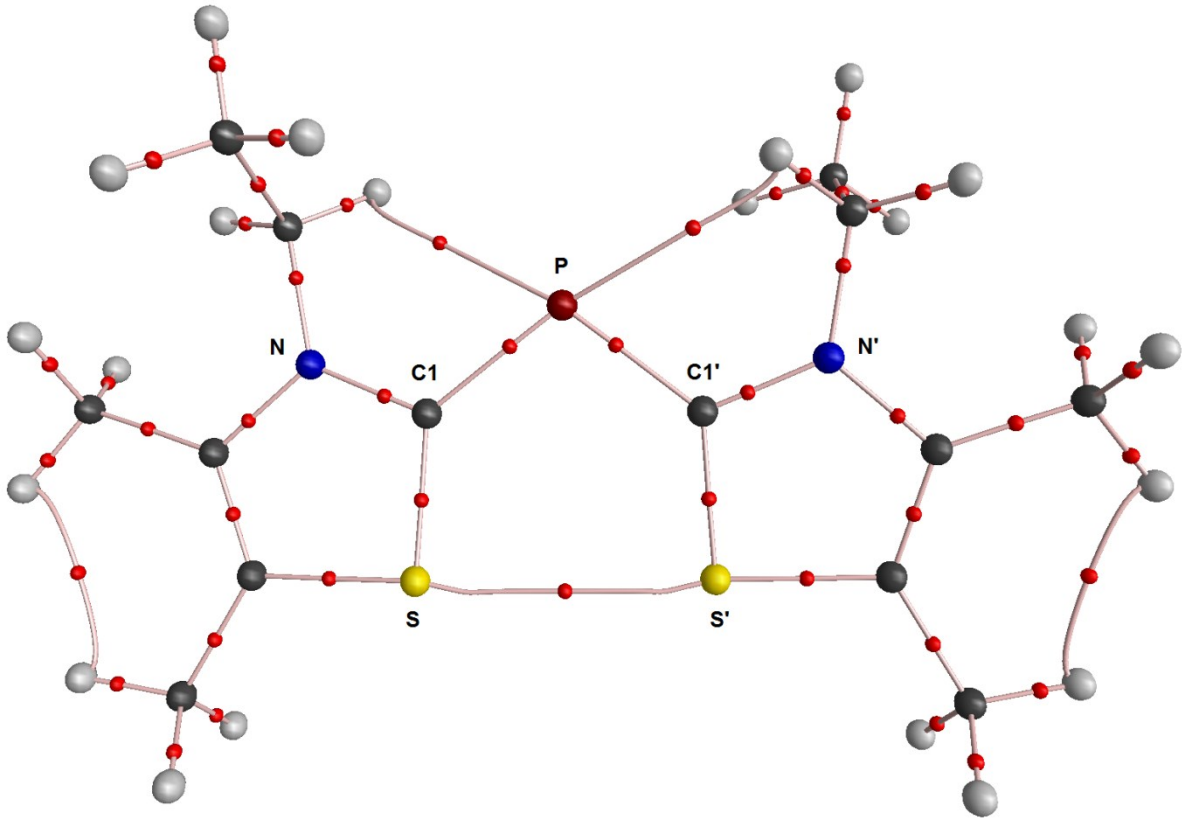
0.0000 0.0001 0.0000 0.0000 0.0000

0.0000 0.0000 0.0000 0.0003 0.5808

0.0111 -0.0020 0.0001 0.0000 0.0000

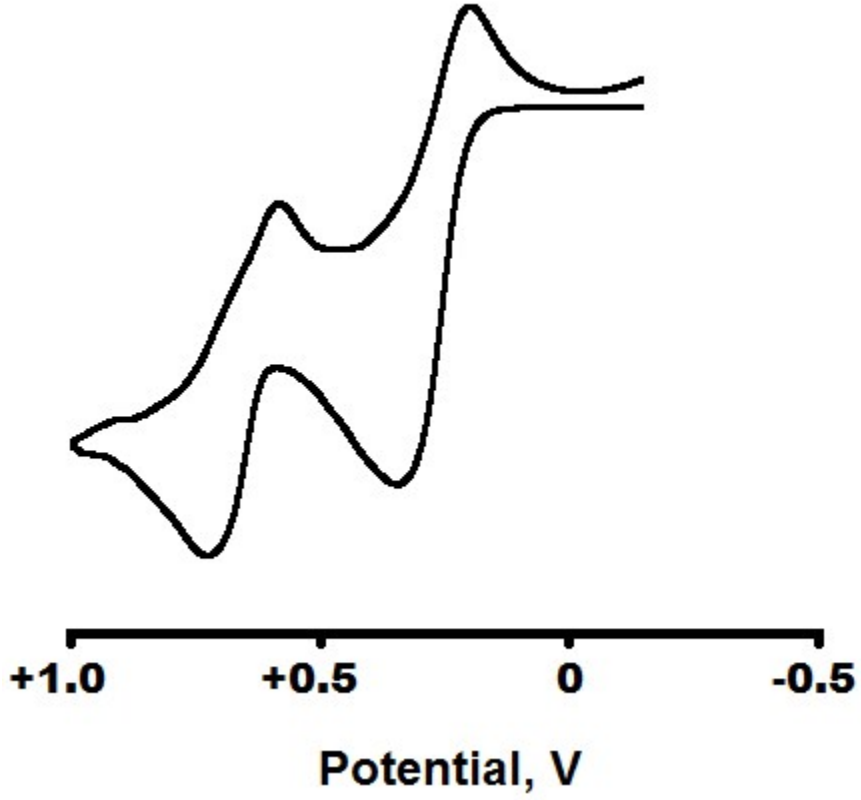
0.0033 -0.0164

AIM Results



Critical Point	ρ	L	KEG	KEK	VIR
P-C1	+0.1481	-0.0567	+0.1738	+0.1170	+0.2908
P-C1`	+0.1481	-0.0567	+0.1738	+0.1170	+0.2908
C1-N	+0.3236	+0.2167	+0.2652	+0.4819	+0.7471
C1`-N1`	+0.3236	+0.2167	+0.2652	+0.4819	+0.7471
C1-S	+0.2092	+0.1092	+0.0765	+0.1857	+0.2623
C1`-S`	+0.2092	+0.1092	+0.0765	+0.1857	+0.2623
S-S`	+0.0156	-0.0119	+0.0109	-0.0011	+0.0098

Cyclic Voltammetry of [$^{Et}TZ_2P$][I]



Cyclic voltammetry was performed in dry MeCN solutions using a [NBu_4][PF_6] (0.1 M) electrolyte with analyte concentration of about 0.01 M. A glassy carbon electrode, a platinum wire, and an Ag/AgCl electrode were used as the working, auxiliary, and reference electrodes, respectively. The experiments were run with a scan rate of 100mV/s and a sensitivity of 100 μA/V. The potential is scaled with respect to the Ag/AgCl reference electrode in the above voltammogram.

References:

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