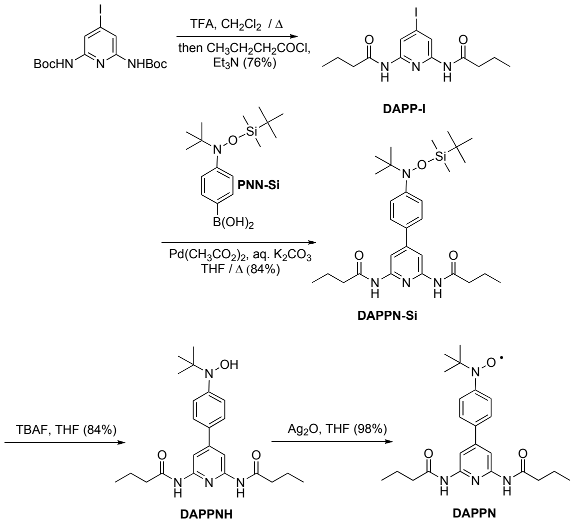
Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information for

Molecular recognition in a heteromolecular radical pair system with complementary multipoint hydrogen bonding

Hidenori Murata, Paul M. Lahti,* Safo Aboaku

Experimental Procedures.



2,6-Di-tert-butoxycarbonylamino-4-iodo-pyridine was prepared according to the procedure in Pauvert, M.; Laine, P.; Jonas, M.; Wiest, O., *J. Org. Chem.,* **2004**, *69*, 543-548.

2,6-Di-n-butyrylamino-4-iodo-pyridine (DAPP-I). Trifluoroacetic acid (5.3 mL) was added to a solution of 2,6-di-*tert*-butoxycarbonylamino-4-iodopyridine (1.50 g, 3.45 mmol) in dichloromethane and refluxed for 2 h. The solution was chilled and triethylamine (19 mL) was added followed by *n*-butyryl chloride (1.62 g, 15.2 mmol). The mixture was stirred at room temperature overnight. To the mixture, brine was added and the solution was extracted with dichloromethane. The organic layer was dried with $MgSO_4$, and evaporated to give the crude product. Chromatography on silica gel with ethyl acetate/hexane (5/5) as the eluent yielded **DAPP-I** (0.983 g, 76%) as a white powder. Mp: 117–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ8.30 (s, 2H), 7.84 (brs, 2H), 2.29 (t, 4H, J = 7.5 Hz), 1.68 (m, 4H), 0.93 (t, 6H, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, ppm): δ171.8, 149.6, 118.5, 109.1, 39.6, 18.8, 13.8. IR (KBr pellet, cm^{-1}): 3246 (NH str), 1668 (C=O str). MS (EI): found m/z = 375, calculated for $C_{13}H_{18}IN_3O_2$ m/z = 375.2. Elemental analysis calculated for $C_{13}H_{18}IN_3O_2$: C, 41.61; H, 4.84; N, 11.20. Found: C 43.52, H 5.28, N 10.88.

Tris[4-(N-tert-butyl-N-[tert-butyldimethylsiloxyl]amino)phenyl]boroxin (*PNN-Si).* This compound was prepared according to the procedure in Field, L. M.; Lahti, P. M., *Chem. Mater.,* **2003**, *15*, 2861-2863.

4-(4'-[N-tert-Butyl-N-(tert-butyldimethylsiloxy)amino])-2,6-di-n-butyrylaminopyridine (DAPPN-Si). A flask containing 2,6-di-*n*-butyrylamino-4-iodopyridine (0.500 g, 1.33 mmol) and palladium acetate (14.9 mg, 66.5 μmol) was evacuated and back filled with argon twice. 3.6 mL of deaerated THF was added by syringe and the mixture was stirred for about 5 min. A solution of tris[4-(*N*-*tert*-butyl-*N*-[*tert*-butyldimethylsiloxyl]amino)phenyl]boroxin (0.517 g, 1.60 mmol) in 3.6 mL of deairated THF was added, followed by 2.8 mL of a 1.2 M aqueous solution of potassium carbonate. The reaction mixture was heated to reflux and allowed to stir overnight under argon. The organic layer was then separated and the aqueous layer was extracted with dichloromethane. The organic layers were combined, dried with $MgSO_4$, filtered and concentrated in vacuo. Chromatography on silica gel with ethyl acetate/hexane (3/7) as the eluent yielded **DAPPN-Si** (0.596 g, 84%) as a white powder. Mp: 180 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ8.20 (s, 2H), 7.69 (brs, 2H), 7.69 (s, 2H), 7.57 (d, 2H, J = 8.8 Hz), 7.26 (d, 2H, J = 7.6

Hz), 2.35 (t, 4H, J = 7.5 Hz), 1.74 (m, 4H), 1.08 (s, 9H), 0.98 (t, 6H, J = 7.5 Hz), 0.89 (s, 9H), -0.14 (s, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 171.7, 153.5, 152.6, 150.1, 134.4, 126.5, 125.5, 107.4, 61.3, 39.9, 26.4, 26.3, 18.9, 18.1, 13.9, -4.5. IR (KBr pellet, cm^{-1}): 3410 (NH str), 1655 (C=O str). MS (EI): found m/z = 526, calculated for $C_{29}H_{46}N_4O_3Si$ m/z = 526.3. Elemental analysis calculated for $C_{29}H_{46}N_4O_3Si$: C, 66.12; H, 8.80; N, 10.64. Found: C 65.97, H 8.97, N 10.51.

*4-(4'-[N-tert-Butyl-N-hydroxylamino])-2,6-di-n-butyrylaminopyridine (**DAPPNH**).* A 1.0 M THF solution of TBAF (2.6 mL, 2.6 mmol) was added dropwise to a solution of **DAPPN-Si** (0.596 mg, 1.13 mmol) in dry THF (6.9 mL). The reaction mixture protected from UV was stirred at room temperature for 12 h. The reaction mixture was concentrated in vacuo. Chromatography on silica gel with ethyl acetate/hexane (3/7) as the eluent yielded **DAPPNH** (0.324 g, 70%) as a orange powder. Mp: 162–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.20 (s, 2H), 7.62 (d, 2H, J = 7.6 Hz), 7.55 (brs, 2H), 7.31 (d, 2H, J = 7.6 Hz), 5.66 (brs, 1H), 2.37 (t, 4H, J = 6.6 Hz), 1.76 (m, 4H), 1.15 (s, 9H), 1.01 (t, 6H, J = 7.3 Hz). ^{13}C NMR (methanol-*d*, ppm): δ 156.4, 152.3, 150.4, 140.0, 127.5, 127.3, 122.3, 120.4, 118.9, 114.8, 114.4, 55.4. IR (KBr pellet, cm^{-1}): 3427 (NH str), 3224 (OH str), 1701 (C=O str). MS (EI): found m/z = 412, calculated for $C_{23}H_{32}N_4O_3$ m/z = 412.5. Elemental analysis calculated for $C_{23}H_{32}N_4O_3$: C, 66.96; H, 7.82; N, 13.58. Found: C 67.18, H 7.92, N 12.56.

*4-(4'-[N-tert-Butyl-N-aminoxyl])-2,6-di-n-butyrylaminopyridine (**DAPPN**).* **DAPPNH** (0.324 g, 785μmol) and freshly prepared silver oxide (0.910 g, 3.93 mmol) were stirred in degassed chloroform (35 mL), protected from UV and under argon, at room temperature for 2 h. The reaction was stopped by rapid filtration through a pad of cotton, washed with chloroform. Concentration under reduced pressure gave a crude product. Chromatography on silica gel with ethyl acetate/hexane (5/5) as the eluent yielded **DAPPN** (0.316 g, 98%) as a bright red powder. Mp: 84–86 °C. IR (KBr pellet, cm^{-1}): 3424 (NH str), 1676 (C=O str). MS (EI): found m/z = 412, calculated for $C_{23}H_{31}N_4O_3$ m/z = 411.5. Elemental analysis calculated for $C_{23}H_{31}N_4O_3$: C, 67.13; H, 7.59; N, 13.61. Found: C 67.93, H 7.86, N 12.07. [A two-year old sample of **DAPPN** was still 97.2% pure by HPLC (C18 column, 1.2 mL/min, 7:3 MeOH:H_2O): R_t = 8.4 min).]

Preparation of Ur6IN·DAPPN Solid Mixture

Ur6IN (0.8 mg, 4.8μmol) and **DAPPN** (1.3 mg, 4.8μmol) were dissolved in toluene (3.3 mL). The solution was slowly evaporated to yield the Ur6IN·DAPPN solid mixture, upon which solid-state EPR measurements were directly performed without further treatment.

Experimental and lineshape simulated EPR spectra of **DAPPN** in toluene. Hfc analysis with program Winsim2002, http://www.niehs.nih.gov/research/resources/software/tools/index.cfm based on work described in D.R. Duling. *J. Magn. Res., Series B* 1994, 104, 105-110.

Date: 11/14/07 Time: 16:4

Winsim v.1.0, 2002

Public EPR Software Tools
National Institute of Environmental Health Sciences
National Institutes of Health, USA
http://epr.niehs.nih.gov/

Spectral Parameters:

Field Center: 3433.400 G
Scan Range: 50.000 G
Data Points: 2048
Mod. Amp.: G
Mod. Freq: KHz

Time Constant:
Rec. Gain:
MW Freq.: GHz
MW Power: mw

Simulation Parameters:

Calculation type: Nitroxide
Number of Species: 1
Domain: CW

Species number: 1

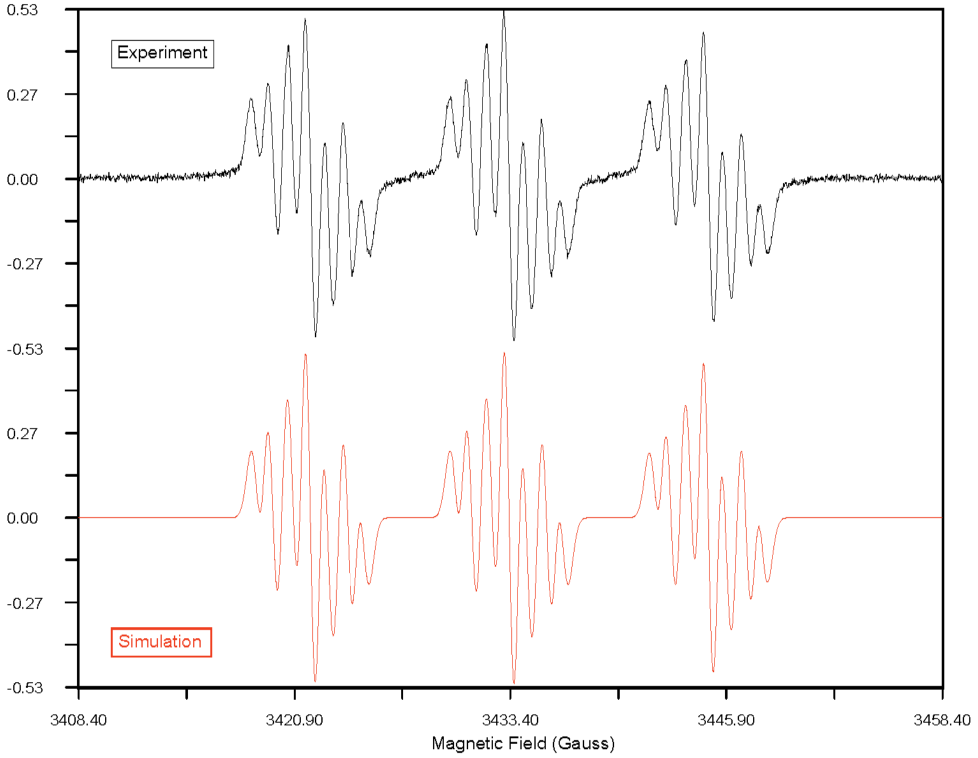
Rel. conc. : 100.000
Line width : 0.500
Lorentzian : 0.000
G-shift : -0.088

Nuclei	Coupling	Spin	Number
1	2.161	0.5	2
2	0.909	0.5	2

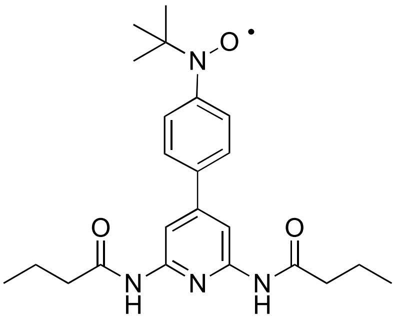
Nitroxide: aN= 11.524, lw1= 0.354, lw2= 0.353, lw3= 0.360

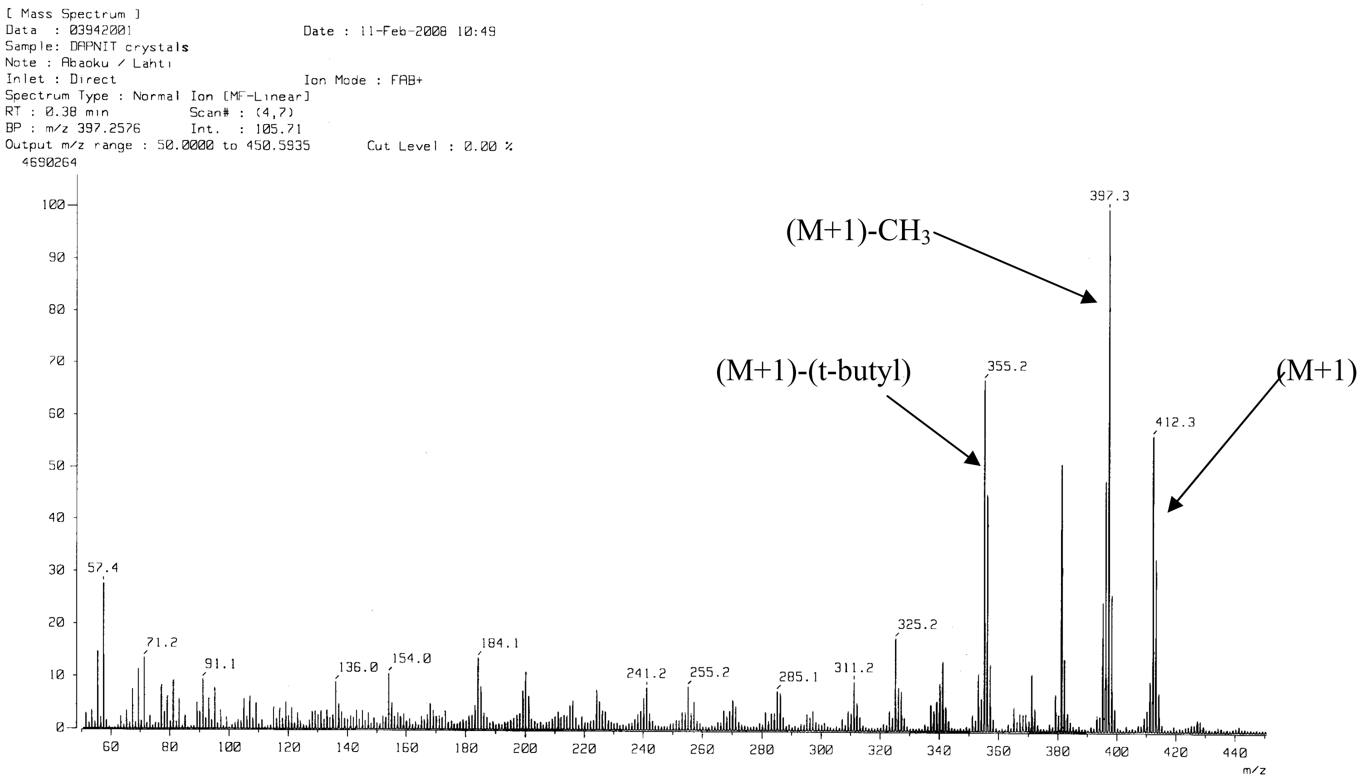
Comment:

FileName:



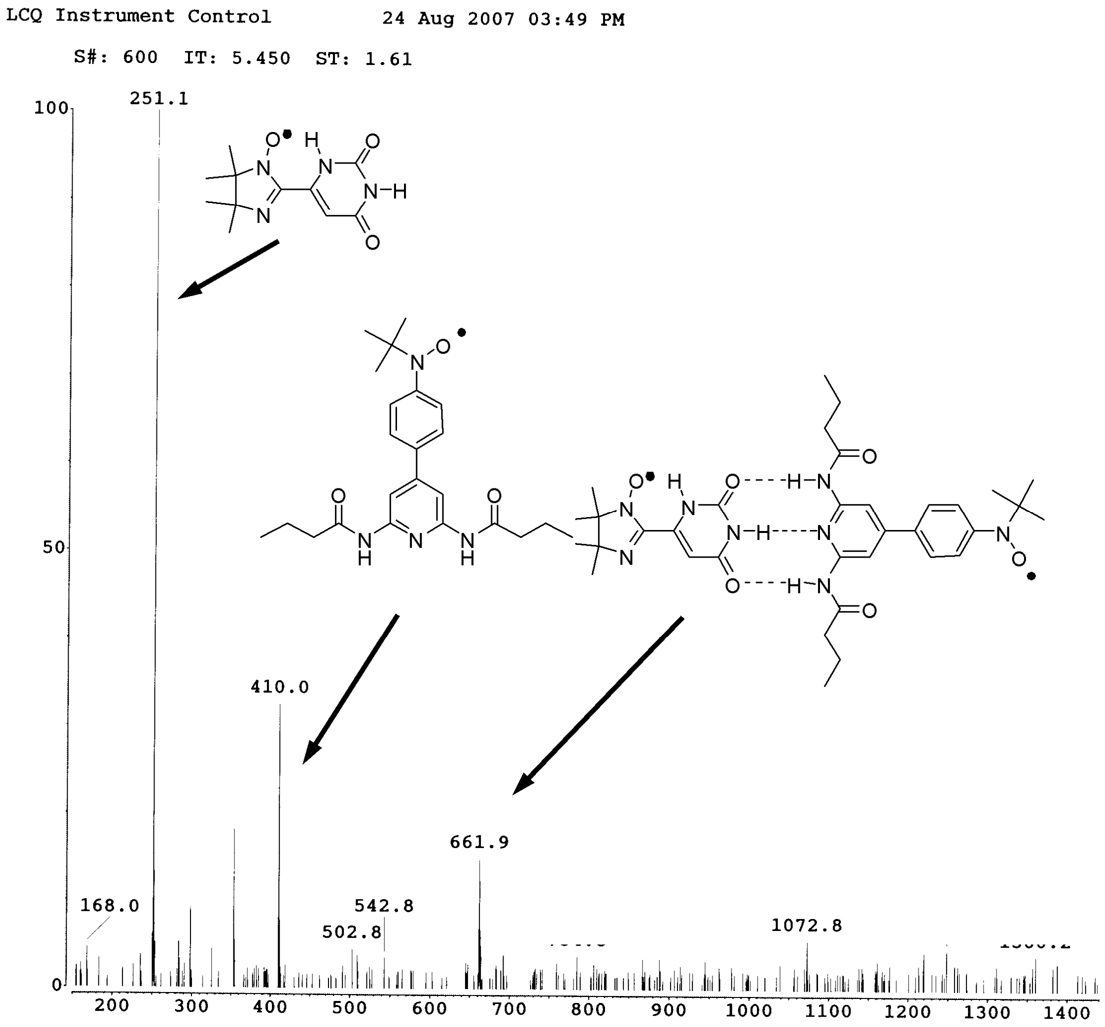
FAB Mass spectrum (positive mode mode) from a single crystal of DAPPN



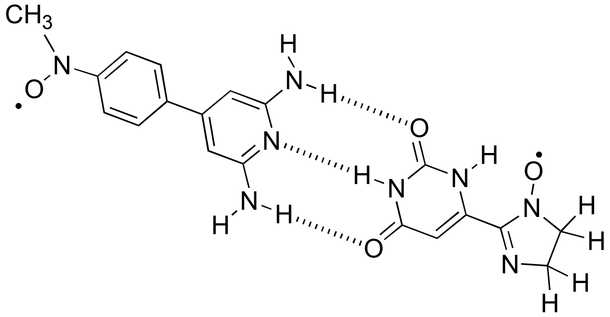


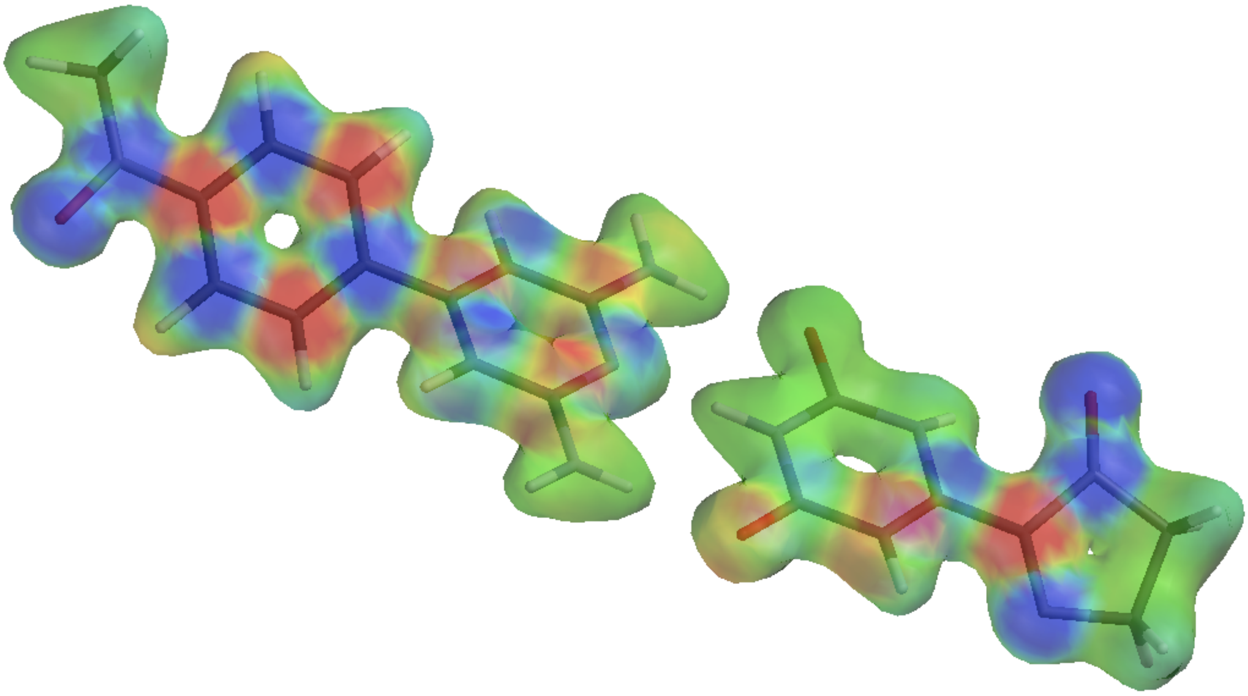
```
[ Mass Spectrum ]
Data   : 03942001                          Date : 11-Feb-2008 10:49
Sample: DAPNIT crystals
Note : Abaoku / Lahti
Inlet : Direct                             Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.38 min          Scan# : (4,7)
BP : m/z 397.2576      Int.   : 105.71
Output m/z range : 50.0000 to 450.5935        Cut Level : 0.00 %
  4690264
```

ESI Mass spectrum of 10 micromolar methanol solution of 1:1 **Ur6IN**:**DAPPN**, positive ion formation method. Instrument is ThermoQuest LCQ-DECA.



Computed spin density map of 1:1 Ur6IN:DAPPN model. Computed using Spartan 2002 for SGI computer with idealized geometry of the molecular fragments (methyl groups removed from IN radical unit and from nitroxide *t*-butyl group), using a semiempirical triplet state PM3 computation. The qualitative spin density distribution is in accord with Figure 1 in the main text. Blue = positive spin density, red = negative spin density; less intense colors indicate smaller spin populations mapped onto the electron density surface.





Computed spin population data for DAPPN: computed using Spartan 2002 for SGI at UB3LYP/6-31G* level.

ATOM	CHARGE	SPIN
1 C	0.599048	-0.000303
2 C	0.507546	-0.009167
3 C	0.500844	-0.009030
4 C	-0.217465	0.024959
5 C	-0.230396	0.026020
6 C	0.120864	-0.025483
7 C	0.088841	0.130891
8 C	-0.180286	-0.071024
9 C	-0.181385	-0.074588
10 C	-0.194632	0.130163
11 C	-0.168042	0.129405
12 C	0.319364	-0.111320
13 C	-0.326449	-0.029790
14 C	-0.539880	0.000015
15 C	0.596927	-0.000311
16 C	-0.543399	0.000024
17 N	-0.680524	-0.000036
18 N	-0.604447	0.019344
19 N	-0.073999	0.339423
20 N	-0.675371	0.000071
21 O	-0.503011	-0.000887
22 O	-0.413701	0.507753
23 O	-0.506245	-0.000569
24 H	0.181792	-0.001131
25 H	0.193658	-0.001088
26 H	0.163021	0.002681
27 H	0.150950	0.002801
28 H	0.139494	-0.006045
29 H	0.169467	-0.006377
30 H	0.175505	0.019093
31 H	0.197327	0.000824
32 H	0.174016	0.013774
33 H	0.198431	-0.000014
34 H	0.153824	-0.000003
35 H	0.187225	-0.000016
36 H	0.176372	-0.000010
37 H	0.199720	0.000002
38 H	0.168943	-0.000005
39 H	0.338790	-0.000030
40 H	0.337262	-0.000020