Supporting Information

Impact of the modulation of electron-electron dipolar interaction on electron spin relaxation of nitroxide diradicals and tetraradical in glassy solvents between 10 and 300 K

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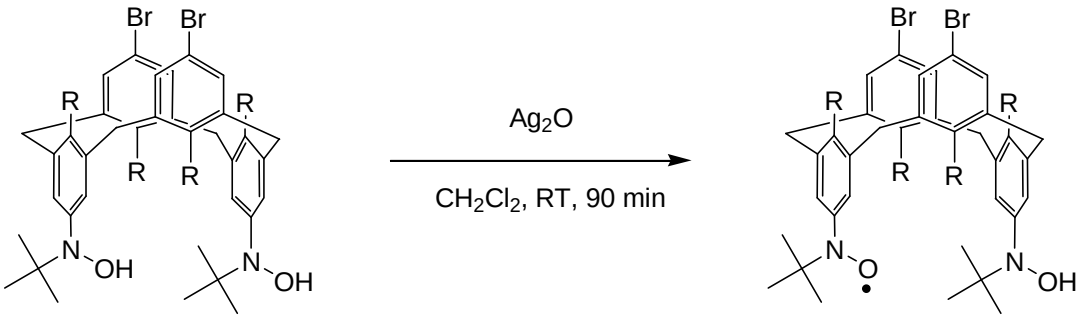
Preparation of Calix[4]arene Nitroxide Monoradical 1c.



R = $OCH_2CH_2OCH_3$

A solution of the dihydroxylamine (34.9 mg, 0.0353 mmol, 1 equiv) in degassed chloroform (3.0 mL) was added onto freshly prepared silver oxide (328 mg, 1.41 mmol, 40 equiv). The reaction mixture, protected from light, was stirred vigorously at room temperature for ~90 min. The crude mixture was centrifuged and the supernatant liquid was filtered through a 0.45-μm filter (Fisher) to remove silver oxide. Concentration under reduced pressure gave a dark orange solid (33.1 mg), which was purified by flash chromatography (TLC-grade silica gel, gradient hexane/ether, 7:3 to 5:5). The silica pad was kept at low temperature, between –5 and 0 °C, by a sleeve filled with EtOH cooled with dry ice. The target material was collected as a pale orange pinkish band (1.3 mg). The EPR spectrum of **1c** in glassy 4:1 toluene:$CHCl_3$ is shown in Figure 5a, top trace. The g and A values are included in Table S1.

Table S1

g values and Nitrogen Hyperfine Couplings

Sample	Temp (K)	g_{xx}, g_{yy}, g_{zz}	A_{zz} (G)[a]
Toluene: $CHCl_3$ (4:1)			
1b (di)	50	2.0093, 2.0058, 2.0026	15.4[b]
1c (mono)	60	2.0091, 2.0056, 2.0024	30.8
2a (di)	70	2.0089, 2.0055, 2.0024	12.5
2b (di)	50	2.0091, 2.0060, 2.0025	12
sucrose octaacetate			
1b (di)	294	2.0080, 2.0043, 2.0022	15.4[b]
2a (di)	294	2.0089, 2.0054, 2.0025	12.5
2a (di)[e]	86	2.0087, 2.0050, 2.0021	12.7
2b (di)	294	2.0089, 2.0054, 2.0025	12.5

[a] Hyperfine values A_{xx} and A_{yy} were not resolved but were assumed to be in the range of 2 to 3 G, which is half the value for the monoradical.

[b] A_{zz} was not resolved in the spectrum and was assumed to be half the value for the monoradical.

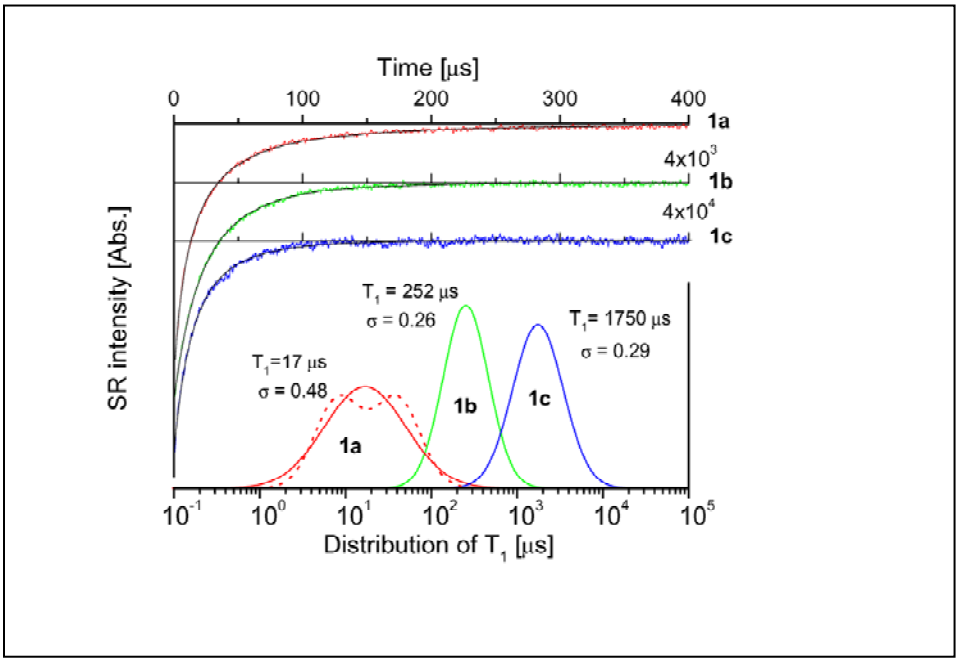


Figure S1. Saturation recovery curves and fit line calculated for a log-normal distributions of T_1 for tetraradical **1a**, diradical **1b** and monoradical **1c** in 4:1 toluene:$CHCl_3$ at 50 K. The distributions, distribution widths and values of T_1 are shown in the lower part of the figure. An alternate modeling of the data for tetraradical **1a** as the sum of two distributions is also shown.

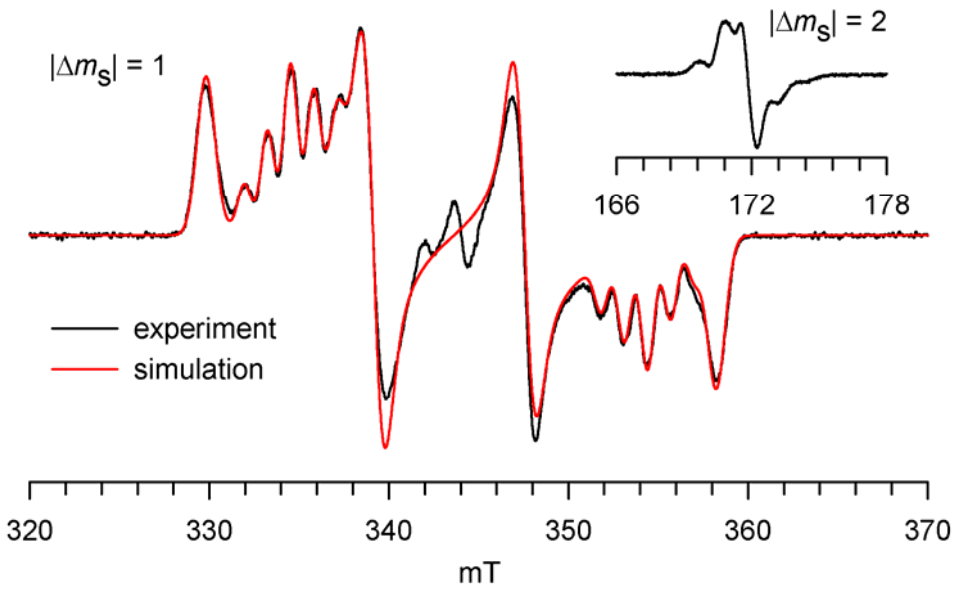
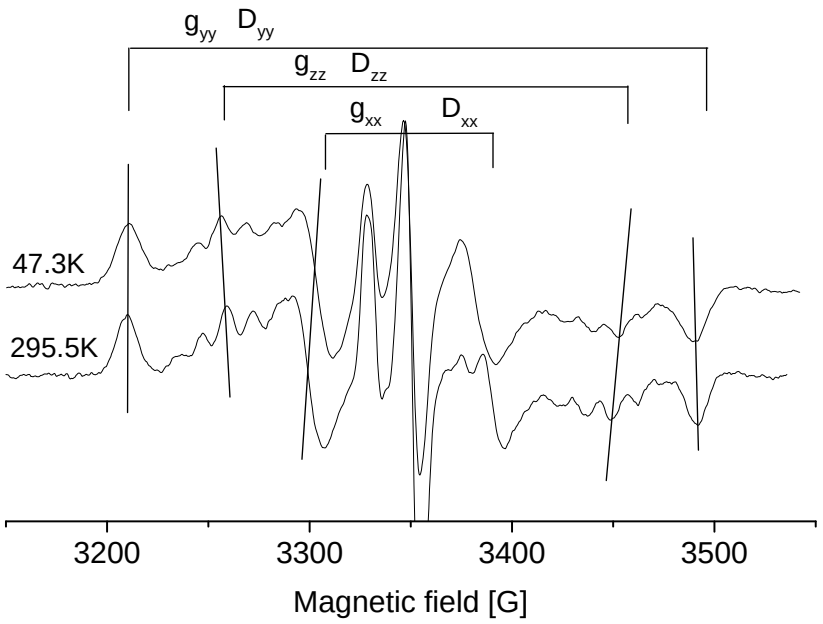


Figure S2. EPR (X-Band, 9.6545 GHz) spectrum of 0.7 mM nitroxide diradical **2a** in ethanol/water (2 : 1) at 140 K. The spectral simulation of the $|\Delta m_s| = 1$ region is shown as red trace. The fitting parameters for the spectral simulation to the $S = 1$ state are: $|D/hc| = 1.328 \times 10^{-2}$ cm^{-1}, $|E/hc| = 1.75 \times 10^{-3}$ cm^{-1}, $|A_{yy}/2hc| = 1.20 \times 10^{-3}$ cm^{-1}, $g_x = 2.0086$, $g_y = 2.0022$, $g_z = 2.0051$, Gaussian line ($L_x = 10$ G, $L_y = 7.5$ G, $L_z = 10$ G). The center lines correspond to an $S = ½$ (monoradical) impurity. The molecular *x*-, *y*-, and *z*-axes for this spectral simulation are set to correspond to the increasing values of the principal components for the spin-spin magnetic dipole tensor, as implemented in WINEPR SimFonia 1.25.

a.



b.

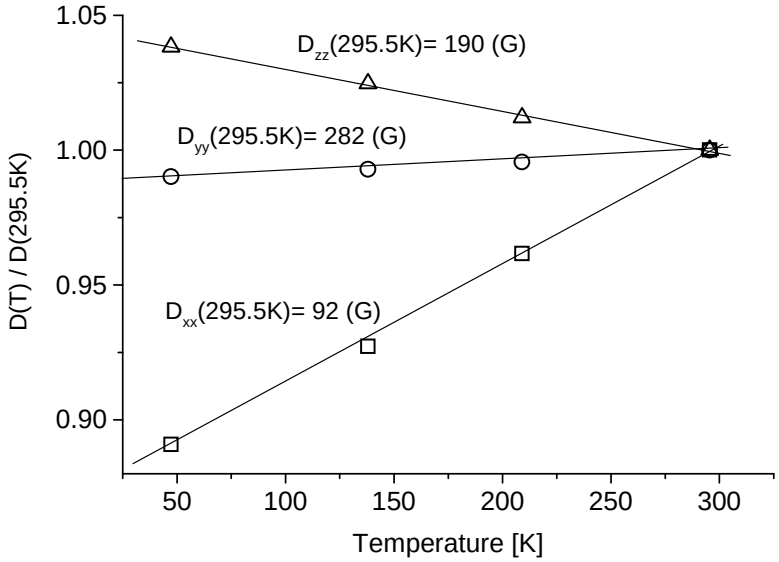


Figure S3. (a) Temperature dependence of X-band CW spectra of diradical **2a** in sucrose octaacetate; (b) temperature dependence of dipolar couplings D_{xx}, D_{yy} and D_{zz} normalized to the values at 295.5 K.

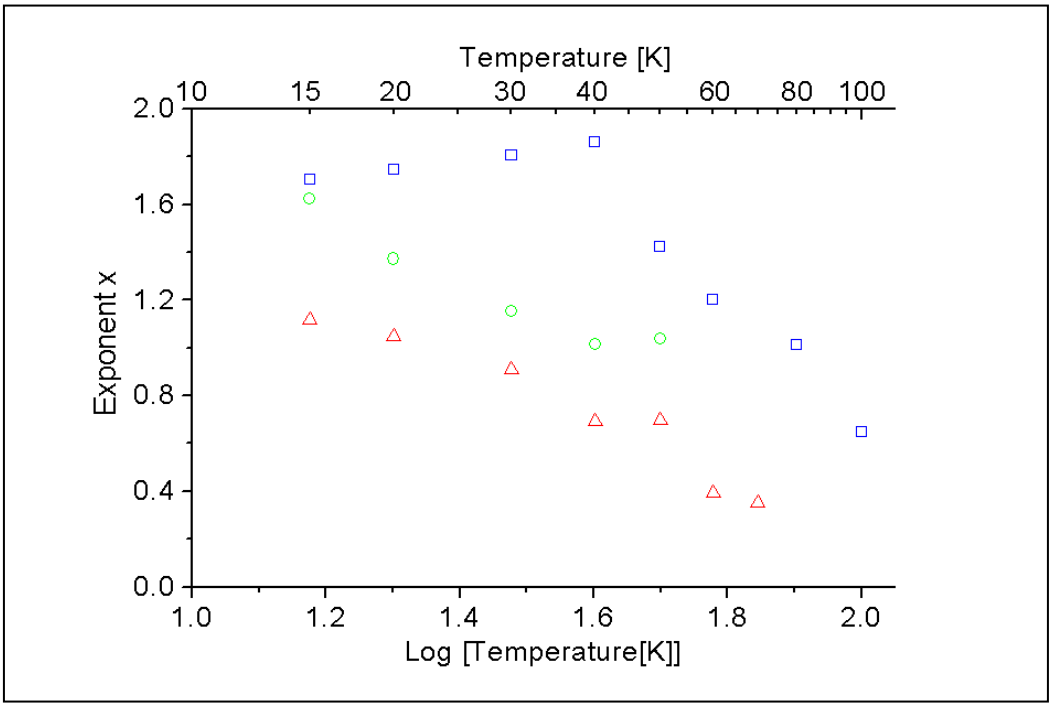


Figure S4: Temperature dependence of exponent x (Equation [3] for spin echo decays for (△) tetraradical **1a**, (○) diradical **1b**, and (□) monoradical **1c** in 4:1 toluene:$CHCl_3$.

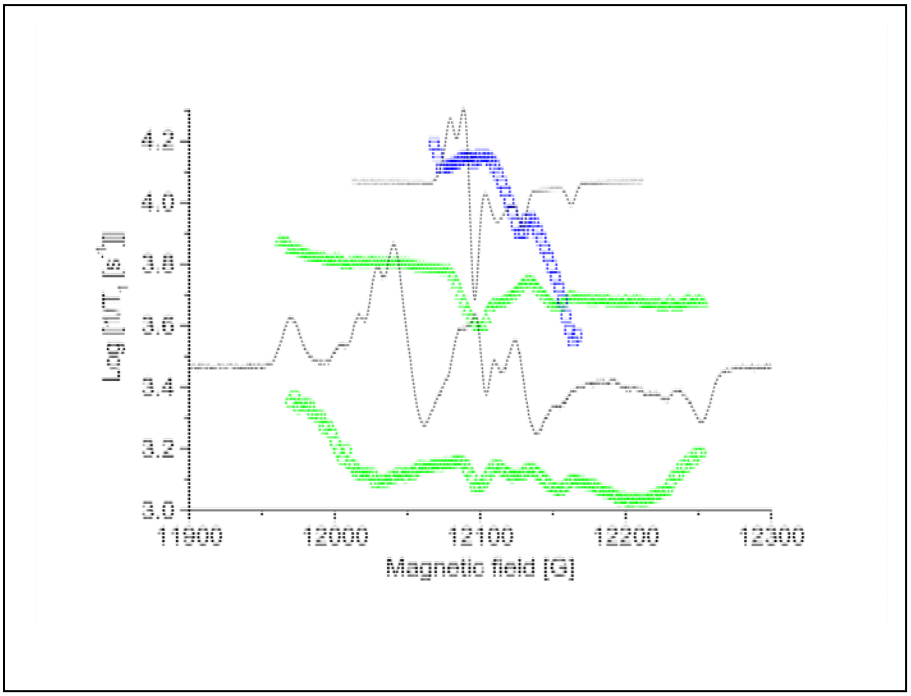


Figure S5. Dependence of $1/T_1$ on position in Q-band spectra at 86 K: (□) tempone in sucrose octaacetate, (○) diradical **2a** in glycerol, and (△) diradical **2a** in sucrose octaacetate. Relaxation rates were estimated by a single exponential fit. The relaxation rates are superimposed on CW spectra in sucrose octaacetate.

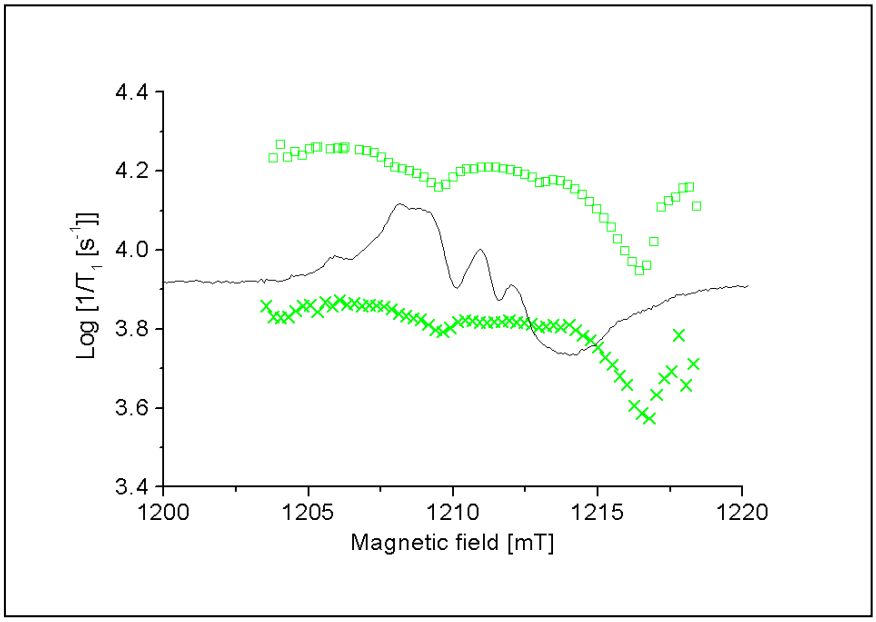


Figure S6. Dependence of $1/T_1$ on position for diradical **3** in Q-band spectra at 86 K: (□) in sucrose octaacetate and (x) in 4:1 toluene:$CHCl_3$. Relaxation rates were estimated by a single exponential fit. The relaxation rates are superimposed on CW spectra in sucrose octaacetate.

Discussion of Figures S5 and S6.

Dependence of $1/T_1$ on Position in the CW Spectra. To enhance orientation selectivity these experiments were performed primarily at Q-band. The variation with position in the spectrum of $1/T_1$ for nitroxide radicals has been reported at X-band.[1] The maximum rates, which are observed near g_{xx} and g_{yy}, are about a factor of 4 faster than the minimum rates that are observed at g_{zz}. This dependence is clearly resolved at Q-band for tempone in sucrose octaacetate at 86 K (Figure S5) where the Raman process is the dominant contribution to $1/T_1$. The rates are similar at X- band and Q-band as expected for the Raman process This orientation dependence, which persists with increasing temperature until the tumbling process dominates, is due to the orientation dependence of spin-orbit coupling or of vibrations.[1]

The relaxation rates for diradical **2a** in the relatively rigid glycerol glass at 86 K at Q-band are shown in Figure S5. The variation with position in the spectrum is only about a factor of 2, which is substantially smaller than for mono-nitroxides. Rates are faster toward the extremes of the spectrum, which is along the g_{yy} axis of the nitroxide and slower near the g_{zz} axis, as in the monoradical. The slightly slower relaxation at the monoradical position (the center of the spectrum) is due to the overlap of the monoradical contribution (**2a_mono**). In sucrose octaacetate, the relaxation for **2a** is faster than in glycerol due to a larger contribution from modulation of the dipole-dipole interaction, which is not strongly dependent on the position in the spectrum (Figure S5). In toluene:$CHCl_3$ solution at X-band the relaxation rates at 50 K for **1b**, **2a**, **2b** show little orientation dependence, similar to that observed for diradical **2a** in sucrose octaacetate.

Well-defined half-field transitions were observed for the diradicals.[2] At 15 to 80 K it was not possible to observe a spin echo, which is attributed to short values of T_m. Values of T_1 were measured by saturation recovery. Signal-to-noise is lower than for the allowed transitions so higher observe powers were used at half-field to observe the recovery, which introduces additional uncertainty in the values. Within that uncertainty, values of T_1 at half-field are similar to those for the allowed transitions. In CW experiments it has been observed that it is more difficult to saturate the half-field transitions than the allowed transitions.[3] The present results show that the difference in power saturation of the

transitions is not due to differences in T_1, but must arise from shorter T_2 and/or the low transition probability for the forbidden transition.

The small dependence of $1/T_1$ on position in the spectrum for **3** is shown in figure S6. The orientation dependence is much less than for monoradicals. Since the nitroxyl rings are non-planar the z axes, which are long the p-π orbital of the nitroxyl nitrogen are not coincident. When the magnetic field is along the z axis for one half of the diradical, which would give a longer T_1 for the monoradical, the field is at an intermediate orientation for the other half of the diradical which would give a shorter T_1. Thus the exchange interaction averages the extremes of monoradical relaxation times.

(1) Du, J.-L.; Eaton, G. R.; Eaton, S. S. *J. Magn. Reson. A* 1995, *115*, 213.
(2) Rajca, A.; Mukherjee, S.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.* 2006, *128*, 13497.
(3) Eaton, S. S.; Eaton, G. R. *J. Amer. Chem. Soc.* 1982, *104*, 5002.

DFT calculations on nitroxide diradical anti-4b at the UB3LYP/6-31G(d) level with Gaussian 03.
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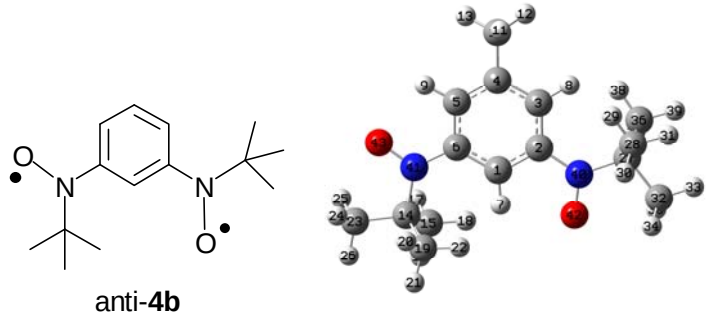

anti-**4b**

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                4-Oct-2007
 *****************************************
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 %mem=8MW
 %nproc=1
 Will use up to    1 processors via shared memory.
 ----------------------------------------------------
 # opt=tight freq ub3lyp/6-31g(d) geom=connectivity
 ----------------------------------------------------

SCF Done:  E(UB+HF-LYP) =  -845.876631256     A.U. after    4 cycles
             Convg  =    0.6886D-08             -V/T =  2.0096
             S**2   =   2.0318
 Annihilation of the first spin contaminant:
 S**2 before annihilation     2.0318,   after     2.0005


Item               Value     Threshold  Converged?
 Maximum Force            0.000000     0.000015     YES
 RMS     Force            0.000000     0.000010     YES
 Maximum Displacement     0.000115     0.000060     NO
 RMS     Displacement     0.000021     0.000040     YES
 Predicted change in Energy=-5.713851D-12
 Optimization completed on the basis of negligible forces.
    -- Stationary point found.
                           ----------------------------
                           !   Optimized Parameters   !
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! (Angstroms and Degrees) !

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! D22   D(3,4,5,9)           -179.6559         -DE/DX =    0.0                 !
! D23   D(10,4,5,6)          -178.6575         -DE/DX =    0.0                 !
! D24   D(10,4,5,9)             1.3962         -DE/DX =    0.0                 !
! D25   D(3,4,10,11)          -80.3422         -DE/DX =    0.0                 !
! D26   D(3,4,10,12)           39.2375         -DE/DX =    0.0                 !
! D27   D(3,4,10,13)          159.9703         -DE/DX =    0.0                 !
! D28   D(5,4,10,11)           98.6095         -DE/DX =    0.0                 !
! D29   D(5,4,10,12)         -141.8108         -DE/DX =    0.0                 !
! D30   D(5,4,10,13)          -21.0779         -DE/DX =    0.0                 !
! D31   D(4,5,6,1)             -0.0689         -DE/DX =    0.0                 !
! D32   D(4,5,6,41)          -179.9811         -DE/DX =    0.0                 !
! D33   D(9,5,6,1)            179.8788         -DE/DX =    0.0                 !
! D34   D(9,5,6,41)            -0.0334         -DE/DX =    0.0                 !
! D35   D(1,6,41,14)           -0.6165         -DE/DX =    0.0                 !
! D36   D(1,6,41,43)          179.4199         -DE/DX =    0.0                 !
! D37   D(5,6,41,14)          179.2917         -DE/DX =    0.0                 !
! D38   D(5,6,41,43)           -0.6719         -DE/DX =    0.0                 !
! D39   D(19,14,15,16)         61.7935         -DE/DX =    0.0                 !
! D40   D(19,14,15,17)       -179.9247         -DE/DX =    0.0                 !
! D41   D(19,14,15,18)        -58.3639         -DE/DX =    0.0                 !
! D42   D(23,14,15,16)        -57.9418         -DE/DX =    0.0                 !
! D43   D(23,14,15,17)         60.34           -DE/DX =    0.0                 !
! D44   D(23,14,15,18)       -178.0992         -DE/DX =    0.0                 !
! D45   D(41,14,15,16)       -174.8282         -DE/DX =    0.0                 !
! D46   D(41,14,15,17)        -56.5464         -DE/DX =    0.0                 !
! D47   D(41,14,15,18)         65.0144         -DE/DX =    0.0                 !
! D48   D(15,14,19,20)        179.8856         -DE/DX =    0.0                 !
! D49   D(15,14,19,21)        -61.8156         -DE/DX =    0.0                 !
! D50   D(15,14,19,22)         58.3448         -DE/DX =    0.0                 !
! D51   D(23,14,19,20)        -60.3862         -DE/DX =    0.0                 !
! D52   D(23,14,19,21)         57.9126         -DE/DX =    0.0                 !
! D53   D(23,14,19,22)        178.073          -DE/DX =    0.0                 !
! D54   D(41,14,19,20)         56.4867         -DE/DX =    0.0                 !
! D55   D(41,14,19,21)        174.7855         -DE/DX =    0.0                 !
! D56   D(41,14,19,22)        -65.0541         -DE/DX =    0.0                 !
! D57   D(15,14,23,24)       -179.246          -DE/DX =    0.0                 !
! D58   D(15,14,23,25)        -58.4372         -DE/DX =    0.0                 !
! D59   D(15,14,23,26)         61.1473         -DE/DX =    0.0                 !
! D60   D(19,14,23,24)         58.2683         -DE/DX =    0.0                 !
! D61   D(19,14,23,25)        179.0772         -DE/DX =    0.0                 !
! D62   D(19,14,23,26)        -61.3384         -DE/DX =    0.0                 !
! D63   D(41,14,23,24)        -60.4702         -DE/DX =    0.0                 !
! D64   D(41,14,23,25)         60.3386         -DE/DX =    0.0                 !
! D65   D(41,14,23,26)        179.9231         -DE/DX =    0.0                 !
! D66   D(15,14,41,6)         -61.9619         -DE/DX =    0.0                 !
! D67   D(15,14,41,43)        118.0018         -DE/DX =    0.0                 !
! D68   D(19,14,41,6)          62.9288         -DE/DX =    0.0                 !
! D69   D(19,14,41,43)       -117.1074         -DE/DX =    0.0                 !
! D70   D(23,14,41,6)        -179.5192         -DE/DX =    0.0                 !
```

```
! D71   D(23,14,41,43)         0.4445         -DE/DX =    0.0                 !
! D72   D(32,27,28,29)       179.3379         -DE/DX =    0.0                 !
! D73   D(32,27,28,30)       -59.4311         -DE/DX =    0.0                 !
! D74   D(32,27,28,31)        58.9463         -DE/DX =    0.0                 !
! D75   D(36,27,28,29)        59.7387         -DE/DX =    0.0                 !
! D76   D(36,27,28,30)      -179.0304         -DE/DX =    0.0                 !
! D77   D(36,27,28,31)       -60.6529         -DE/DX =    0.0                 !
! D78   D(40,27,28,29)       -63.6439         -DE/DX =    0.0                 !
! D79   D(40,27,28,30)        57.587          -DE/DX =    0.0                 !
! D80   D(40,27,28,31)       175.9644         -DE/DX =    0.0                 !
! D81   D(28,27,32,33)       -61.176          -DE/DX =    0.0                 !
! D82   D(28,27,32,34)        58.4002         -DE/DX =    0.0                 !
! D83   D(28,27,32,35)       179.2298         -DE/DX =    0.0                 !
! D84   D(36,27,32,33)        61.3727         -DE/DX =    0.0                 !
! D85   D(36,27,32,34)      -179.0512         -DE/DX =    0.0                 !
! D86   D(36,27,32,35)       -58.2216         -DE/DX =    0.0                 !
! D87   D(40,27,32,33)      -179.9381         -DE/DX =    0.0                 !
! D88   D(40,27,32,34)       -60.3619         -DE/DX =    0.0                 !
! D89   D(40,27,32,35)        60.4676         -DE/DX =    0.0                 !
! D90   D(28,27,36,37)       179.0137         -DE/DX =    0.0                 !
! D91   D(28,27,36,38)       -59.7927         -DE/DX =    0.0                 !
! D92   D(28,27,36,39)        60.6205         -DE/DX =    0.0                 !
! D93   D(32,27,36,37)        59.4159         -DE/DX =    0.0                 !
! D94   D(32,27,36,38)      -179.3905         -DE/DX =    0.0                 !
! D95   D(32,27,36,39)       -58.9773         -DE/DX =    0.0                 !
! D96   D(40,27,36,37)       -57.5689         -DE/DX =    0.0                 !
! D97   D(40,27,36,38)        63.6248         -DE/DX =    0.0                 !
! D98   D(40,27,36,39)      -175.962          -DE/DX =    0.0                 !
! D99   D(28,27,40,2)         61.7512         -DE/DX =    0.0                 !
! D100  D(28,27,40,42)      -118.1207         -DE/DX =    0.0                 !
! D101  D(32,27,40,2)        179.248          -DE/DX =    0.0                 !
! D102  D(32,27,40,42)        -0.6239         -DE/DX =    0.0                 !
! D103  D(36,27,40,2)        -63.2863         -DE/DX =    0.0                 !
! D104  D(36,27,40,42)       116.8418         -DE/DX =    0.0                 !
--------------------------------------------------------------------------------
GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad

                         Input orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic              Coordinates (Angstroms)
Number     Number      Type              X           Y           Z
---------------------------------------------------------------------
   1          6             0        0.128374    0.157637   -0.020905
   2          6             0        0.067122   -0.279707    1.314933
   3          6             0        1.259655   -0.539036    2.013031
   4          6             0        2.498554   -0.358180    1.382891
   5          6             0        2.551496    0.071561    0.061111
   6          6             0        1.362980    0.334720   -0.654258
   7          1             0       -0.812330    0.338349   -0.508166
   8          1             0        1.254900   -0.881186    3.037285
   9          1             0        3.498439    0.211189   -0.442766
  10          6             0        3.775143   -0.609653    2.154397
  11          1             0        4.027743    0.247387    2.792587
  12          1             0        3.684312   -1.484800    2.807704
  13          1             0        4.620504   -0.776353    1.480134
  14          6             0        0.362122    1.091956   -2.949712
  15          6             0       -0.501601   -0.163423   -3.190413
  16          1             0       -1.258811    0.064336   -3.948588
  17          1             0        0.120928   -0.981088   -3.568941
  18          1             0       -1.022061   -0.517510   -2.299435
  19          6             0       -0.456500    2.284154   -2.412468
  20          1             0        0.197296    3.148637   -2.255640
  21          1             0       -1.212685    2.561839   -3.154873
  22          1             0       -0.974405    2.075746   -1.475155
  23          6             0        0.994146    1.505568   -4.288319
```

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   24          1             0        1.630707    2.385716   -4.177116
   25          1             0        1.601965    0.702585   -4.710428
   26          1             0        0.185808    1.741279   -4.988957
   27          6             0       -1.555839   -0.874503    3.280308
   28          6             0       -0.979435    0.135148    4.293921
   29          1             0        0.109373    0.201618    4.277617
   30          1             0       -1.381068    1.134688    4.097400
   31          1             0       -1.281097   -0.158355    5.305340
   32          6             0       -3.086326   -0.876119    3.424044
   33          1             0       -3.332040   -1.192466    4.443606
   34          1             0       -3.506832    0.116967    3.253075
   35          1             0       -3.555477   -1.565467    2.719266
   36          6             0       -1.050113   -2.313119    3.512753
   37          1             0       -1.500661   -2.991476    2.780755
   38          1             0        0.033878   -2.414758    3.441810
   39          1             0       -1.352080   -2.644196    4.512449
   40          7             0       -1.234354   -0.433077    1.864736
   41          7             0        1.500232    0.768764   -1.997069
   42          8             0       -2.233852   -0.174290    1.101268
   43          8             0        2.692390    0.901278   -2.453176
 ---------------------------------------------------------------------
```
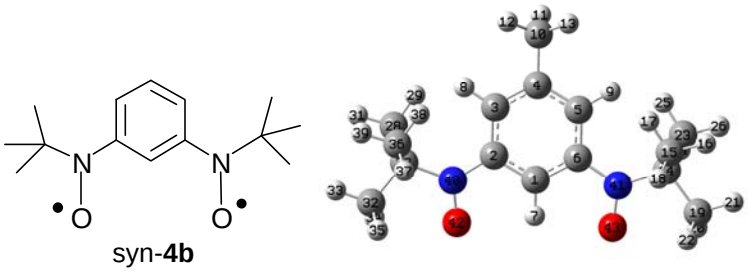

DFT calculations on nitroxide diradical syn-4b at the UB3LYP/6-31G(d) level with Gaussian 03

File: DiNO_C4dft.log



syn-**4b**

```
*****************************************
 Gaussian 03:  IA32W-G03RevC.02 12-Jun-2004
               22-Oct-2007
 *****************************************
 %chk=DiNO_C4dft.chk
 %mem=8MW
 %nproc=1
 Will use up to    1 processors via shared memory.
 ----------------------------------------------------
 # opt=tight freq ub3lyp/6-31g(d) geom=connectivity
 ----------------------------------------------------

SCF Done:  E(UB+HF-LYP) =  -845.873725530     A.U. after   10 cycles
             Convg  =    0.7542D-08             -V/T =  2.0096
             S**2   =   2.0307
 Annihilation of the first spin contaminant:
 S**2 before annihilation     2.0307,   after     2.0005


Item               Value     Threshold  Converged?
 Maximum Force            0.000000     0.000015     YES
 RMS     Force            0.000000     0.000010     YES
 Maximum Displacement     0.013707     0.000060     NO
```

```
RMS     Displacement     0.001876     0.000040     NO
Predicted change in Energy=-1.466410D-09
Optimization completed on the basis of negligible forces.
   -- Stationary point found.
                          ----------------------------
                          !   Optimized Parameters   !
                          ! (Angstroms and Degrees)  !
--------------------------                           --------------------------
! Name  Definition              Value          Derivative Info.                !
--------------------------------------------------------------------------------
! R1    R(1,2)                  1.402          -DE/DX =    0.0                 !
! R2    R(1,6)                  1.402          -DE/DX =    0.0                 !
! R3    R(1,7)                  1.078          -DE/DX =    0.0                 !
! R4    R(2,3)                  1.4096         -DE/DX =    0.0                 !
! R5    R(2,40)                 1.4206         -DE/DX =    0.0                 !
! R6    R(3,4)                  1.3967         -DE/DX =    0.0                 !
! R7    R(3,8)                  1.0798         -DE/DX =    0.0                 !
! R8    R(4,5)                  1.3966         -DE/DX =    0.0                 !
! R9    R(4,10)                 1.5132         -DE/DX =    0.0                 !
! R10   R(5,6)                  1.4097         -DE/DX =    0.0                 !
! R11   R(5,9)                  1.0798         -DE/DX =    0.0                 !
! R12   R(6,41)                 1.4206         -DE/DX =    0.0                 !
! R13   R(10,11)                1.0981         -DE/DX =    0.0                 !
! R14   R(10,12)                1.0951         -DE/DX =    0.0                 !
! R15   R(10,13)                1.0951         -DE/DX =    0.0                 !
! R16   R(14,15)                1.5423         -DE/DX =    0.0                 !
! R17   R(14,19)                1.5372         -DE/DX =    0.0                 !
! R18   R(14,23)                1.543          -DE/DX =    0.0                 !
! R19   R(14,41)                1.5176         -DE/DX =    0.0                 !
! R20   R(15,16)                1.0956         -DE/DX =    0.0                 !
! R21   R(15,17)                1.0909         -DE/DX =    0.0                 !
! R22   R(15,18)                1.095          -DE/DX =    0.0                 !
! R23   R(19,20)                1.0914         -DE/DX =    0.0                 !
! R24   R(19,21)                1.0955         -DE/DX =    0.0                 !
! R25   R(19,22)                1.0921         -DE/DX =    0.0                 !
! R26   R(23,24)                1.0949         -DE/DX =    0.0                 !
! R27   R(23,25)                1.0913         -DE/DX =    0.0                 !
! R28   R(23,26)                1.0956         -DE/DX =    0.0                 !
! R29   R(27,28)                1.543          -DE/DX =    0.0                 !
! R30   R(27,32)                1.5372         -DE/DX =    0.0                 !
! R31   R(27,36)                1.5422         -DE/DX =    0.0                 !
! R32   R(27,40)                1.5176         -DE/DX =    0.0                 !
! R33   R(28,29)                1.0913         -DE/DX =    0.0                 !
! R34   R(28,30)                1.0949         -DE/DX =    0.0                 !
! R35   R(28,31)                1.0956         -DE/DX =    0.0                 !
! R36   R(32,33)                1.0955         -DE/DX =    0.0                 !
! R37   R(32,34)                1.0914         -DE/DX =    0.0                 !
! R38   R(32,35)                1.0921         -DE/DX =    0.0                 !
! R39   R(36,37)                1.095          -DE/DX =    0.0                 !
! R40   R(36,38)                1.0909         -DE/DX =    0.0                 !
! R41   R(36,39)                1.0955         -DE/DX =    0.0                 !
! R42   R(40,42)                1.2823         -DE/DX =    0.0                 !
! R43   R(41,43)                1.2823         -DE/DX =    0.0                 !
! A1    A(2,1,6)              120.7063         -DE/DX =    0.0                 !
! A2    A(2,1,7)              119.6461         -DE/DX =    0.0                 !
! A3    A(6,1,7)              119.6464         -DE/DX =    0.0                 !
! A4    A(1,2,3)              119.3258         -DE/DX =    0.0                 !
! A5    A(1,2,40)             116.681          -DE/DX =    0.0                 !
! A6    A(3,2,40)             123.9926         -DE/DX =    0.0                 !
! A7    A(2,3,4)              120.2365         -DE/DX =    0.0                 !
! A8    A(2,3,8)              121.6546         -DE/DX =    0.0                 !
! A9    A(4,3,8)              118.1052         -DE/DX =    0.0                 !
! A10   A(3,4,5)              120.1657         -DE/DX =    0.0                 !
! A11   A(3,4,10)             119.9055         -DE/DX =    0.0                 !
! A12   A(5,4,10)             119.9076         -DE/DX =    0.0                 !
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! A13	A(4,5,6)	120.2384	-DE/DX =	0.0 !
! A14	A(4,5,9)	118.1012	-DE/DX =	0.0 !
! A15	A(6,5,9)	121.6568	-DE/DX =	0.0 !
! A16	A(1,6,5)	119.3228	-DE/DX =	0.0 !
! A17	A(1,6,41)	116.6804	-DE/DX =	0.0 !
! A18	A(5,6,41)	123.9964	-DE/DX =	0.0 !
! A19	A(4,10,11)	111.221	-DE/DX =	0.0 !
! A20	A(4,10,12)	111.4995	-DE/DX =	0.0 !
! A21	A(4,10,13)	111.4995	-DE/DX =	0.0 !
! A22	A(11,10,12)	107.2662	-DE/DX =	0.0 !
! A23	A(11,10,13)	107.2677	-DE/DX =	0.0 !
! A24	A(12,10,13)	107.8684	-DE/DX =	0.0 !
! A25	A(15,14,19)	108.0895	-DE/DX =	0.0 !
! A26	A(15,14,23)	112.8586	-DE/DX =	0.0 !
! A27	A(15,14,41)	110.2137	-DE/DX =	0.0 !
! A28	A(19,14,23)	108.205	-DE/DX =	0.0 !
! A29	A(19,14,41)	107.2873	-DE/DX =	0.0 !
! A30	A(23,14,41)	109.9928	-DE/DX =	0.0 !
! A31	A(14,15,16)	109.1436	-DE/DX =	0.0 !
! A32	A(14,15,17)	113.8279	-DE/DX =	0.0 !
! A33	A(14,15,18)	110.0402	-DE/DX =	0.0 !
! A34	A(16,15,17)	107.7503	-DE/DX =	0.0 !
! A35	A(16,15,18)	107.9933	-DE/DX =	0.0 !
! A36	A(17,15,18)	107.9073	-DE/DX =	0.0 !
! A37	A(14,19,20)	111.6082	-DE/DX =	0.0 !
! A38	A(14,19,21)	108.18	-DE/DX =	0.0 !
! A39	A(14,19,22)	111.4333	-DE/DX =	0.0 !
! A40	A(20,19,21)	108.856	-DE/DX =	0.0 !
! A41	A(20,19,22)	107.9141	-DE/DX =	0.0 !
! A42	A(21,19,22)	108.7864	-DE/DX =	0.0 !
! A43	A(14,23,24)	109.9649	-DE/DX =	0.0 !
! A44	A(14,23,25)	113.6868	-DE/DX =	0.0 !
! A45	A(14,23,26)	109.2733	-DE/DX =	0.0 !
! A46	A(24,23,25)	107.943	-DE/DX =	0.0 !
! A47	A(24,23,26)	108.0692	-DE/DX =	0.0 !
! A48	A(25,23,26)	107.7357	-DE/DX =	0.0 !
! A49	A(28,27,32)	108.2076	-DE/DX =	0.0 !
! A50	A(28,27,36)	112.8567	-DE/DX =	0.0 !
! A51	A(28,27,40)	109.9893	-DE/DX =	0.0 !
! A52	A(32,27,36)	108.0894	-DE/DX =	0.0 !
! A53	A(32,27,40)	107.2861	-DE/DX =	0.0 !
! A54	A(36,27,40)	110.2178	-DE/DX =	0.0 !
! A55	A(27,28,29)	113.6835	-DE/DX =	0.0 !
! A56	A(27,28,30)	109.964	-DE/DX =	0.0 !
! A57	A(27,28,31)	109.2757	-DE/DX =	0.0 !
! A58	A(29,28,30)	107.9443	-DE/DX =	0.0 !
! A59	A(29,28,31)	107.7352	-DE/DX =	0.0 !
! A60	A(30,28,31)	108.0705	-DE/DX =	0.0 !
! A61	A(27,32,33)	108.1812	-DE/DX =	0.0 !
! A62	A(27,32,34)	111.6102	-DE/DX =	0.0 !
! A63	A(27,32,35)	111.4315	-DE/DX =	0.0 !
! A64	A(33,32,34)	108.8563	-DE/DX =	0.0 !
! A65	A(33,32,35)	108.7846	-DE/DX =	0.0 !
! A66	A(34,32,35)	107.9142	-DE/DX =	0.0 !
! A67	A(27,36,37)	110.042	-DE/DX =	0.0 !
! A68	A(27,36,38)	113.8286	-DE/DX =	0.0 !
! A69	A(27,36,39)	109.1412	-DE/DX =	0.0 !
! A70	A(37,36,38)	107.9076	-DE/DX =	0.0 !
! A71	A(37,36,39)	107.9926	-DE/DX =	0.0 !
! A72	A(38,36,39)	107.7503	-DE/DX =	0.0 !
! A73	A(2,40,27)	125.898	-DE/DX =	0.0 !
! A74	A(2,40,42)	117.4357	-DE/DX =	0.0 !
! A75	A(27,40,42)	116.6608	-DE/DX =	0.0 !
! A76	A(6,41,14)	125.8993	-DE/DX =	0.0 !
! A77	A(6,41,43)	117.4364	-DE/DX =	0.0 !

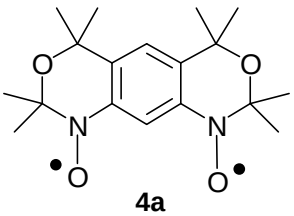
```
! A78   A(14,41,43)          116.6591         -DE/DX =    0.0                 !
! D1    D(6,1,2,3)             0.5235         -DE/DX =    0.0                 !
! D2    D(6,1,2,40)         -179.7436         -DE/DX =    0.0                 !
! D3    D(7,1,2,3)          -179.8764         -DE/DX =    0.0                 !
! D4    D(7,1,2,40)           -0.1435         -DE/DX =    0.0                 !
! D5    D(2,1,6,5)            -0.5207         -DE/DX =    0.0                 !
! D6    D(2,1,6,41)          179.7272         -DE/DX =    0.0                 !
! D7    D(7,1,6,5)           179.8792         -DE/DX =    0.0                 !
! D8    D(7,1,6,41)            0.1271         -DE/DX =    0.0                 !
! D9    D(1,2,3,4)             0.0271         -DE/DX =    0.0                 !
! D10   D(1,2,3,8)           179.3077         -DE/DX =    0.0                 !
! D11   D(40,2,3,4)         -179.6851         -DE/DX =    0.0                 !
! D12   D(40,2,3,8)           -0.4045         -DE/DX =    0.0                 !
! D13   D(1,2,40,27)         173.2829         -DE/DX =    0.0                 !
! D14   D(1,2,40,42)          -5.8328         -DE/DX =    0.0                 !
! D15   D(3,2,40,27)          -6.9979         -DE/DX =    0.0                 !
! D16   D(3,2,40,42)         173.8864         -DE/DX =    0.0                 !
! D17   D(2,3,4,5)            -0.5763         -DE/DX =    0.0                 !
! D18   D(2,3,4,10)          177.7459         -DE/DX =    0.0                 !
! D19   D(8,3,4,5)          -179.8821         -DE/DX =    0.0                 !
! D20   D(8,3,4,10)           -1.5599         -DE/DX =    0.0                 !
! D21   D(3,4,5,6)             0.5791         -DE/DX =    0.0                 !
! D22   D(3,4,5,9)           179.9            -DE/DX =    0.0                 !
! D23   D(10,4,5,6)         -177.743          -DE/DX =    0.0                 !
! D24   D(10,4,5,9)            1.5779         -DE/DX =    0.0                 !
! D25   D(3,4,10,11)         -89.0926         -DE/DX =    0.0                 !
! D26   D(3,4,10,12)          30.588          -DE/DX =    0.0                 !
! D27   D(3,4,10,13)         151.225          -DE/DX =    0.0                 !
! D28   D(5,4,10,11)          89.2339         -DE/DX =    0.0                 !
! D29   D(5,4,10,12)        -151.0855         -DE/DX =    0.0                 !
! D30   D(5,4,10,13)         -30.4485         -DE/DX =    0.0                 !
! D31   D(4,5,6,1)            -0.0327         -DE/DX =    0.0                 !
! D32   D(4,5,6,41)          179.7002         -DE/DX =    0.0                 !
! D33   D(9,5,6,1)          -179.3289         -DE/DX =    0.0                 !
! D34   D(9,5,6,41)            0.4039         -DE/DX =    0.0                 !
! D35   D(1,6,41,14)        -173.4745         -DE/DX =    0.0                 !
! D36   D(1,6,41,43)           5.6641         -DE/DX =    0.0                 !
! D37   D(5,6,41,14)           6.7862         -DE/DX =    0.0                 !
! D38   D(5,6,41,43)        -174.0752         -DE/DX =    0.0                 !
! D39   D(19,14,15,16)        59.4514         -DE/DX =    0.0                 !
! D40   D(19,14,15,17)       179.8552         -DE/DX =    0.0                 !
! D41   D(19,14,15,18)       -58.8873         -DE/DX =    0.0                 !
! D42   D(23,14,15,16)       -60.1772         -DE/DX =    0.0                 !
! D43   D(23,14,15,17)        60.2266         -DE/DX =    0.0                 !
! D44   D(23,14,15,18)      -178.5159         -DE/DX =    0.0                 !
! D45   D(41,14,15,16)       176.4136         -DE/DX =    0.0                 !
! D46   D(41,14,15,17)       -63.1825         -DE/DX =    0.0                 !
! D47   D(41,14,15,18)        58.0749         -DE/DX =    0.0                 !
! D48   D(15,14,19,20)       179.9495         -DE/DX =    0.0                 !
! D49   D(15,14,19,21)       -60.3174         -DE/DX =    0.0                 !
! D50   D(15,14,19,22)        59.2248         -DE/DX =    0.0                 !
! D51   D(23,14,19,20)       -57.5289         -DE/DX =    0.0                 !
! D52   D(23,14,19,21)        62.2042         -DE/DX =    0.0                 !
! D53   D(23,14,19,22)      -178.2537         -DE/DX =    0.0                 !
! D54   D(41,14,19,20)        61.1108         -DE/DX =    0.0                 !
! D55   D(41,14,19,21)      -179.156          -DE/DX =    0.0                 !
! D56   D(41,14,19,22)       -59.6139         -DE/DX =    0.0                 !
! D57   D(15,14,23,24)       179.7525         -DE/DX =    0.0                 !
! D58   D(15,14,23,25)       -59.0968         -DE/DX =    0.0                 !
! D59   D(15,14,23,26)        61.2877         -DE/DX =    0.0                 !
! D60   D(19,14,23,24)        60.1906         -DE/DX =    0.0                 !
! D61   D(19,14,23,25)      -178.6588         -DE/DX =    0.0                 !
! D62   D(19,14,23,26)       -58.2742         -DE/DX =    0.0                 !
! D63   D(41,14,23,24)       -56.7161         -DE/DX =    0.0                 !
! D64   D(41,14,23,25)        64.4346         -DE/DX =    0.0                 !
```

```
! D65   D(41,14,23,26)       -175.1809         -DE/DX =    0.0                 !
! D66   D(15,14,41,6)          57.5048         -DE/DX =    0.0                 !
! D67   D(15,14,41,43)       -121.6398         -DE/DX =    0.0                 !
! D68   D(19,14,41,6)         174.9646         -DE/DX =    0.0                 !
! D69   D(19,14,41,43)          -4.18           -DE/DX =    0.0                 !
! D70   D(23,14,41,6)          -67.5571         -DE/DX =    0.0                 !
! D71   D(23,14,41,43)         113.2984         -DE/DX =    0.0                 !
! D72   D(32,27,28,29)         178.6336         -DE/DX =    0.0                 !
! D73   D(32,27,28,30)         -60.2171         -DE/DX =    0.0                 !
! D74   D(32,27,28,31)          58.2502         -DE/DX =    0.0                 !
! D75   D(36,27,28,29)          59.0711         -DE/DX =    0.0                 !
! D76   D(36,27,28,30)        -179.7796         -DE/DX =    0.0                 !
! D77   D(36,27,28,31)         -61.3123         -DE/DX =    0.0                 !
! D78   D(40,27,28,29)         -64.4617         -DE/DX =    0.0                 !
! D79   D(40,27,28,30)          56.6876         -DE/DX =    0.0                 !
! D80   D(40,27,28,31)         175.1549         -DE/DX =    0.0                 !
! D81   D(28,27,32,33)         -62.227          -DE/DX =    0.0                 !
! D82   D(28,27,32,34)          57.5085         -DE/DX =    0.0                 !
! D83   D(28,27,32,35)         178.2335         -DE/DX =    0.0                 !
! D84   D(36,27,32,33)          60.2939         -DE/DX =    0.0                 !
! D85   D(36,27,32,34)        -179.9706         -DE/DX =    0.0                 !
! D86   D(36,27,32,35)         -59.2457         -DE/DX =    0.0                 !
! D87   D(40,27,32,33)         179.1367         -DE/DX =    0.0                 !
! D88   D(40,27,32,34)         -61.1278         -DE/DX =    0.0                 !
! D89   D(40,27,32,35)          59.5972         -DE/DX =    0.0                 !
! D90   D(28,27,36,37)         178.5234         -DE/DX =    0.0                 !
! D91   D(28,27,36,38)         -60.2168         -DE/DX =    0.0                 !
! D92   D(28,27,36,39)          60.1858         -DE/DX =    0.0                 !
! D93   D(32,27,36,37)          58.8928         -DE/DX =    0.0                 !
! D94   D(32,27,36,38)        -179.8475         -DE/DX =    0.0                 !
! D95   D(32,27,36,39)         -59.4449         -DE/DX =    0.0                 !
! D96   D(40,27,36,37)         -58.0703         -DE/DX =    0.0                 !
! D97   D(40,27,36,38)          63.1895         -DE/DX =    0.0                 !
! D98   D(40,27,36,39)        -176.4079         -DE/DX =    0.0                 !
! D99   D(28,27,40,2)           67.7111         -DE/DX =    0.0                 !
! D100  D(28,27,40,42)        -113.1671         -DE/DX =    0.0                 !
! D101  D(32,27,40,2)         -174.8101         -DE/DX =    0.0                 !
! D102  D(32,27,40,42)           4.3117         -DE/DX =    0.0                 !
! D103  D(36,27,40,2)          -57.3488         -DE/DX =    0.0                 !
! D104  D(36,27,40,42)         121.7729         -DE/DX =    0.0                 !
--------------------------------------------------------------------------------
GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad

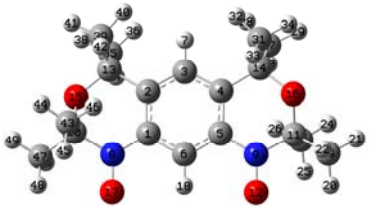
                         Input orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic              Coordinates (Angstroms)
Number     Number      Type              X           Y           Z
---------------------------------------------------------------------
   1          6             0       -0.087431   -0.663471   -0.029287
   2          6             0       -0.092106   -0.626378    1.372197
   3          6             0        1.134579   -0.607916    2.066454
   4          6             0        2.341100   -0.625874    1.363155
   5          6             0        2.339160   -0.674392   -0.032645
   6          6             0        1.120324   -0.693229   -0.740633
   7          1             0       -1.022556   -0.675708   -0.565508
   8          1             0        1.174889   -0.568263    3.144768
   9          1             0        3.290928   -0.685333   -0.542507
  10          6             0        3.653072   -0.554306    2.113801
  11          1             0        3.969020    0.486621    2.263609
  12          1             0        3.574750   -1.015912    3.103809
  13          1             0        4.455598   -1.062369    1.568694
  14          6             0        2.183418   -0.912813   -3.122094
  15          6             0        2.937333   -2.222733   -2.815034
  16          1             0        3.728198   -2.365104   -3.559678
  17          1             0        3.402078   -2.242829   -1.828297
```

18	1	0	2.252363	-3.074467	-2.882008
19	6	0	1.588129	-1.024652	-4.534911
20	1	0	1.038263	-0.123457	-4.811870
21	1	0	2.411982	-1.168247	-5.242561
22	1	0	0.904702	-1.872778	-4.614008
23	6	0	3.098347	0.329016	-3.081404
24	1	0	2.517707	1.228824	-3.309673
25	1	0	3.588944	0.480766	-2.118462
26	1	0	3.880343	0.227148	-3.842014
27	6	0	-1.616072	-0.706985	3.498378
28	6	0	-1.086307	0.554699	4.211397
29	1	0	-0.003711	0.674611	4.143515
30	1	0	-1.552187	1.448849	3.784369
31	1	0	-1.350967	0.507898	5.273558
32	6	0	-3.138582	-0.769550	3.700872
33	1	0	-3.337201	-0.860037	4.774411
34	1	0	-3.631268	0.129089	3.325504
35	1	0	-3.574198	-1.630230	3.188870
36	6	0	-1.005228	-2.009781	4.053442
37	1	0	-1.431143	-2.874860	3.534444
38	1	0	0.080255	-2.062857	3.958842
39	1	0	-1.252496	-2.097798	5.117087
40	7	0	-1.363572	-0.603788	2.005478
41	7	0	1.025267	-0.735869	-2.157435
42	8	0	-2.396846	-0.503252	1.252750
43	8	0	-0.143490	-0.631510	-2.674603

DFT calculations on nitroxide diradical 4a at the UB3LYP/6-31G(d) level with Gaussian 03



4a



```
*****************************************
 Gaussian 03:  IA32W-G03RevC.02 12-Jun-2004
               28-Sep-2007
 *****************************************
 %chk=C:\G03W\Radicals\Oxazene NO\Freq_Oxaxene_MTDiNO_B3LYP_S1r1.chk
 %mem=6MW
 %nproc=1
 Will use up to    1 processors via shared memory.
 -------------------------------------------
 # opt freq ub3lyp/6-31g(d) geom=connectivity
 -------------------------------------------

SCF Done:  E(UB+HF-LYP) =  -1111.85524353     A.U. after   18 cycles
             Convg  =    0.9640D-08             -V/T =  2.0093
             S**2   =   2.0340
 Annihilation of the first spin contaminant:
 S**2 before annihilation     2.0340,   after     2.0006
```

```
Item               Value     Threshold  Converged?
 Maximum Force            0.000006     0.000450     YES
 RMS     Force            0.000002     0.000300     YES
 Maximum Displacement     0.000554     0.001800     YES
 RMS     Displacement     0.000103     0.001200     YES
 Predicted change in Energy=-4.120980D-09
 Optimization completed.
    -- Stationary point found.
                           ----------------------------
                           !   Optimized Parameters   !
                           ! (Angstroms and Degrees)  !
 --------------------------                            -------------------------
 ! Name  Definition              Value          Derivative Info.                !
 ---------------------------------------------------------------------------------
 ! R1    R(1,2)                  1.4141         -DE/DX =    0.0                 !
 ! R2    R(1,6)                  1.3979         -DE/DX =    0.0                 !
 ! R3    R(1,8)                  1.3998         -DE/DX =    0.0                 !
 ! R4    R(2,3)                  1.3968         -DE/DX =    0.0                 !
 ! R5    R(2,13)                 1.522          -DE/DX =    0.0                 !
 ! R6    R(3,4)                  1.3968         -DE/DX =    0.0                 !
 ! R7    R(3,7)                  1.0862         -DE/DX =    0.0                 !
 ! R8    R(4,5)                  1.4141         -DE/DX =    0.0                 !
 ! R9    R(4,14)                 1.522          -DE/DX =    0.0                 !
 ! R10   R(5,6)                  1.3979         -DE/DX =    0.0                 !
 ! R11   R(5,9)                  1.3998         -DE/DX =    0.0                 !
 ! R12   R(6,18)                 1.0806         -DE/DX =    0.0                 !
 ! R13   R(8,10)                 1.4964         -DE/DX =    0.0                 !
 ! R14   R(8,17)                 1.279          -DE/DX =    0.0                 !
 ! R15   R(9,11)                 1.4964         -DE/DX =    0.0                 !
 ! R16   R(9,12)                 1.279          -DE/DX =    0.0                 !
 ! R17   R(10,15)                1.4146         -DE/DX =    0.0                 !
 ! R18   R(10,43)                1.5373         -DE/DX =    0.0                 !
 ! R19   R(10,47)                1.5264         -DE/DX =    0.0                 !
 ! R20   R(11,16)                1.4146         -DE/DX =    0.0                 !
 ! R21   R(11,19)                1.5264         -DE/DX =    0.0                 !
 ! R22   R(11,23)                1.5373         -DE/DX =    0.0                 !
 ! R23   R(13,15)                1.4453         -DE/DX =    0.0                 !
 ! R24   R(13,35)                1.5401         -DE/DX =    0.0                 !
 ! R25   R(13,39)                1.5415         -DE/DX =    0.0                 !
 ! R26   R(14,16)                1.4453         -DE/DX =    0.0                 !
 ! R27   R(14,27)                1.5415         -DE/DX =    0.0                 !
 ! R28   R(14,31)                1.5401         -DE/DX =    0.0                 !
 ! R29   R(19,20)                1.0902         -DE/DX =    0.0                 !
 ! R30   R(19,21)                1.0936         -DE/DX =    0.0                 !
 ! R31   R(19,22)                1.0929         -DE/DX =    0.0                 !
 ! R32   R(23,24)                1.0941         -DE/DX =    0.0                 !
 ! R33   R(23,25)                1.094          -DE/DX =    0.0                 !
 ! R34   R(23,26)                1.0931         -DE/DX =    0.0                 !
 ! R35   R(27,28)                1.0953         -DE/DX =    0.0                 !
 ! R36   R(27,29)                1.0948         -DE/DX =    0.0                 !
 ! R37   R(27,30)                1.0922         -DE/DX =    0.0                 !
 ! R38   R(31,32)                1.0943         -DE/DX =    0.0                 !
 ! R39   R(31,33)                1.0934         -DE/DX =    0.0                 !
 ! R40   R(31,34)                1.0949         -DE/DX =    0.0                 !
 ! R41   R(35,36)                1.0943         -DE/DX =    0.0                 !
 ! R42   R(35,37)                1.0934         -DE/DX =    0.0                 !
 ! R43   R(35,38)                1.0949         -DE/DX =    0.0                 !
 ! R44   R(39,40)                1.0953         -DE/DX =    0.0                 !
 ! R45   R(39,41)                1.0948         -DE/DX =    0.0                 !
 ! R46   R(39,42)                1.0922         -DE/DX =    0.0                 !
 ! R47   R(43,44)                1.0941         -DE/DX =    0.0                 !
 ! R48   R(43,45)                1.0939         -DE/DX =    0.0                 !
 ! R49   R(43,46)                1.0931         -DE/DX =    0.0                 !
 ! R50   R(47,48)                1.0902         -DE/DX =    0.0                 !
 ! R51   R(47,49)                1.0936         -DE/DX =    0.0                 !
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```
! R52   R(47,50)              1.0929         -DE/DX =    0.0                 !
! A1    A(2,1,6)             121.0099        -DE/DX =    0.0                 !
! A2    A(2,1,8)             119.972         -DE/DX =    0.0                 !
! A3    A(6,1,8)             119.0139        -DE/DX =    0.0                 !
! A4    A(1,2,3)             117.5756        -DE/DX =    0.0                 !
! A5    A(1,2,13)            121.1151        -DE/DX =    0.0                 !
! A6    A(3,2,13)            121.2589        -DE/DX =    0.0                 !
! A7    A(2,3,4)             123.1597        -DE/DX =    0.0                 !
! A8    A(2,3,7)             118.4202        -DE/DX =    0.0                 !
! A9    A(4,3,7)             118.4201        -DE/DX =    0.0                 !
! A10   A(3,4,5)             117.5756        -DE/DX =    0.0                 !
! A11   A(3,4,14)            121.2588        -DE/DX =    0.0                 !
! A12   A(5,4,14)            121.1152        -DE/DX =    0.0                 !
! A13   A(4,5,6)             121.0098        -DE/DX =    0.0                 !
! A14   A(4,5,9)             119.9722        -DE/DX =    0.0                 !
! A15   A(6,5,9)             119.0137        -DE/DX =    0.0                 !
! A16   A(1,6,5)             119.5876        -DE/DX =    0.0                 !
! A17   A(1,6,18)            120.2062        -DE/DX =    0.0                 !
! A18   A(5,6,18)            120.2062        -DE/DX =    0.0                 !
! A19   A(1,8,10)            119.1342        -DE/DX =    0.0                 !
! A20   A(1,8,17)            121.1201        -DE/DX =    0.0                 !
! A21   A(10,8,17)           118.2972        -DE/DX =    0.0                 !
! A22   A(5,9,11)            119.1343        -DE/DX =    0.0                 !
! A23   A(5,9,12)            121.1201        -DE/DX =    0.0                 !
! A24   A(11,9,12)           118.2972        -DE/DX =    0.0                 !
! A25   A(8,10,15)           109.1165        -DE/DX =    0.0                 !
! A26   A(8,10,43)           107.8879        -DE/DX =    0.0                 !
! A27   A(8,10,47)           108.9441        -DE/DX =    0.0                 !
! A28   A(15,10,43)          114.1742        -DE/DX =    0.0                 !
! A29   A(15,10,47)          105.117         -DE/DX =    0.0                 !
! A30   A(43,10,47)          111.4908        -DE/DX =    0.0                 !
! A31   A(9,11,16)           109.1165        -DE/DX =    0.0                 !
! A32   A(9,11,19)           108.9437        -DE/DX =    0.0                 !
! A33   A(9,11,23)           107.8876        -DE/DX =    0.0                 !
! A34   A(16,11,19)          105.1164        -DE/DX =    0.0                 !
! A35   A(16,11,23)          114.1759        -DE/DX =    0.0                 !
! A36   A(19,11,23)          111.4901        -DE/DX =    0.0                 !
! A37   A(2,13,15)           111.0969        -DE/DX =    0.0                 !
! A38   A(2,13,35)           110.1798        -DE/DX =    0.0                 !
! A39   A(2,13,39)           112.6354        -DE/DX =    0.0                 !
! A40   A(15,13,35)          102.8563        -DE/DX =    0.0                 !
! A41   A(15,13,39)          110.0406        -DE/DX =    0.0                 !
! A42   A(35,13,39)          109.5908        -DE/DX =    0.0                 !
! A43   A(4,14,16)           111.0968        -DE/DX =    0.0                 !
! A44   A(4,14,27)           112.6359        -DE/DX =    0.0                 !
! A45   A(4,14,31)           110.1793        -DE/DX =    0.0                 !
! A46   A(16,14,27)          110.042         -DE/DX =    0.0                 !
! A47   A(16,14,31)          102.8556        -DE/DX =    0.0                 !
! A48   A(27,14,31)          109.5899        -DE/DX =    0.0                 !
! A49   A(10,15,13)          122.118         -DE/DX =    0.0                 !
! A50   A(11,16,14)          122.1193        -DE/DX =    0.0                 !
! A51   A(11,19,20)          110.6554        -DE/DX =    0.0                 !
! A52   A(11,19,21)          108.7195        -DE/DX =    0.0                 !
! A53   A(11,19,22)          109.7515        -DE/DX =    0.0                 !
! A54   A(20,19,21)          109.7477        -DE/DX =    0.0                 !
! A55   A(20,19,22)          109.1404        -DE/DX =    0.0                 !
! A56   A(21,19,22)          108.7988        -DE/DX =    0.0                 !
! A57   A(11,23,24)          109.7843        -DE/DX =    0.0                 !
! A58   A(11,23,25)          109.2112        -DE/DX =    0.0                 !
! A59   A(11,23,26)          111.7446        -DE/DX =    0.0                 !
! A60   A(24,23,25)          109.1508        -DE/DX =    0.0                 !
! A61   A(24,23,26)          108.9729        -DE/DX =    0.0                 !
! A62   A(25,23,26)          107.9255        -DE/DX =    0.0                 !
! A63   A(14,27,28)          110.7529        -DE/DX =    0.0                 !
! A64   A(14,27,29)          109.2049        -DE/DX =    0.0                 !
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! A65   A(14,27,30)          112.1626         -DE/DX =    0.0                 !
! A66   A(28,27,29)          108.2375         -DE/DX =    0.0                 !
! A67   A(28,27,30)          107.7919         -DE/DX =    0.0                 !
! A68   A(29,27,30)          108.5873         -DE/DX =    0.0                 !
! A69   A(14,31,32)          111.1818         -DE/DX =    0.0                 !
! A70   A(14,31,33)          110.1439         -DE/DX =    0.0                 !
! A71   A(14,31,34)          109.4655         -DE/DX =    0.0                 !
! A72   A(32,31,33)          108.769          -DE/DX =    0.0                 !
! A73   A(32,31,34)          108.6414         -DE/DX =    0.0                 !
! A74   A(33,31,34)          108.5842         -DE/DX =    0.0                 !
! A75   A(13,35,36)          111.1818         -DE/DX =    0.0                 !
! A76   A(13,35,37)          110.144          -DE/DX =    0.0                 !
! A77   A(13,35,38)          109.4655         -DE/DX =    0.0                 !
! A78   A(36,35,37)          108.7689         -DE/DX =    0.0                 !
! A79   A(36,35,38)          108.6414         -DE/DX =    0.0                 !
! A80   A(37,35,38)          108.5842         -DE/DX =    0.0                 !
! A81   A(13,39,40)          110.7529         -DE/DX =    0.0                 !
! A82   A(13,39,41)          109.205          -DE/DX =    0.0                 !
! A83   A(13,39,42)          112.1621         -DE/DX =    0.0                 !
! A84   A(40,39,41)          108.2376         -DE/DX =    0.0                 !
! A85   A(40,39,42)          107.7921         -DE/DX =    0.0                 !
! A86   A(41,39,42)          108.5873         -DE/DX =    0.0                 !
! A87   A(10,43,44)          109.7842         -DE/DX =    0.0                 !
! A88   A(10,43,45)          109.2114         -DE/DX =    0.0                 !
! A89   A(10,43,46)          111.7444         -DE/DX =    0.0                 !
! A90   A(44,43,45)          109.1509         -DE/DX =    0.0                 !
! A91   A(44,43,46)          108.9727         -DE/DX =    0.0                 !
! A92   A(45,43,46)          107.9257         -DE/DX =    0.0                 !
! A93   A(10,47,48)          110.6554         -DE/DX =    0.0                 !
! A94   A(10,47,49)          108.7195         -DE/DX =    0.0                 !
! A95   A(10,47,50)          109.7515         -DE/DX =    0.0                 !
! A96   A(48,47,49)          109.7477         -DE/DX =    0.0                 !
! A97   A(48,47,50)          109.1404         -DE/DX =    0.0                 !
! A98   A(49,47,50)          108.7987         -DE/DX =    0.0                 !
! D1    D(6,1,2,3)            -2.6644         -DE/DX =    0.0                 !
! D2    D(6,1,2,13)          174.7841         -DE/DX =    0.0                 !
! D3    D(8,1,2,3)           176.5777         -DE/DX =    0.0                 !
! D4    D(8,1,2,13)           -5.9738         -DE/DX =    0.0                 !
! D5    D(2,1,6,5)             1.3716         -DE/DX =    0.0                 !
! D6    D(2,1,6,18)         -178.6286         -DE/DX =    0.0                 !
! D7    D(8,1,6,5)          -177.8777         -DE/DX =    0.0                 !
! D8    D(8,1,6,18)            2.1222         -DE/DX =    0.0                 !
! D9    D(2,1,8,10)          -13.2867         -DE/DX =    0.0                 !
! D10   D(2,1,8,17)         -179.3204         -DE/DX =    0.0                 !
! D11   D(6,1,8,10)          165.9705         -DE/DX =    0.0                 !
! D12   D(6,1,8,17)           -0.0632         -DE/DX =    0.0                 !
! D13   D(1,2,3,4)             1.3048         -DE/DX =    0.0                 !
! D14   D(1,2,3,7)          -178.6954         -DE/DX =    0.0                 !
! D15   D(13,2,3,4)         -176.1398         -DE/DX =    0.0                 !
! D16   D(13,2,3,7)            3.8601         -DE/DX =    0.0                 !
! D17   D(1,2,13,15)           -2.185          -DE/DX =    0.0                 !
! D18   D(1,2,13,35)        -115.5061         -DE/DX =    0.0                 !
! D19   D(1,2,13,39)         121.7902         -DE/DX =    0.0                 !
! D20   D(3,2,13,15)         175.1691         -DE/DX =    0.0                 !
! D21   D(3,2,13,35)          61.8481         -DE/DX =    0.0                 !
! D22   D(3,2,13,39)         -60.8557         -DE/DX =    0.0                 !
! D23   D(2,3,4,5)             1.3039         -DE/DX =    0.0                 !
! D24   D(2,3,4,14)         -176.1397         -DE/DX =    0.0                 !
! D25   D(7,3,4,5)          -178.6959         -DE/DX =    0.0                 !
! D26   D(7,3,4,14)            3.8605         -DE/DX =    0.0                 !
! D27   D(3,4,5,6)            -2.6641         -DE/DX =    0.0                 !
! D28   D(3,4,5,9)           176.5793         -DE/DX =    0.0                 !
! D29   D(14,4,5,6)          174.7834         -DE/DX =    0.0                 !
! D30   D(14,4,5,9)           -5.9732         -DE/DX =    0.0                 !
! D31   D(3,4,14,16)         175.1696         -DE/DX =    0.0                 !
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! D32   D(3,4,14,27)          -60.853          -DE/DX =    0.0                 !
! D33   D(3,4,14,31)           61.8496         -DE/DX =    0.0                 !
! D34   D(5,4,14,16)           -2.1836         -DE/DX =    0.0                 !
! D35   D(5,4,14,27)          121.7938         -DE/DX =    0.0                 !
! D36   D(5,4,14,31)         -115.5035         -DE/DX =    0.0                 !
! D37   D(4,5,6,1)              1.3719         -DE/DX =    0.0                 !
! D38   D(4,5,6,18)          -178.6279         -DE/DX =    0.0                 !
! D39   D(9,5,6,1)           -177.8786         -DE/DX =    0.0                 !
! D40   D(9,5,6,18)             2.1215         -DE/DX =    0.0                 !
! D41   D(4,5,9,11)           -13.288          -DE/DX =    0.0                 !
! D42   D(4,5,9,12)          -179.3217         -DE/DX =    0.0                 !
! D43   D(6,5,9,11)           165.9705         -DE/DX =    0.0                 !
! D44   D(6,5,9,12)            -0.0633         -DE/DX =    0.0                 !
! D45   D(1,8,10,15)           38.822          -DE/DX =    0.0                 !
! D46   D(1,8,10,43)          -85.74           -DE/DX =    0.0                 !
! D47   D(1,8,10,47)          153.0761         -DE/DX =    0.0                 !
! D48   D(17,8,10,15)        -154.7496         -DE/DX =    0.0                 !
! D49   D(17,8,10,43)          80.6885         -DE/DX =    0.0                 !
! D50   D(17,8,10,47)         -40.4955         -DE/DX =    0.0                 !
! D51   D(5,9,11,16)           38.8215         -DE/DX =    0.0                 !
! D52   D(5,9,11,19)          153.0748         -DE/DX =    0.0                 !
! D53   D(5,9,11,23)          -85.7425         -DE/DX =    0.0                 !
! D54   D(12,9,11,16)        -154.7499         -DE/DX =    0.0                 !
! D55   D(12,9,11,19)         -40.4967         -DE/DX =    0.0                 !
! D56   D(12,9,11,23)          80.6861         -DE/DX =    0.0                 !
! D57   D(8,10,15,13)         -50.3662         -DE/DX =    0.0                 !
! D58   D(43,10,15,13)         70.4251         -DE/DX =    0.0                 !
! D59   D(47,10,15,13)       -167.0804         -DE/DX =    0.0                 !
! D60   D(8,10,43,44)         176.3371         -DE/DX =    0.0                 !
! D61   D(8,10,43,45)         -64.0234         -DE/DX =    0.0                 !
! D62   D(8,10,43,46)          55.3096         -DE/DX =    0.0                 !
! D63   D(15,10,43,44)         54.8651         -DE/DX =    0.0                 !
! D64   D(15,10,43,45)        174.5046         -DE/DX =    0.0                 !
! D65   D(15,10,43,46)        -66.1624         -DE/DX =    0.0                 !
! D66   D(47,10,43,44)        -64.0787         -DE/DX =    0.0                 !
! D67   D(47,10,43,45)         55.5608         -DE/DX =    0.0                 !
! D68   D(47,10,43,46)        174.8938         -DE/DX =    0.0                 !
! D69   D(8,10,47,48)          59.4631         -DE/DX =    0.0                 !
! D70   D(8,10,47,49)        -179.9395         -DE/DX =    0.0                 !
! D71   D(8,10,47,50)         -61.0459         -DE/DX =    0.0                 !
! D72   D(15,10,47,48)        176.2951         -DE/DX =    0.0                 !
! D73   D(15,10,47,49)        -63.1076         -DE/DX =    0.0                 !
! D74   D(15,10,47,50)         55.7861         -DE/DX =    0.0                 !
! D75   D(43,10,47,48)        -59.4937         -DE/DX =    0.0                 !
! D76   D(43,10,47,49)         61.1037         -DE/DX =    0.0                 !
! D77   D(43,10,47,50)       -180.0027         -DE/DX =    0.0                 !
! D78   D(9,11,16,14)          -50.3637         -DE/DX =    0.0                 !
! D79   D(19,11,16,14)        -167.0772         -DE/DX =    0.0                 !
! D80   D(23,11,16,14)          70.4284         -DE/DX =    0.0                 !
! D81   D(9,11,19,20)           59.4633         -DE/DX =    0.0                 !
! D82   D(9,11,19,21)         -179.9394         -DE/DX =    0.0                 !
! D83   D(9,11,19,22)          -61.0457         -DE/DX =    0.0                 !
! D84   D(16,11,19,20)         176.2949         -DE/DX =    0.0                 !
! D85   D(16,11,19,21)         -63.1078         -DE/DX =    0.0                 !
! D86   D(16,11,19,22)          55.7859         -DE/DX =    0.0                 !
! D87   D(23,11,19,20)         -59.4925         -DE/DX =    0.0                 !
! D88   D(23,11,19,21)          61.1048         -DE/DX =    0.0                 !
! D89   D(23,11,19,22)        -180.0015         -DE/DX =    0.0                 !
! D90   D(9,11,23,24)          176.3343         -DE/DX =    0.0                 !
! D91   D(9,11,23,25)          -64.0263         -DE/DX =    0.0                 !
! D92   D(9,11,23,26)           55.3064         -DE/DX =    0.0                 !
! D93   D(16,11,23,24)          54.8613         -DE/DX =    0.0                 !
! D94   D(16,11,23,25)         174.5007         -DE/DX =    0.0                 !
! D95   D(16,11,23,26)         -66.1666         -DE/DX =    0.0                 !
! D96   D(19,11,23,24)         -64.0825         -DE/DX =    0.0                 !
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 ! D97   D(19,11,23,25)        55.5569         -DE/DX =    0.0                 !
 ! D98   D(19,11,23,26)       174.8896         -DE/DX =    0.0                 !
 ! D99   D(2,13,15,10)         32.8129         -DE/DX =    0.0                 !
 ! D100  D(35,13,15,10)       150.6727         -DE/DX =    0.0                 !
 ! D101  D(39,13,15,10)       -92.626          -DE/DX =    0.0                 !
 ! D102  D(2,13,35,36)        -64.2477         -DE/DX =    0.0                 !
 ! D103  D(2,13,35,37)         56.3958         -DE/DX =    0.0                 !
 ! D104  D(2,13,35,38)        175.716          -DE/DX =    0.0                 !
 ! D105  D(15,13,35,36)       177.2478         -DE/DX =    0.0                 !
 ! D106  D(15,13,35,37)       -62.1087         -DE/DX =    0.0                 !
 ! D107  D(15,13,35,38)        57.2115         -DE/DX =    0.0                 !
 ! D108  D(39,13,35,36)        60.2265         -DE/DX =    0.0                 !
 ! D109  D(39,13,35,37)      -179.13           -DE/DX =    0.0                 !
 ! D110  D(39,13,35,38)       -59.8098         -DE/DX =    0.0                 !
 ! D111  D(2,13,39,40)         65.5341         -DE/DX =    0.0                 !
 ! D112  D(2,13,39,41)       -175.3624         -DE/DX =    0.0                 !
 ! D113  D(2,13,39,42)        -54.9418         -DE/DX =    0.0                 !
 ! D114  D(15,13,39,40)      -169.9088         -DE/DX =    0.0                 !
 ! D115  D(15,13,39,41)       -50.8054         -DE/DX =    0.0                 !
 ! D116  D(15,13,39,42)        69.6152         -DE/DX =    0.0                 !
 ! D117  D(35,13,39,40)       -57.4993         -DE/DX =    0.0                 !
 ! D118  D(35,13,39,41)        61.6041         -DE/DX =    0.0                 !
 ! D119  D(35,13,39,42)      -177.9752         -DE/DX =    0.0                 !
 ! D120  D(4,14,16,11)         32.81           -DE/DX =    0.0                 !
 ! D121  D(27,14,16,11)       -92.6305         -DE/DX =    0.0                 !
 ! D122  D(31,14,16,11)       150.6688         -DE/DX =    0.0                 !
 ! D123  D(4,14,27,28)         65.5346         -DE/DX =    0.0                 !
 ! D124  D(4,14,27,29)       -175.3622         -DE/DX =    0.0                 !
 ! D125  D(4,14,27,30)        -54.9413         -DE/DX =    0.0                 !
 ! D126  D(16,14,27,28)      -169.907          -DE/DX =    0.0                 !
 ! D127  D(16,14,27,29)       -50.8038         -DE/DX =    0.0                 !
 ! D128  D(16,14,27,30)        69.617          -DE/DX =    0.0                 !
 ! D129  D(31,14,27,28)       -57.498          -DE/DX =    0.0                 !
 ! D130  D(31,14,27,29)        61.6052         -DE/DX =    0.0                 !
 ! D131  D(31,14,27,30)      -177.9739         -DE/DX =    0.0                 !
 ! D132  D(4,14,31,32)        -64.2477         -DE/DX =    0.0                 !
 ! D133  D(4,14,31,33)         56.3957         -DE/DX =    0.0                 !
 ! D134  D(4,14,31,34)        175.716          -DE/DX =    0.0                 !
 ! D135  D(16,14,31,32)       177.2484         -DE/DX =    0.0                 !
 ! D136  D(16,14,31,33)       -62.1081         -DE/DX =    0.0                 !
 ! D137  D(16,14,31,34)        57.2121         -DE/DX =    0.0                 !
 ! D138  D(27,14,31,32)        60.2262         -DE/DX =    0.0                 !
 ! D139  D(27,14,31,33)      -179.1304         -DE/DX =    0.0                 !
 ! D140  D(27,14,31,34)       -59.8101         -DE/DX =    0.0                 !
```

Repeat geometry optimization for 4a with “tight” convergence constraints

```
******************************************
 Gaussian 03:  IA32W-G03RevC.02 12-Jun-2004
               08-Oct-2007
 ******************************************
 %chk=C:\G03W\Radicals\Oxazene NO\Freq2_Oxaxene_MTDiNO_B3LYP_S1r1.chk
 %mem=8MW
 %nproc=1
 Will use up to    1 processors via shared memory.
 ------------------------------------------------
 # opt=tight freq ub3lyp/6-31g(d) geom=connectivity
 ------------------------------------------------
Step number 136 out of a maximum of 300
SCF Done:  E(UB+HF-LYP) =  -1111.85524353     A.U. after   23 cycles
             Convg  =    0.8097D-08             -V/T =  2.0093
             S**2   =   2.0340
 Annihilation of the first spin contaminant:
 S**2 before annihilation     2.0340,   after     2.0006
```

```
Item               Value     Threshold  Converged?
 Maximum Force            0.000001     0.000015     YES
 RMS     Force            0.000000     0.000010     YES
 Maximum Displacement     0.002057     0.000060     NO
 RMS     Displacement     0.000408     0.000040     NO
 Predicted change in Energy=-8.517637D-10
 GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad

                         Input orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0       -0.000059    0.000118   -0.000004
    2          6             0       -0.000055   -0.000040    1.414126
    3          6             0        1.238069   -0.000099    2.060714
    4          6             0        2.456445    0.026621    1.378166
    5          6             0        2.414465    0.083417   -0.034202
    6          6             0        1.196754    0.055937   -0.720186
    7          1             0        1.254203   -0.021954    3.146599
    8          7             0       -1.210488   -0.072256   -0.699288
    9          7             0        3.603619    0.184587   -0.765672
   10          6             0       -2.456891   -0.447946    0.038743
   11          6             0        4.871757    0.530594   -0.050501
   12          8             0        3.590477    0.250615   -2.042851
   13          6             0       -1.301815    0.057968    2.200652
   14          6             0        3.780954   -0.062081    2.122724
   15          8             0       -2.440103    0.160089    1.315901
   16          8             0        4.892341   -0.128274    1.201130
   17          8             0       -1.235384   -0.086551   -1.977916
   18          1             0        1.180701    0.077700   -1.800478
   19          6             0        6.051857   -0.049864   -0.825331
   20          1             0        6.081998    0.352229   -1.838241
   21          1             0        6.976269    0.204303   -0.299221
   22          1             0        5.962236   -1.138005   -0.874244
   23          6             0        4.958232    2.062630    0.042918
   24          1             0        5.843235    2.349191    0.618881
   25          1             0        5.035055    2.480923   -0.964974
   26          1             0        4.071396    2.490089    0.517863
   27          6             0        3.984129    1.101895    3.112740
   28          1             0        3.247801    1.055849    3.922254
   29          1             0        4.983424    1.029120    3.553984
   30          1             0        3.887425    2.076135    2.628695
   31          6             0        3.879038   -1.402544    2.874614
   32          1             0        3.114522   -1.475515    3.654153
   33          1             0        3.751514   -2.235397    2.177718
   34          1             0        4.865243   -1.487051    3.342620
   35          6             0       -1.376790    1.367306    3.008008
   36          1             0       -0.589414    1.409594    3.766787
   37          1             0       -1.269553    2.227382    2.341419
   38          1             0       -2.348615    1.432452    3.508092
   39          6             0       -1.476100   -1.144716    3.149029
   40          1             0       -0.715927   -1.130638    3.937413
   41          1             0       -2.461741   -1.090166    3.622439
   42          1             0       -1.394519   -2.098795    2.623789
   43          6             0       -2.540884   -1.982578    0.073082
   44          1             0       -3.408659   -2.292903    0.662785
   45          1             0       -2.647337   -2.360163   -0.948103
   46          1             0       -1.640577   -2.427872    0.504277
   47          6             0       -3.659369    0.162023   -0.676730
   48          1             0       -3.720022   -0.199466   -1.703483
   49          1             0       -4.567725   -0.113555   -0.133706
   50          1             0       -3.570758    1.251313   -0.684980
```