

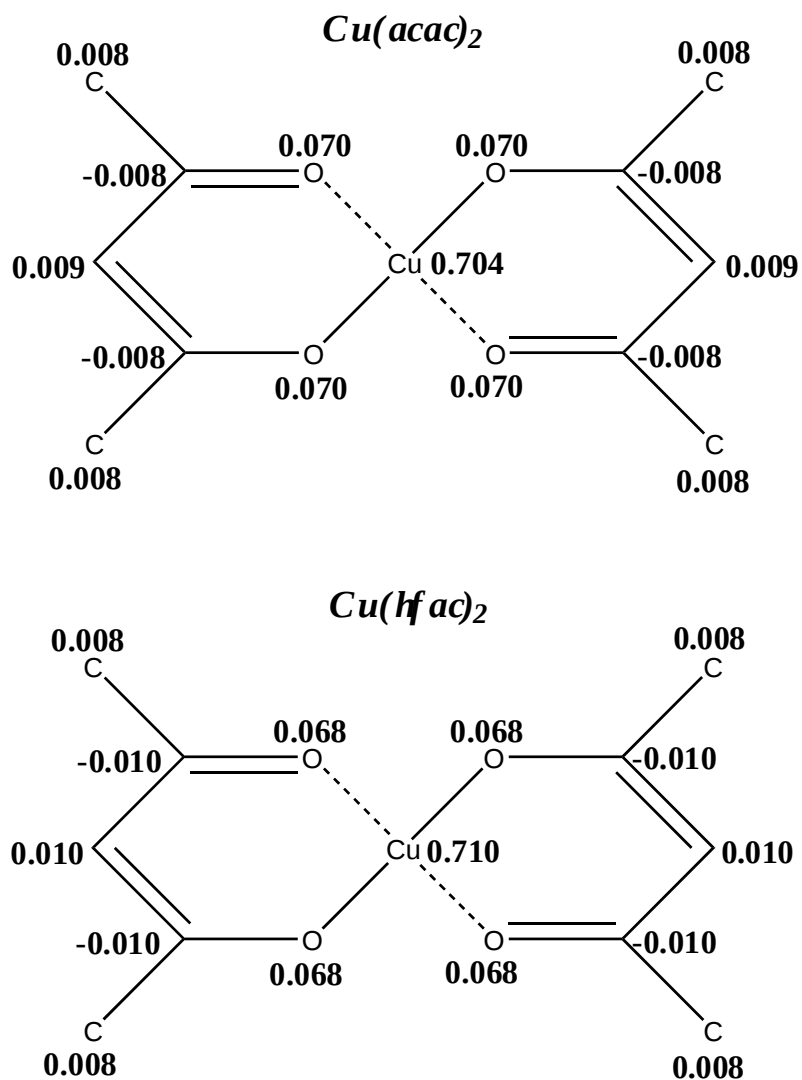


Fig. S1: UB3LYP/6-31G\* Mulliken atomic spin density distribution in Cu(acac)<sub>2</sub> (top) and Cu(hfac)<sub>2</sub> (bottom). Spin densities of hydrogen and fluorine atoms are not shown because they are smaller than 0.003.

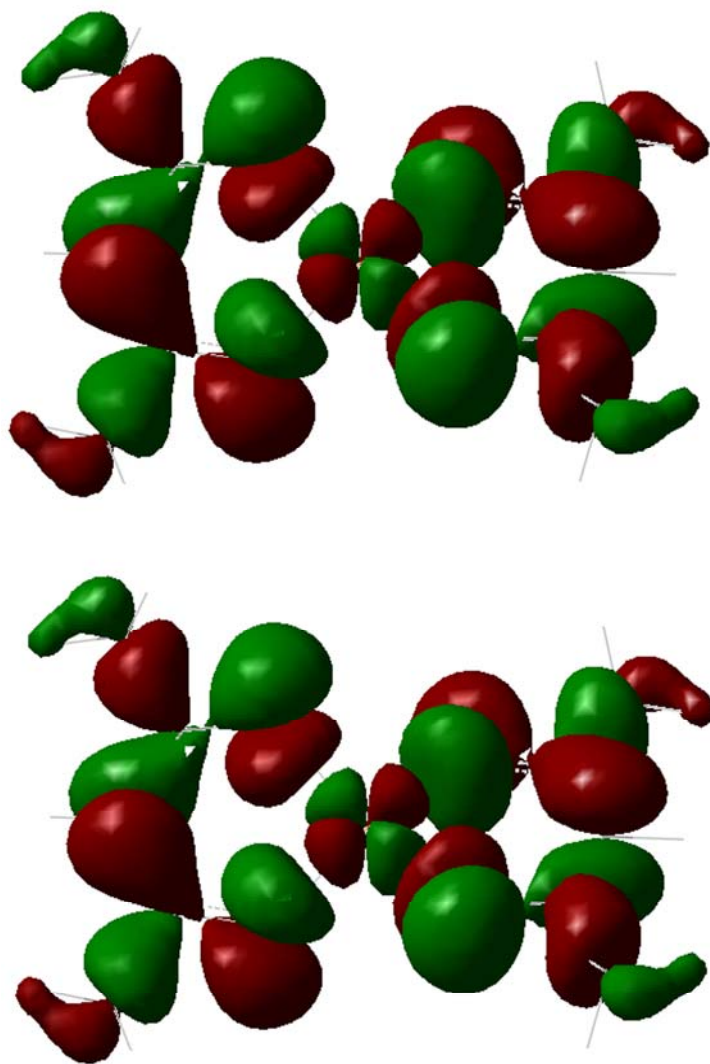


Fig. S2: Singly occupied canonical orbital of  $\text{Cu}(\text{acac})_2$  (top) and  $\text{Cu}(\text{hfac})_2$  (bottom). Contour value 0.02.

**UB3LYP/6-31G\* SCF-energies of the separate spin-states of the X-ray geometries, energy**

|             | Energy Doublet | Energy Quartet | delta E [a.u.] |
|-------------|----------------|----------------|----------------|
| Meta Xray H | -3401.18234510 | -3401.18204530 | -0.00029980    |
| Meta Xray F | -4592.04687850 | -4592.04654330 | -0.00033520    |
| Para xray H | -3401.61035460 | -3401.61092880 | 0.00057420     |
| Para xray F | -4592.47840420 | -4592.47897910 | 0.00057490     |

**UB3LYP/6-31G\* atomic spin densities of the crystallographic geometry of Meta- and Para**

|       | Meta Xray H Doublet | Meta Xray F Doublet |
|-------|---------------------|---------------------|
| 1 Cu  | -0.753              | -0.759              |
| 2 H/F | -0.002              | -0.001              |
| 3 H/F | 0.000               | 0.000               |
| 4 H/F | 0.000               | 0.000               |
| 5 H/F | 0.000               | 0.000               |
| 6 H/F | 0.000               | 0.000               |
| 7 H/F | 0.000               | 0.000               |
| 8 O   | -0.072              | -0.062              |
| 9 O   | 0.002               | 0.003               |
| 10 O  | 0.544               | 0.550               |
| 11 N  | -0.065              | -0.073              |
| 12 N  | 0.397               | 0.390               |
| 13 C  | -0.042              | -0.042              |
| 14 C  | 0.004               | 0.003               |
| 15 C  | 0.001               | 0.001               |
| 16 C  | -0.026              | -0.027              |
| 17 C  | 0.047               | 0.047               |
| 18 C  | -0.015              | -0.014              |
| 19 C  | 0.046               | 0.046               |
| 20 C  | 0.000               | 0.000               |
| 21 C  | -0.009              | -0.007              |
| 22 C  | 0.000               | 0.000               |
| 23 C  | 0.003               | 0.003               |
| 24 C  | 0.000               | 0.000               |
| 25 C  | 0.026               | 0.026               |
| 26 C  | 0.042               | 0.043               |
| 27 H  | 0.000               | 0.000               |
| 28 H  | -0.002              | -0.002              |
| 29 H  | -0.001              | -0.001              |
| 30 H  | 0.000               | 0.000               |
| 31 H  | -0.003              | -0.003              |
| 32 H  | 0.002               | 0.002               |
| 33 H  | 0.000               | 0.000               |
| 34 H  | -0.001              | 0.000               |
| 35 H  | 0.001               | 0.001               |
| 36 H  | -0.001              | -0.001              |
| 37 H  | -0.001              | -0.001              |
| 38 H  | 0.002               | 0.003               |
| 39 H  | -0.002              | -0.002              |
| 40 H  | -0.001              | -0.001              |

|        |        |        |
|--------|--------|--------|
| 41 H/F | -0.002 | -0.001 |
| 42 H/F | 0.000  | 0.000  |
| 43 H/F | 0.000  | 0.000  |
| 44 H/F | 0.000  | 0.000  |
| 45 H/F | 0.000  | 0.000  |
| 46 H/F | 0.000  | 0.000  |
| 47 O   | -0.072 | -0.062 |
| 48 O   | 0.002  | 0.003  |
| 49 O   | 0.544  | 0.550  |
| 50 N   | -0.065 | -0.073 |
| 51 N   | 0.397  | 0.390  |
| 52 C   | -0.042 | -0.042 |
| 53 C   | 0.004  | 0.003  |
| 54 C   | 0.001  | 0.001  |
| 55 C   | -0.026 | -0.027 |
| 56 C   | 0.047  | 0.047  |
| 57 C   | -0.015 | -0.014 |
| 58 C   | 0.046  | 0.046  |
| 59 C   | 0.000  | 0.000  |
| 60 C   | -0.009 | -0.007 |
| 61 C   | 0.000  | 0.000  |
| 62 C   | 0.003  | 0.003  |
| 63 C   | 0.000  | 0.000  |
| 64 C   | 0.026  | 0.026  |
| 65 C   | 0.042  | 0.043  |
| 66 H   | 0.000  | 0.000  |
| 67 H   | -0.002 | -0.002 |
| 68 H   | -0.001 | -0.001 |
| 69 H   | 0.000  | 0.000  |
| 70 H   | -0.003 | -0.003 |
| 71 H   | 0.002  | 0.002  |
| 72 H   | 0.000  | 0.000  |
| 73 H   | -0.001 | 0.000  |
| 74 H   | 0.001  | 0.001  |
| 75 H   | -0.001 | -0.001 |
| 76 H   | -0.001 | -0.001 |
| 77 H   | 0.002  | 0.003  |
| 78 H   | -0.002 | -0.002 |
| 79 H   | -0.001 | -0.001 |

|      | Para Xray H Doublet | Para Xray F Doublet |
|------|---------------------|---------------------|
| 1 Cu | -0.756              | -0.765              |
| 2 O  | 0.003               | 0.003               |
| 3 O  | -0.070              | -0.060              |
| 4 O  | 0.518               | 0.524               |
| 5 N  | 0.052               | 0.043               |
| 6 N  | 0.337               | 0.327               |
| 7 C  | 0.000               | 0.000               |
| 8 C  | 0.001               | 0.001               |
| 9 C  | 0.000               | 0.000               |
| 10 C | 0.003               | 0.003               |

|      |        |        |
|------|--------|--------|
| 11 C | -0.009 | -0.007 |
| 12 C | -0.046 | -0.042 |
| 13 C | 0.115  | 0.111  |
| 14 C | -0.078 | -0.071 |
| 15 C | 0.104  | 0.100  |
| 16 C | -0.043 | -0.039 |
| 17 C | -0.023 | -0.023 |
| 18 C | 0.010  | 0.010  |
| 19 C | 0.012  | 0.011  |
| 20 C | -0.001 | -0.001 |
| 21 O | 0.003  | 0.003  |
| 22 O | -0.070 | -0.060 |
| 23 O | 0.518  | 0.524  |
| 24 N | 0.052  | 0.043  |
| 25 N | 0.337  | 0.327  |
| 26 C | 0.000  | 0.000  |
| 27 C | 0.001  | 0.001  |
| 28 C | 0.000  | 0.000  |
| 29 C | 0.003  | 0.003  |
| 30 C | -0.009 | -0.007 |
| 31 C | -0.046 | -0.042 |
| 32 C | 0.115  | 0.111  |
| 33 C | -0.078 | -0.071 |
| 34 C | 0.104  | 0.100  |
| 35 C | -0.043 | -0.039 |
| 36 C | -0.023 | -0.023 |
| 37 C | 0.010  | 0.010  |
| 38 C | 0.012  | 0.011  |
| 39 C | -0.001 | -0.001 |
| 40 F | 0.000  | 0.000  |
| 41 F | 0.000  | 0.000  |
| 42 F | 0.000  | 0.000  |
| 43 H | 0.000  | 0.000  |
| 44 F | -0.002 | -0.001 |
| 45 F | 0.000  | 0.000  |
| 46 F | 0.000  | 0.000  |
| 47 H | 0.001  | 0.000  |
| 48 H | -0.006 | -0.006 |
| 49 H | -0.005 | -0.005 |
| 50 H | 0.001  | 0.000  |
| 51 H | 0.002  | 0.002  |
| 52 H | 0.000  | 0.000  |
| 53 H | 0.000  | 0.000  |
| 54 H | 0.004  | 0.004  |
| 55 H | -0.001 | -0.001 |
| 56 H | 0.000  | 0.000  |
| 57 H | -0.002 | -0.002 |
| 58 H | 0.001  | 0.001  |
| 59 H | 0.001  | 0.001  |
| 60 F | 0.000  | 0.000  |
| 61 F | 0.000  | 0.000  |

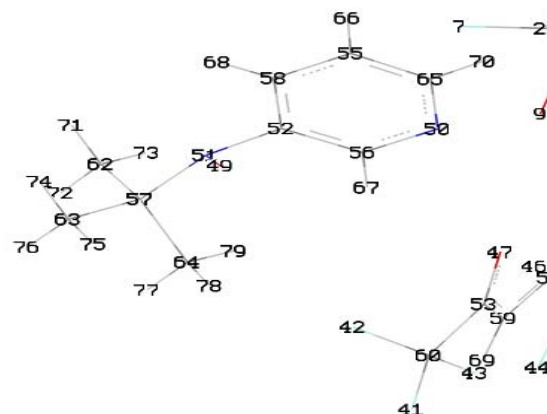
|      |        |        |
|------|--------|--------|
| 62 F | 0.000  | 0.000  |
| 63 H | 0.000  | 0.000  |
| 64 F | -0.002 | -0.001 |
| 65 F | 0.000  | 0.000  |
| 66 F | 0.000  | 0.000  |
| 67 H | 0.001  | 0.000  |
| 68 H | -0.006 | -0.006 |
| 69 H | -0.005 | -0.005 |
| 70 H | 0.001  | 0.000  |
| 71 H | 0.002  | 0.002  |
| 72 H | 0.000  | 0.000  |
| 73 H | 0.000  | 0.000  |
| 74 H | 0.004  | 0.004  |
| 75 H | -0.001 | -0.001 |
| 76 H | 0.000  | 0.000  |
| 77 H | -0.002 | -0.002 |
| 78 H | 0.001  | 0.001  |
| 79 H | 0.001  | 0.001  |

**y of the doublet-quartet splitting and J estimates of Cu(hfac)2(Py-tBu-NO)2 and Cu(acac)2(Py-tl**

| delta E [K] | J=delta E/2 [K] |
|-------------|-----------------|
| -94.67      | -47.33462003    |
| -105.85     | -52.92383139    |
| 181.32      | 90.65890199     |
| 181.54      | 90.76942317     |

**a- Cu(hfac)2(Py-tBu-NO)2 and Cu(acac)2(Py-tBu-NO)2 in doublet and quartet state**

| Meta Xray H Quartet | Meta Xray F Quartet |
|---------------------|---------------------|
| 0.755               | 0.762               |
| 0.002               | 0.001               |
| 0.000               | 0.000               |
| 0.000               | 0.000               |
| 0.000               | 0.000               |
| 0.000               | 0.000               |
| 0.000               | 0.000               |
| 0.000               | 0.000               |
| 0.072               | 0.063               |
| -0.002              | -0.003              |
| 0.545               | 0.550               |
| 0.033               | 0.041               |
| 0.398               | 0.391               |
| -0.033              | -0.032              |
| -0.003              | -0.002              |
| -0.001              | -0.001              |
| -0.016              | -0.016              |
| 0.036               | 0.035               |
| -0.015              | -0.014              |
| 0.037               | 0.037               |
| 0.000               | 0.000               |
| 0.009               | 0.007               |
| 0.000               | 0.000               |
| 0.003               | 0.003               |
| 0.000               | 0.001               |
| 0.026               | 0.026               |
| 0.031               | 0.032               |
| 0.001               | 0.001               |
| 0.000               | 0.000               |
| -0.001              | -0.001              |
| 0.000               | 0.000               |
| -0.001              | -0.001              |
| 0.002               | 0.002               |
| 0.000               | 0.000               |
| -0.001              | -0.001              |
| 0.001               | 0.001               |
| -0.001              | -0.001              |
| -0.001              | -0.001              |
| 0.002               | 0.003               |
| -0.002              | -0.002              |
| -0.001              | -0.001              |

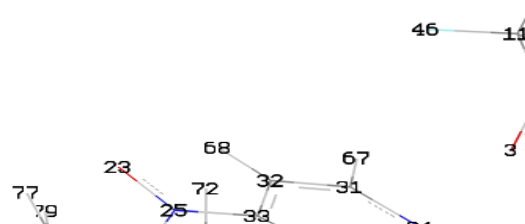


|        |        |
|--------|--------|
| 0.002  | 0.001  |
| 0.000  | 0.000  |
| 0.000  | 0.000  |
| 0.000  | 0.000  |
| 0.000  | 0.000  |
| 0.000  | 0.000  |
| 0.072  | 0.063  |
| -0.002 | -0.003 |
| 0.545  | 0.550  |
| 0.033  | 0.041  |
| 0.398  | 0.391  |
| -0.033 | -0.032 |
| -0.003 | -0.002 |
| -0.001 | -0.001 |
| -0.016 | -0.016 |
| 0.036  | 0.035  |
| -0.015 | -0.014 |
| 0.037  | 0.037  |
| 0.000  | 0.000  |
| 0.009  | 0.007  |
| 0.000  | 0.000  |
| 0.003  | 0.003  |
| 0.000  | 0.001  |
| 0.026  | 0.026  |
| 0.031  | 0.032  |
| 0.001  | 0.001  |
| 0.000  | 0.000  |
| -0.001 | -0.001 |
| 0.000  | 0.000  |
| -0.001 | -0.001 |
| 0.002  | 0.002  |
| 0.000  | 0.000  |
| -0.001 | -0.001 |
| 0.001  | 0.001  |
| -0.001 | -0.001 |
| -0.001 | -0.001 |
| 0.002  | 0.003  |
| -0.002 | -0.002 |
| -0.001 | -0.001 |

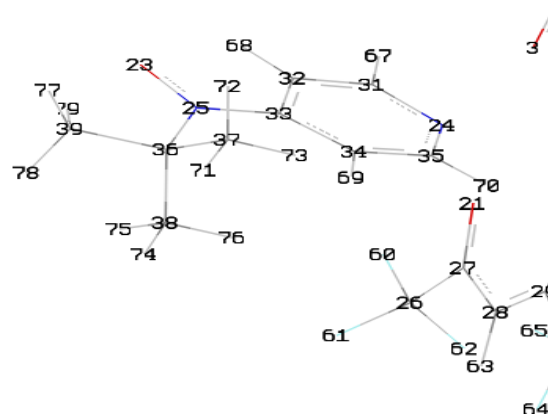
Para Xray H Quartet

Para Xray F Quartet

|        |        |
|--------|--------|
| 0.756  | 0.763  |
| 0.000  | -0.001 |
| 0.071  | 0.061  |
| 0.517  | 0.523  |
| 0.153  | 0.157  |
| 0.336  | 0.326  |
| 0.000  | 0.000  |
| -0.001 | -0.001 |
| 0.001  | 0.000  |
| -0.004 | -0.003 |

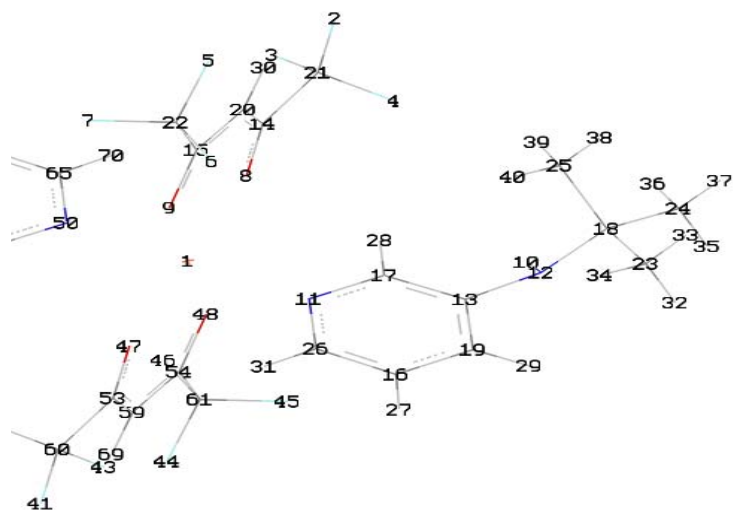


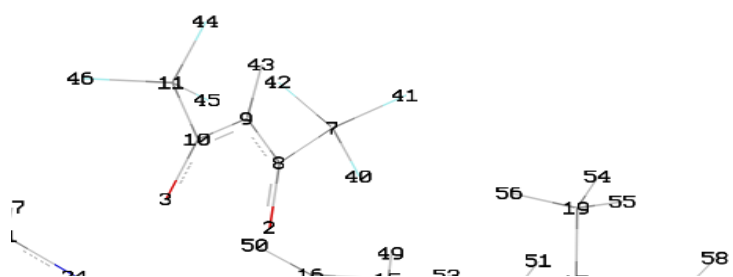
|        |        |
|--------|--------|
| 0.009  | 0.007  |
| -0.055 | -0.052 |
| 0.123  | 0.121  |
| -0.085 | -0.078 |
| 0.113  | 0.110  |
| -0.053 | -0.048 |
| -0.023 | -0.023 |
| 0.010  | 0.010  |
| 0.012  | 0.011  |
| -0.001 | -0.001 |
| 0.000  | -0.001 |
| 0.071  | 0.061  |
| 0.517  | 0.523  |
| 0.153  | 0.157  |
| 0.336  | 0.326  |
| 0.000  | 0.000  |
| -0.001 | -0.001 |
| 0.001  | 0.000  |
| -0.004 | -0.003 |
| 0.009  | 0.007  |
| -0.055 | -0.052 |
| 0.123  | 0.121  |
| -0.085 | -0.078 |
| 0.113  | 0.110  |
| -0.053 | -0.048 |
| -0.023 | -0.023 |
| 0.010  | 0.010  |
| 0.012  | 0.011  |
| -0.001 | -0.001 |
| 0.000  | 0.000  |
| 0.000  | 0.000  |
| 0.000  | 0.000  |
| 0.000  | 0.000  |
| 0.000  | 0.000  |
| 0.002  | 0.001  |
| 0.000  | 0.000  |
| 0.000  | 0.000  |
| 0.003  | 0.003  |
| -0.006 | -0.005 |
| -0.005 | -0.004 |
| 0.003  | 0.003  |
| 0.002  | 0.002  |
| 0.000  | 0.000  |
| 0.000  | 0.000  |
| 0.004  | 0.004  |
| -0.001 | -0.001 |
| 0.000  | 0.000  |
| -0.002 | -0.002 |
| 0.001  | 0.001  |
| 0.001  | 0.001  |
| 0.000  | 0.000  |
| 0.000  | 0.000  |

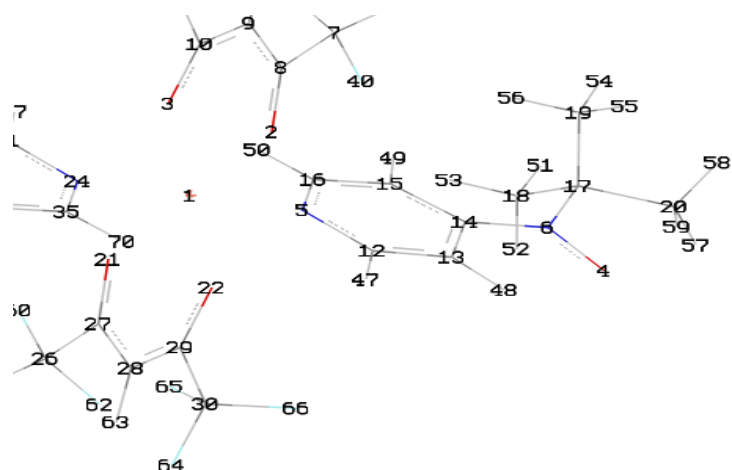


|        |        |
|--------|--------|
| 0.000  | 0.000  |
| 0.000  | 0.000  |
| 0.002  | 0.001  |
| 0.000  | 0.000  |
| 0.000  | 0.000  |
| 0.003  | 0.003  |
| -0.006 | -0.005 |
| -0.005 | -0.004 |
| 0.003  | 0.003  |
| 0.002  | 0.002  |
| 0.000  | 0.000  |
| 0.000  | 0.000  |
| 0.004  | 0.004  |
| -0.001 | -0.001 |
| 0.000  | 0.000  |
| -0.002 | -0.002 |
| 0.001  | 0.001  |
| 0.001  | 0.001  |

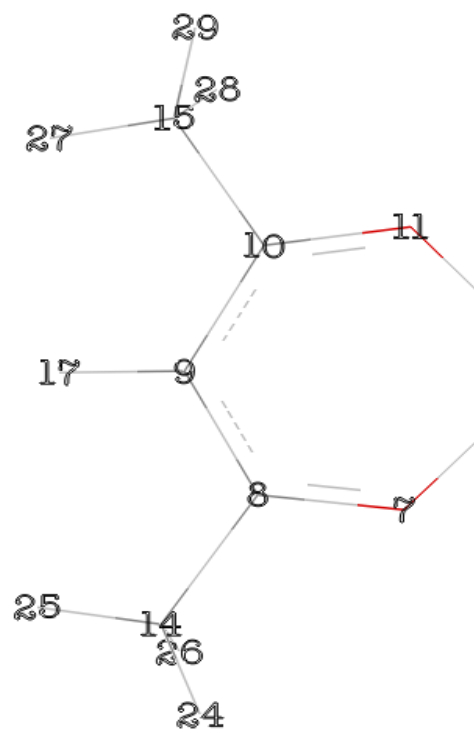
Bu-NO)<sub>2</sub>







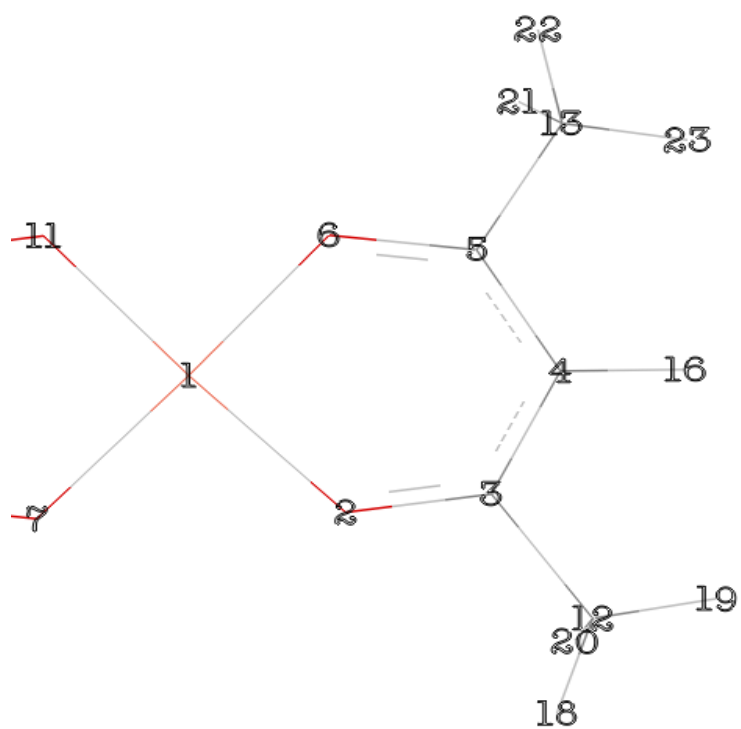
|            | Cu(acac) <sub>2</sub> | Cu(hfac) <sub>2</sub> | $\Delta X = X(\text{acac}) - X(\text{hfac})$ | X=R,A,D                   |
|------------|-----------------------|-----------------------|----------------------------------------------|---------------------------|
| R(1,2)     | 1.900                 | 1.901                 | 0.000                                        |                           |
| R(1,6)     | 1.900                 | 1.901                 | 0.000                                        | $\Delta R_{\text{ave}} =$ |
| R(1,7)     | 1.900                 | 1.901                 | 0.000                                        | -0.013 Å                  |
| R(1,11)    | 1.900                 | 1.901                 | 0.000                                        | $\Delta A_{\text{ave}} =$ |
| R(2,3)     | 1.278                 | 1.268                 | 0.010                                        | 0.027 °                   |
| R(3,4)     | 1.405                 | 1.398                 | 0.007                                        | $\Delta D_{\text{ave}} =$ |
| R(3,12)    | 1.513                 | 1.538                 | -0.026                                       | 1.712 °                   |
| R(4,5)     | 1.405                 | 1.398                 | 0.007                                        |                           |
| R(4,16)    | 1.083                 | 1.079                 | 0.004                                        |                           |
| R(5,6)     | 1.278                 | 1.268                 | 0.010                                        |                           |
| R(5,13)    | 1.513                 | 1.538                 | -0.026                                       |                           |
| R(7,8)     | 1.278                 | 1.268                 | 0.010                                        |                           |
| R(8,9)     | 1.405                 | 1.398                 | 0.007                                        |                           |
| R(8,14)    | 1.513                 | 1.538                 | -0.026                                       |                           |
| R(9,10)    | 1.405                 | 1.398                 | 0.007                                        |                           |
| R(9,17)    | 1.083                 | 1.079                 | 0.004                                        |                           |
| R(10,11)   | 1.278                 | 1.268                 | 0.010                                        |                           |
| R(10,15)   | 1.513                 | 1.538                 | -0.026                                       |                           |
| R(12,18)   | 1.096                 | 1.340                 | -0.245                                       |                           |
| R(12,19)   | 1.093                 | 1.346                 | -0.254                                       |                           |
| R(12,20)   | 1.096                 | 1.344                 | -0.248                                       |                           |
| R(13,21)   | 1.096                 | 1.346                 | -0.250                                       |                           |
| R(13,22)   | 1.096                 | 1.344                 | -0.248                                       |                           |
| R(13,23)   | 1.093                 | 1.341                 | -0.248                                       |                           |
| R(14,24)   | 1.096                 | 1.340                 | -0.244                                       |                           |
| R(14,25)   | 1.093                 | 1.346                 | -0.254                                       |                           |
| R(14,26)   | 1.096                 | 1.344                 | -0.248                                       |                           |
| R(15,27)   | 1.093                 | 1.344                 | -0.251                                       |                           |
| R(15,28)   | 1.096                 | 1.340                 | -0.244                                       |                           |
| R(15,29)   | 1.096                 | 1.346                 | -0.250                                       |                           |
| A(2,1,6)   | 94.969                | 94.430                | 0.539                                        |                           |
| A(2,1,7)   | 92.350                | 92.458                | -0.108                                       |                           |
| A(6,1,11)  | 92.350                | 92.468                | -0.117                                       |                           |
| A(7,1,11)  | 94.967                | 94.430                | 0.537                                        |                           |
| A(1,2,3)   | 125.279               | 124.715               | 0.564                                        |                           |
| A(2,3,4)   | 125.259               | 127.510               | -2.250                                       |                           |
| A(2,3,12)  | 115.022               | 113.221               | 1.801                                        |                           |
| A(3,4,5)   | 123.929               | 121.089               | 2.840                                        |                           |
| A(3,4,16)  | 118.035               | 119.456               | -1.421                                       |                           |
| A(4,5,6)   | 125.259               | 127.506               | -2.247                                       |                           |
| A(4,5,13)  | 119.721               | 119.267               | 0.454                                        |                           |
| A(1,6,5)   | 125.281               | 124.724               | 0.558                                        |                           |
| A(1,7,8)   | 125.284               | 124.726               | 0.558                                        |                           |
| A(7,8,9)   | 125.259               | 127.505               | -2.245                                       |                           |
| A(7,8,14)  | 115.020               | 113.223               | 1.797                                        |                           |
| A(8,9,10)  | 123.928               | 121.088               | 2.840                                        |                           |
| A(8,9,17)  | 118.037               | 119.459               | -1.422                                       |                           |
| A(9,10,11) | 125.259               | 127.512               | -2.252                                       |                           |
| A(9,10,15) | 119.718               | 119.267               | 0.451                                        |                           |



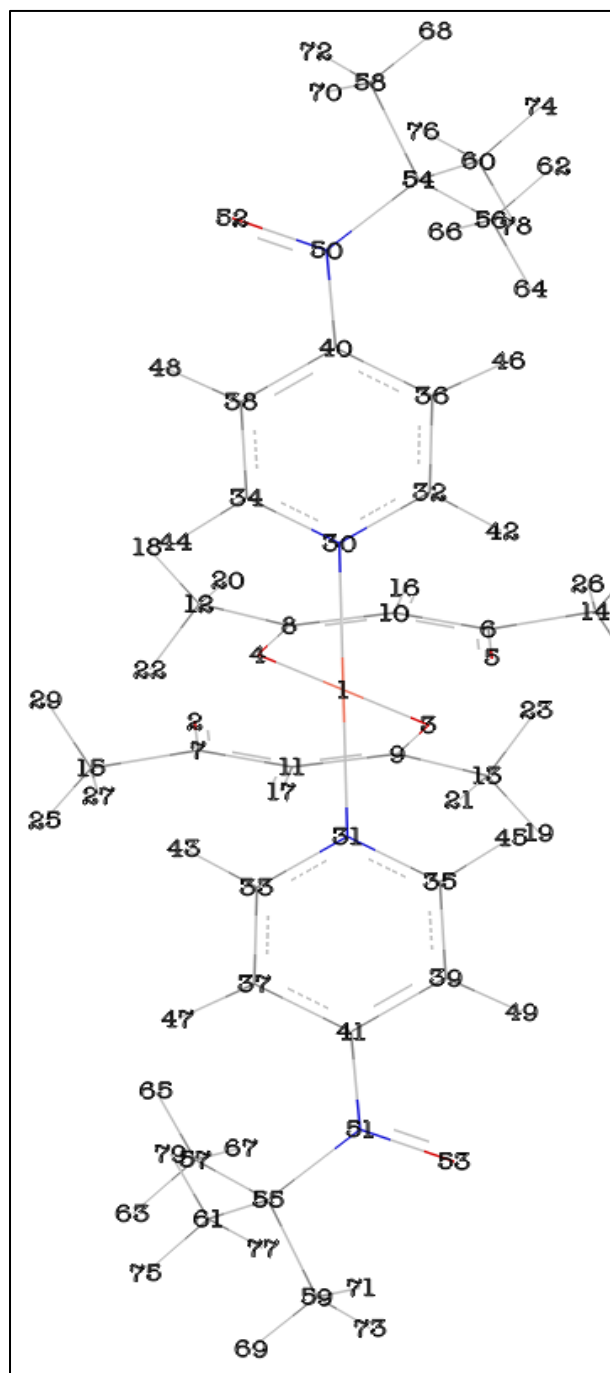
|              |          |          |        |
|--------------|----------|----------|--------|
| A(1,11,10)   | 125.280  | 124.713  | 0.567  |
| A(3,12,18)   | 109.316  | 110.212  | -0.896 |
| A(3,12,19)   | 112.626  | 112.134  | 0.492  |
| A(3,12,20)   | 109.335  | 109.603  | -0.269 |
| A(18,12,19)  | 109.281  | 108.240  | 1.040  |
| A(18,12,20)  | 106.961  | 108.465  | -1.504 |
| A(19,12,20)  | 109.161  | 108.090  | 1.071  |
| A(5,13,21)   | 109.335  | 112.132  | -2.797 |
| A(5,13,22)   | 109.315  | 109.613  | -0.298 |
| A(5,13,23)   | 112.628  | 110.203  | 2.425  |
| A(21,13,22)  | 106.961  | 108.093  | -1.132 |
| A(21,13,23)  | 109.163  | 108.238  | 0.925  |
| A(22,13,23)  | 109.278  | 108.466  | 0.813  |
| A(8,14,24)   | 109.317  | 110.214  | -0.897 |
| A(8,14,25)   | 112.627  | 112.133  | 0.494  |
| A(8,14,26)   | 109.334  | 109.601  | -0.267 |
| A(24,14,25)  | 109.284  | 108.245  | 1.040  |
| A(24,14,26)  | 106.962  | 108.466  | -1.504 |
| A(25,14,26)  | 109.156  | 108.087  | 1.070  |
| A(10,15,27)  | 112.627  | 109.602  | 3.025  |
| A(10,15,28)  | 109.335  | 110.208  | -0.872 |
| A(10,15,29)  | 109.316  | 112.139  | -2.823 |
| A(27,15,28)  | 109.161  | 108.464  | 0.697  |
| A(27,15,29)  | 109.281  | 108.093  | 1.188  |
| A(28,15,29)  | 106.960  | 108.239  | -1.279 |
| D(6,1,2,3)   | 0.725    | 0.810    | -0.084 |
| D(7,1,2,3)   | 152.382  | 153.284  | -0.902 |
| D(2,1,6,5)   | 0.732    | 0.715    | 0.017  |
| D(11,1,6,5)  | 152.359  | 153.134  | -0.775 |
| D(2,1,7,8)   | 152.357  | 153.190  | -0.833 |
| D(11,1,7,8)  | 0.730    | 0.773    | -0.044 |
| D(6,1,11,10) | 152.370  | 153.239  | -0.869 |
| D(7,1,11,10) | 0.714    | 0.763    | -0.049 |
| D(1,2,3,4)   | -1.500   | -1.670   | 0.170  |
| D(1,2,3,12)  | 178.679  | 177.788  | 0.891  |
| D(2,3,4,5)   | 0.819    | 0.916    | -0.098 |
| D(2,3,4,16)  | -179.178 | -179.092 | -0.086 |
| D(12,3,4,5)  | -179.368 | -178.513 | -0.855 |
| D(12,3,4,16) | 0.636    | 1.479    | -0.843 |
| D(2,3,12,18) | 57.908   | 55.138   | 2.770  |
| D(2,3,12,19) | 179.587  | 175.791  | 3.796  |
| D(2,3,12,20) | -58.873  | -64.163  | 5.290  |
| D(4,3,12,18) | -121.924 | -125.355 | 3.431  |
| D(4,3,12,19) | -0.245   | -4.702   | 4.457  |
| D(4,3,12,20) | 121.295  | 115.344  | 5.950  |
| D(3,4,5,6)   | 0.827    | 0.894    | -0.067 |
| D(3,4,5,13)  | -179.364 | -178.532 | -0.832 |
| D(16,4,5,6)  | -179.176 | -179.097 | -0.079 |
| D(16,4,5,13) | 0.633    | 1.477    | -0.844 |
| D(4,5,6,1)   | -1.508   | -1.594   | 0.086  |
| D(4,5,13,21) | 121.344  | 115.369  | 5.974  |

|                |          |          |        |
|----------------|----------|----------|--------|
| D(4,5,13,22)   | -121.876 | -125.328 | 3.452  |
| D(4,5,13,23)   | -0.200   | -4.686   | 4.487  |
| D(6,5,13,21)   | -58.829  | -64.135  | 5.306  |
| D(6,5,13,22)   | 57.952   | 55.167   | 2.784  |
| D(6,5,13,23)   | 179.628  | 175.809  | 3.819  |
| D(1,7,8,9)     | -1.496   | -1.641   | 0.146  |
| D(1,7,8,14)    | 178.674  | 177.829  | 0.845  |
| D(7,8,9,10)    | 0.815    | 0.900    | -0.084 |
| D(7,8,9,17)    | -179.184 | -179.091 | -0.094 |
| D(14,8,9,10)   | -179.361 | -178.543 | -0.819 |
| D(14,8,9,17)   | 0.639    | 1.467    | -0.828 |
| D(7,8,14,24)   | 57.818   | 55.177   | 2.641  |
| D(7,8,14,25)   | 179.502  | 175.835  | 3.667  |
| D(7,8,14,26)   | -58.964  | -64.125  | 5.161  |
| D(9,8,14,24)   | -122.023 | -125.305 | 3.281  |
| D(9,8,14,25)   | -0.339   | -4.646   | 4.308  |
| D(9,8,14,26)   | 121.195  | 115.394  | 5.802  |
| D(8,9,10,11)   | 0.815    | 0.924    | -0.109 |
| D(8,9,10,15)   | -179.367 | -178.497 | -0.870 |
| D(17,9,10,11)  | -179.185 | -179.085 | -0.100 |
| D(17,9,10,15)  | 0.633    | 1.493    | -0.860 |
| D(9,10,11,1)   | -1.484   | -1.646   | 0.162  |
| D(15,10,11,1)  | 178.690  | 177.805  | 0.885  |
| D(9,10,15,27)  | -0.261   | -4.709   | 4.448  |
| D(9,10,15,28)  | 121.279  | 115.344  | 5.936  |
| D(9,10,15,29)  | -121.940 | -125.360 | 3.420  |
| D(11,10,15,27) | 179.575  | 175.791  | 3.785  |
| D(11,10,15,28) | -58.885  | -64.157  | 5.272  |
| D(11,10,15,29) | 57.896   | 55.139   | 2.757  |

(no C-F and corresponding C-H bonds)



|    |         |         |         |
|----|---------|---------|---------|
| Cu | 0.0000  | 0.0000  | 0.0000  |
| O  | -0.1285 | 0.0307  | 2.3193  |
| O  | 1.9752  | -0.0113 | 0.2040  |
| O  | -1.9752 | 0.0113  | -0.2040 |
| O  | 0.1285  | -0.0307 | -2.3193 |
| C  | -0.8924 | -0.0380 | -3.0408 |
| C  | 0.8924  | 0.0380  | 3.0408  |
| C  | -2.6823 | 0.0051  | -1.2625 |
| C  | 2.6823  | -0.0051 | 1.2625  |
| C  | -2.2375 | -0.0177 | -2.5858 |
| C  | 2.2375  | 0.0177  | 2.5858  |
| C  | -4.1768 | 0.0258  | -1.0087 |
| C  | 4.1768  | -0.0258 | 1.0087  |
| C  | -0.6642 | -0.0776 | -4.5442 |
| C  | 0.6642  | 0.0776  | 4.5442  |
| H  | -3.0071 | -0.0225 | -3.3483 |
| H  | 3.0071  | 0.0225  | 3.3483  |
| H  | -4.4320 | 0.9233  | -0.4342 |
| H  | 4.4320  | -0.9233 | 0.4342  |
| H  | -4.7628 | 0.0109  | -1.9300 |
| H  | 4.7628  | -0.0109 | 1.9300  |
| H  | -4.4504 | -0.8384 | -0.3930 |
| H  | 4.4504  | 0.8384  | 0.3930  |
| H  | -0.0075 | 0.7517  | -4.8284 |
| H  | 0.0075  | -0.7517 | 4.8284  |
| H  | -1.5888 | -0.0215 | -5.1236 |
| H  | 1.5888  | 0.0215  | 5.1236  |
| H  | -0.1394 | -1.0054 | -4.7993 |
| H  | 0.1394  | 1.0054  | 4.7993  |
| N  | 0.0150  | 1.9990  | -0.0293 |
| N  | -0.0150 | -1.9990 | 0.0293  |
| C  | 0.8238  | 2.6639  | -0.8562 |
| C  | -0.8238 | -2.6639 | 0.8562  |
| C  | -0.7825 | 2.7151  | 0.7732  |
| C  | 0.7825  | -2.7151 | -0.7732 |
| C  | 0.8758  | 4.0436  | -0.9223 |
| C  | -0.8758 | -4.0436 | 0.9223  |
| C  | -0.8025 | 4.0931  | 0.7814  |
| C  | 0.8025  | -4.0931 | -0.7814 |
| C  | 0.0447  | 4.8005  | -0.0853 |
| C  | -0.0447 | -4.8005 | 0.0853  |
| H  | 1.4523  | 2.0529  | -1.4948 |
| H  | -1.4523 | -2.0529 | 1.4948  |
| H  | -1.4235 | 2.1413  | 1.4333  |
| H  | 1.4235  | -2.1413 | -1.4333 |
| H  | 1.5607  | 4.4873  | -1.6253 |
| H  | -1.5607 | -4.4873 | 1.6253  |
| H  | -1.4618 | 4.6304  | 1.4475  |
| H  | 1.4618  | -4.6304 | -1.4475 |
| N  | -0.0013 | 6.2097  | -0.0526 |
| N  | 0.0013  | -6.2097 | 0.0526  |
| O  | -0.8193 | 6.7436  | 0.7639  |
| O  | 0.8193  | -6.7436 | -0.7639 |
| C  | 0.8397  | 7.1489  | -0.9051 |
| C  | -0.8397 | -7.1489 | 0.9051  |



|   |         |         |         |
|---|---------|---------|---------|
| C | 2.3308  | 6.9477  | -0.5895 |
| C | -2.3308 | -6.9477 | 0.5895  |
| C | 0.4547  | 8.5807  | -0.5221 |
| C | -0.4547 | -8.5807 | 0.5221  |
| C | 0.5111  | 6.9404  | -2.3924 |
| C | -0.5111 | -6.9404 | 2.3924  |
| H | 2.9135  | 7.6900  | -1.1441 |
| H | -2.9135 | -7.6900 | 1.1441  |
| H | 2.7084  | 5.9612  | -0.8593 |
| H | -2.7084 | -5.9612 | 0.8593  |
| H | 2.5145  | 7.1010  | 0.4784  |
| H | -2.5145 | -7.1010 | -0.4784 |
| H | 1.0555  | 9.2642  | -1.1302 |
| H | -1.0555 | -9.2642 | 1.1302  |
| H | 0.6529  | 8.7823  | 0.5320  |
| H | -0.6529 | -8.7823 | -0.5320 |
| H | -0.6016 | 8.7779  | -0.7124 |
| H | 0.6016  | -8.7779 | 0.7124  |
| H | 1.0592  | 7.6809  | -2.9835 |
| H | -1.0592 | -7.6809 | 2.9835  |
| H | -0.5586 | 7.0912  | -2.5671 |
| H | 0.5586  | -7.0912 | 2.5671  |
| H | 0.7790  | 5.9526  | -2.7678 |
| H | -0.7790 | -5.9526 | 2.7678  |

74

62

4

26 24  
14  
28

13

19

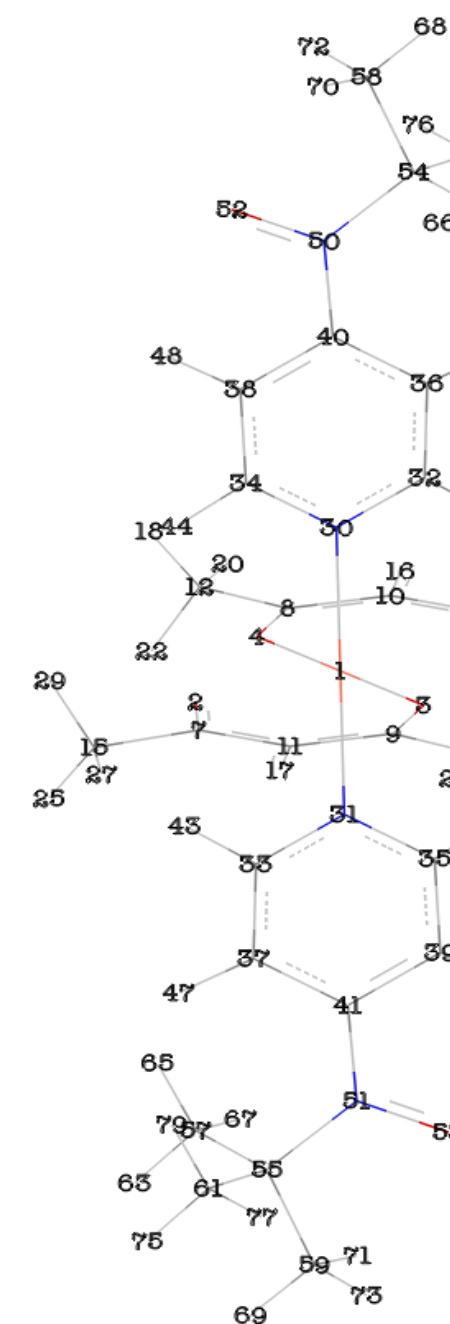
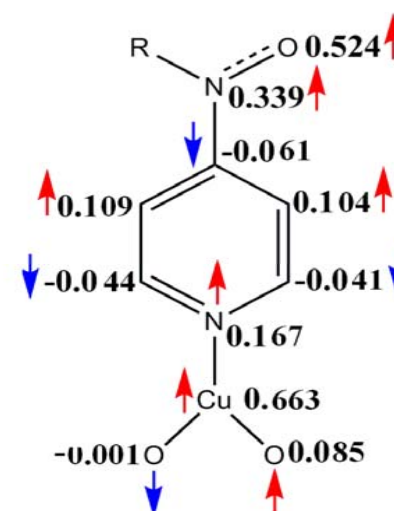
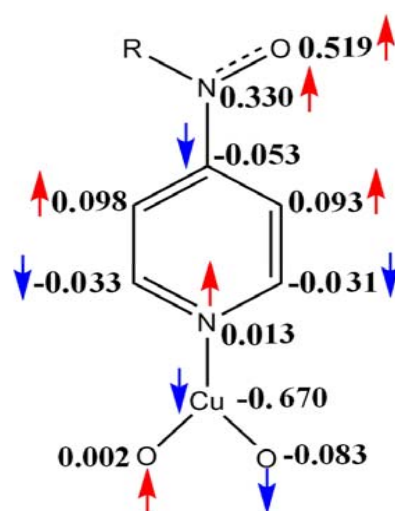
1

Spin densities in the optimized Rh-Para obtained with the DK-basis set

|      | Doublet | Quartet |
|------|---------|---------|
| 1 Cu | -0.670  | 0.663   |
| 2 O  | 0.002   | -0.001  |
| 3 O  | -0.083  | 0.085   |
| 4 O  | -0.083  | 0.085   |
| 5 O  | 0.002   | -0.001  |
| 6 C  | 0.000   | 0.000   |
| 7 C  | 0.000   | 0.000   |
| 8 C  | 0.003   | -0.003  |
| 9 C  | 0.003   | -0.003  |
| 10 C | 0.000   | 0.000   |
| 11 C | 0.000   | 0.000   |
| 12 C | -0.008  | 0.008   |
| 13 C | -0.008  | 0.008   |
| 14 C | 0.000   | 0.000   |
| 15 C | 0.000   | 0.000   |
| 16 H | 0.000   | 0.000   |
| 17 H | 0.000   | 0.000   |
| 18 H | 0.000   | 0.000   |
| 19 H | 0.000   | 0.000   |
| 20 H | -0.002  | 0.002   |
| 21 H | -0.002  | 0.002   |
| 22 H | 0.000   | 0.000   |
| 23 H | 0.000   | 0.000   |
| 24 H | 0.000   | 0.000   |
| 25 H | 0.000   | 0.000   |
| 26 H | 0.000   | 0.000   |
| 27 H | 0.000   | 0.000   |
| 28 H | 0.000   | 0.000   |
| 29 H | 0.000   | 0.000   |
| 30 N | 0.013   | 0.167   |
| 31 N | 0.013   | 0.167   |
| 32 C | -0.031  | -0.041  |
| 33 C | -0.031  | -0.041  |
| 34 C | -0.036  | -0.044  |
| 35 C | -0.036  | -0.044  |
| 36 C | 0.093   | 0.104   |
| 37 C | 0.093   | 0.104   |
| 38 C | 0.098   | 0.109   |
| 39 C | 0.098   | 0.109   |
| 40 C | -0.053  | -0.061  |
| 41 C | -0.053  | -0.061  |
| 42 H | 0.000   | 0.004   |
| 43 H | 0.000   | 0.004   |
| 44 H | 0.000   | 0.004   |
| 45 H | 0.000   | 0.004   |
| 46 H | -0.005  | -0.004  |
| 47 H | -0.005  | -0.004  |
| 48 H | -0.006  | -0.005  |
| 49 H | -0.006  | -0.005  |
| 50 N | 0.330   | 0.329   |
| 51 N | 0.330   | 0.329   |
| 52 O | 0.519   | 0.517   |
| 53 O | 0.519   | 0.517   |

Geometry of Rh-Para optimized as doublet and quartet (and deviation from the X-ray parameters) obtained with the D

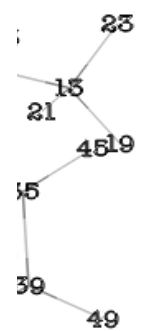
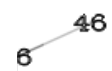
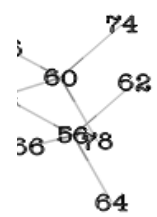
|                  | X ray | D     | deltD  | Q     | deltQ  |
|------------------|-------|-------|--------|-------|--------|
| Cu – O'          | 2.294 | 2.322 | -0.028 | 2.323 | -0.029 |
| Cu – O           | 2.036 | 1.983 | 0.053  | 1.986 | 0.050  |
| Cu – N           | 2.045 | 2.005 | 0.040  | 1.999 | 0.046  |
| N – O            | 1.28  | 1.273 | 0.007  | 1.273 | 0.007  |
| N – CtBu         | 1.39  | 1.522 | -0.132 | 1.522 | -0.132 |
| O'– Cu – O       | 85    | 87.28 | -2.28  | 87.28 | -2.28  |
| O'– Cu – O*      | 95    | 92.72 | 2.28   | 92.72 | 2.28   |
| O – Cu – N       | 89.4  | 89.98 | -0.58  | 89.99 | -0.59  |
| O – Cu – N*      | 90.6  | 90.02 | 0.58   | 90.01 | 0.59   |
| O'– Cu – N       | 91.4  | 90.10 | 1.30   | 90.11 | 1.29   |
| O'– Cu – N*      | 88.6  | 89.90 | -1.30  | 89.89 | -1.29  |
| C1 – C2 – N3 –O4 | 5.88  | 0.63  | 5.25   | 0.29  | 5.59   |



|      |        |        |
|------|--------|--------|
| 54 C | -0.026 | -0.026 |
| 55 C | -0.026 | -0.026 |
| 56 C | 0.013  | 0.013  |
| 57 C | 0.013  | 0.013  |
| 58 C | 0.000  | 0.000  |
| 59 C | 0.000  | 0.000  |
| 60 C | 0.013  | 0.013  |
| 61 C | 0.013  | 0.013  |
| 62 H | 0.002  | 0.002  |
| 63 H | 0.002  | 0.002  |
| 64 H | -0.001 | -0.001 |
| 65 H | -0.001 | -0.001 |
| 66 H | -0.001 | -0.001 |
| 67 H | -0.001 | -0.001 |
| 68 H | -0.001 | -0.001 |
| 69 H | -0.001 | -0.001 |
| 70 H | 0.000  | 0.000  |
| 71 H | 0.000  | 0.000  |
| 72 H | 0.000  | 0.000  |
| 73 H | 0.000  | 0.000  |
| 74 H | 0.002  | 0.002  |
| 75 H | 0.002  | 0.002  |
| 76 H | -0.001 | -0.001 |
| 77 H | -0.001 | -0.001 |
| 78 H | -0.001 | -0.001 |
| 79 H | -0.001 | -0.001 |

1K-basis set

8



53