Supporting Information for: Substituent Effects on the Thermal Decomposition of Phosphate Esters on Ferrous Surfaces

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Bonds Broken within the Phosphate Ester Molecules

Fig. S1 shows the change in the number of bonds remaining within the phosphate ester molecules (TNBP, TIBP, TSBP, TTBP, TCP) adsorbed on the Fe_3O_4(001) surface.

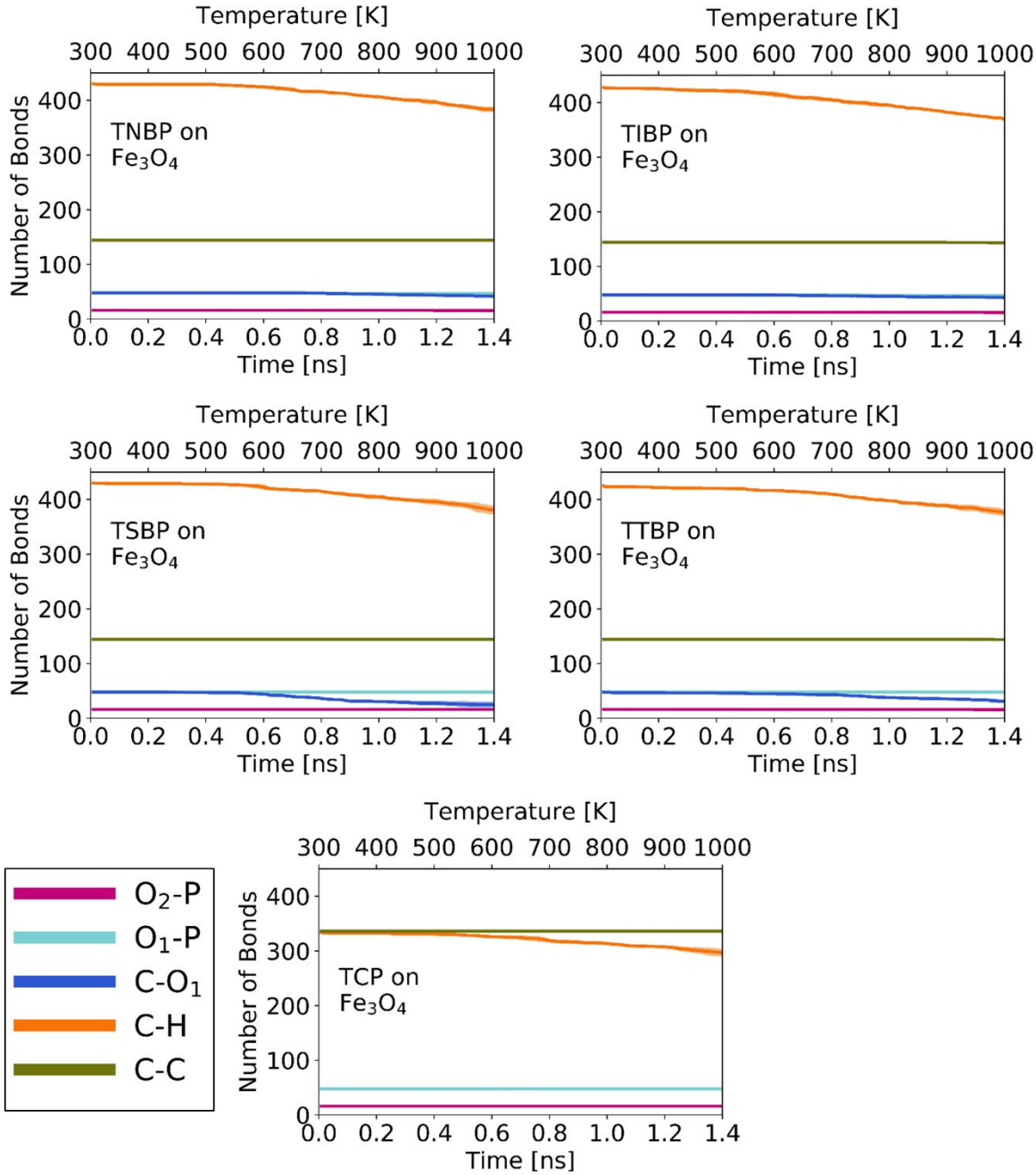

Figure S1. Change in the number of bonds within the TNBP, TIBP, TSBP, TTBP, and TCP molecules on the Fe_3O_4(001) surface. Solid lines are means of three independent simulations, shaded areas represent one standard deviation. Used for the percentages in Fig. 4.

Fig. S2 shows the change in the number of bonds remaining in some of the phosphate ester molecules (TNBP, TSBP) on different ferrous surfaces: α-Fe(110) and *a*-Fe_3O_4-OH.

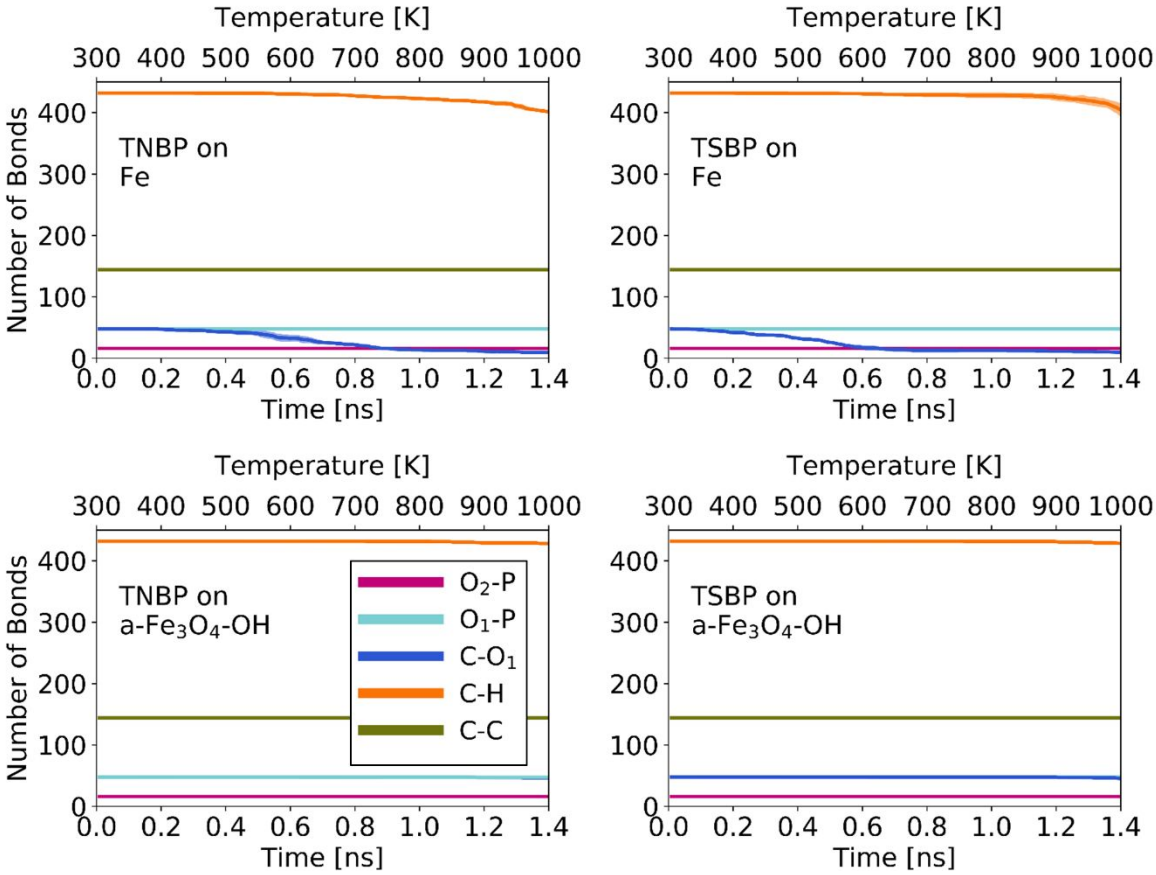

Figure S2. Change in the number of bonds within the TNBP and TSBP molecules on the α-Fe(110) and *a*-Fe_3O_4-OH surfaces. Solid lines are means of three independent simulations, shaded areas represent one standard deviation. Used for the percentages in Fig. 7.

ReaxFF Parameter File

Reactive MD-force field: C/H/O/Fe/P force field 2017_water

```
 39       ! Number of general parameters
   50.0000 !Overcoordination parameter
    9.5469 !Overcoordination parameter
   26.5405 !Valency angle conjugation parameter
    1.7224 !Triple bond stabilisation parameter
    6.8702 !Triple bond stabilisation parameter
   60.4850 !C2-correction
    1.0588 !Undercoordination parameter
    4.6000 !Triple bond stabilisation parameter
   12.1176 !Undercoordination parameter
   13.3056 !Undercoordination parameter
  -70.5044 !Triple bond stabilization energy
    0.0000 !Lower Taper-radius
   10.0000 !Upper Taper-radius
    2.8793 !Not used
   33.8667 !Valency undercoordination
    6.0891 !Valency angle/lone pair parameter
    1.0563 !Valency angle
    2.0384 !Valency angle parameter
    6.1431 !Not used
    6.9290 !Double bond/angle parameter
    0.3989 !Double bond/angle parameter: overcoord
    3.9954 !Double bond/angle parameter: overcoord
   -2.4837 !Not used
    5.7796 !Torsion/BO parameter
   10.0000 !Torsion overcoordination
    1.9487 !Torsion overcoordination
   -1.2327 !Conjugation 0 (not used)
    2.1645 !Conjugation
    1.5591 !vdWaals shielding
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  0.1000 !Cutoff for bond order (*100)
  2.1365 !Valency angle conjugation parameter
  0.6991 !Overcoordination parameter
 50.0000 !Overcoordination parameter
  1.8512 !Valency/lone pair parameter
  0.5000 !Not used
 20.0000 !Not used
  5.0000 !Molecular energy (not used)
  0.0000 !Molecular energy (not used)
  2.6962 !Valency angle conjugation parameter
 5    ! Nr of atoms; cov.r; valency;a.m;Rvdw;Evdw;gammaEEM;cov.r2;#
            alfa;gammavdW;valency;Eunder;Eover;chiEEM;etaEEM;n.u.

            cov r3;Elp;Heat inc.;n.u.;n.u.;n.u.;n.u.

            ov/un;val1;n.u.;val3,vval4

C    1.3817   4.0000  12.0000   1.8903   0.1838   0.9000   1.1341   4.0000
     9.7559   2.1346   4.0000  34.9350  79.5548   5.9666   7.0000   0.0000
     1.2114   0.0000 202.5551   8.9539  34.9289  13.5366   0.8563   0.0000
    -2.8983   2.5000   1.0564   4.0000   2.9663   0.0000   0.0000   0.0000
H    0.8930   1.0000   1.0080   1.3550   0.0930   0.8203  -0.1000   1.0000
     8.2230  33.2894   1.0000   0.0000 121.1250   3.7248   9.6093   1.0000
    -0.1000   0.0000  61.6606   3.0408   2.4197   0.0003   1.0698   0.0000
   -19.4571   4.2733   1.0338   1.0000   2.8793   0.0000   0.0000   0.0000
O    1.2450   2.0000  15.9990   2.3890   0.1000   1.0898   1.0548   6.0000
     9.7300  13.8449   4.0000  37.5000 116.0768   8.5000   8.3122   2.0000
     0.9049   0.4056  59.0626   3.5027   0.7640   0.0021   0.9745   0.0000
    -3.5500   2.9000   1.0493   4.0000   2.9225   0.0000   0.0000   0.0000
Fe   1.9029   3.0000  55.8450   2.0990   0.1181   0.4744  -1.6836   3.0000
    10.8548   2.6084   3.0000   0.0000  18.3725   1.7785   8.6281   0.0000
    -1.2000   0.0000 102.1000  25.3430  10.1260   0.7590   0.8563   0.0000
   -16.0573   2.6997   1.0338   6.0000   2.5791   0.0000   0.0000   0.0000
P    1.5994   3.0000  30.9738   1.7000   0.1743   1.0000   1.3000   5.0000
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```
   9.1909  14.2932   5.0000   0.0000   0.0000   1.8292   7.2520   0.0000
  -1.0000  10.2596   1.5000   0.2205  16.7429  15.9629   0.0000   0.0000
  -2.5000   1.6114   1.0338   5.0000   2.8793   0.0000   0.0000   0.0000
15      ! Nr of bonds; Edis1;LPpen;n.u.;pbe1;pbo5;13corr;pbo6

                    pbe2;pbo3;pbo4;n.u.;pbo1;pbo2;ovcorr

 1  1 158.2004  99.1897  78.0000  -0.7738  -0.4550   1.0000  37.6117   0.4147
      0.4590  -0.1000   9.1628   1.0000  -0.0777   6.7268   1.0000   0.0000
 1  2 169.4760   0.0000   0.0000  -0.6083   0.0000   1.0000   6.0000   0.7652
      5.2290   1.0000   0.0000   1.0000  -0.0500   6.9136   0.0000   0.0000
 2  2 153.3934   0.0000   0.0000  -0.4600   0.0000   1.0000   6.0000   0.7300
      6.2500   1.0000   0.0000   1.0000  -0.0790   6.0552   0.0000   0.0000
 1  3 164.4303  82.6772  60.8077  -0.3739  -0.2351   1.0000  10.5036   1.0000
      0.4475  -0.2288   7.0250   1.0000  -0.1363   4.8734   0.0000   0.0000
 2  3 160.0000   0.0000   0.0000  -0.5725   0.0000   1.0000   6.0000   0.5626
      1.1150   1.0000   0.0000   0.0000  -0.0920   4.2790   0.0000   0.0000
 3  3 142.2858 145.0000  50.8293   0.2506  -0.1000   1.0000  29.7503   0.6051
      0.3451  -0.1055   9.0000   1.0000  -0.1225   5.5000   1.0000   0.0000
 1  4 109.5214   0.0000   0.0000   0.6663  -0.3000   1.0000  36.0000   0.0100
      1.0648  -0.3500  15.0000   1.0000  -0.1512   4.1708   1.0000   0.0000
 2  4  78.2669   0.0000   0.0000   0.4668   0.0000   1.0000   6.0000   0.1766
      0.5673   1.0000   0.0000   1.0000  -0.1543   5.4965   0.0000   0.0000
 3  4  67.5128   0.0000   0.0000   0.1301  -0.3000   0.0000  36.0000   0.0852
      1.0000  -0.3500  15.0000   1.0000  -0.0629   7.1208   0.0000   0.0000
 4  4  41.4611   0.0000   0.0000   0.2931  -0.2000   0.0000  16.0000   0.2682
      0.6294  -0.2000  15.0000   1.0000  -0.0512   6.8013   0.0000   0.0000
 1  5 110.0000  92.0000   0.0000   0.2171  -0.1418   1.0000  13.1260   0.6000
      0.3601  -0.1310  10.7257   1.0000  -0.0869   5.3302   1.0000   0.0000
 2  5   0.1466   0.0000   0.0000   0.2250  -0.1418   1.0000  13.1260   0.6000
      0.3912  -0.1310   0.0000   1.0000  -0.1029   9.3302   0.0000   0.0000
 3  5 202.5868 164.1808   0.0000   0.5506  -0.5000   1.0000  25.0000   0.4300
      0.0912  -0.1285  16.0342   1.0000  -0.2008   6.2678   1.0000   0.0000
 4  5 267.6410   0.0000   0.0000  -0.9090  -0.3000   0.0000  36.0000   0.1000
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      1.7768  -0.3500  15.0000   1.0000  -0.0992   5.7752   0.0000   0.0000
 5  5   0.0000   0.0000   0.0000   0.2171  -0.5000   1.0000  35.0000   0.6000
      0.5000  -0.5000  20.0000   1.0000  -0.2000  10.0000   1.0000   0.0000
 8    ! Nr of off-diagonal terms; Ediss;Ro;gamma;rsigma;rpi;rpi2
 1  2   0.1239   1.4004   9.8467   1.1210  -1.0000  -1.0000
 1  3   0.1345   1.8422   9.7725   1.2835   1.1576   1.0637
 2  3   0.0283   1.2885  10.9190   0.9215  -1.0000  -1.0000
 1  4   0.4204   1.4900  11.0144   1.4071  -1.0000  -1.0000
 2  4   0.0200   1.9451  10.8595   1.4157  -1.0000  -1.0000
 3  4   0.1000   1.8000   9.1989   1.7050  -1.0000  -1.0000
 3  5   0.0611   1.7624  10.2685   1.7989   1.4523  -1.0000
 4  5   0.2619   2.1638  11.2236   1.8799  -1.0000  -1.0000
52    ! Nr of angles;at1;at2;at3;Thetao,o;ka;kb;pv1;pv2
 1  1  1  59.0573  30.7029   0.7606   0.0000   0.7180   6.2933   1.1244
 1  1  2  65.7758  14.5234   6.2481   0.0000   0.5665   0.0000   1.6255
 2  1  2  70.2607  25.2202   3.7312   0.0000   0.0050   0.0000   2.7500
 1  2  1   0.0000   3.4110   7.7350   0.0000   0.0000   0.0000   1.0400
 1  2  2   0.0000   0.0000   6.0000   0.0000   0.0000   0.0000   1.0400
 2  2  2   0.0000  27.9213   5.8635   0.0000   0.0000   0.0000   1.0400
 1  1  3  53.9517   7.8968   2.6122   0.0000   3.0000  58.6562   1.0338
 3  1  3  76.9627  44.2852   2.4177 -25.3063   1.6334 -50.0000   2.7392
 1  3  1  72.6199  42.5510   0.7205   0.0000   2.9294   0.0000   1.3096
 1  3  3  81.9029  32.2258   1.7397   0.0000   0.9888  68.1072   1.7777
 3  3  3  80.7324  30.4554   0.9953   0.0000   3.0000  50.0000   1.0783
 2  1  3  65.0000  16.3141   5.2730   0.0000   0.4448   0.0000   1.4077
 1  3  2  70.1101  13.1217   4.4734   0.0000   0.8433   0.0000   3.0000
 2  3  3  75.6935  50.0000   2.0000   0.0000   1.0000   0.0000   1.1680
 2  3  2  85.8000   9.8453   2.2720   0.0000   2.8635   0.0000   1.5800
 1  2  3   0.0000  25.0000   3.0000   0.0000   1.0000   0.0000   1.0400
 2  2  3   0.0000   8.5744   3.0000   0.0000   0.0000   0.0000   1.0421
 3  2  3   0.0000  15.0000   2.8900   0.0000   0.0000   0.0000   2.8774
 1  4  1   0.1000  42.2980   0.3169   0.0000   1.1069   0.0000   2.3466
 1  1  4  74.8790  30.0000   2.0000   0.0000   2.0334   0.0000   1.0928
 1  4  4  47.9341   1.0246   7.9341   0.0000   2.8853   0.0000   1.0000
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4  1  4  33.2812  34.6443   3.0111   0.0000   0.1701   0.0000   1.0510
2  4  2  20.3683   0.0100   2.2825   0.0000   0.7660   0.0000   1.3788
2  2  4   0.0000   0.0100   1.0568   0.0000   1.8595   0.0000   3.6142
4  2  4   0.0000  10.4428   7.9607   0.0000   2.3717   0.0000   1.1970
2  4  4  48.4128   4.0632   0.6773   0.0000   2.2274   0.0000   1.8605
2  1  4   2.6539  32.1638   0.9167   0.0000   0.0240   0.0000   1.1158
1  4  2  42.7140   0.1451   0.2500   0.0000   0.0851   0.0000   2.8955
1  2  4   0.0000   0.0100   2.2066   0.0000   1.9789   0.0000   1.4466
1  3  4  90.0000  42.4716   6.6776   0.0000   2.4560   0.0000   1.6221
3  1  4  54.6900  12.6123   2.3543   0.0000   2.0000   0.0000   1.2513
1  4  3  38.2755  19.3103   0.1151   0.0000   0.7569   0.0000   2.3113
2  3  4  26.0012  49.6772   0.0500   0.0000   1.1589   0.0000   1.0000
3  2  4   0.0000   0.0100   3.2567   0.0000   2.0582   0.0000   1.3513
2  4  3  38.5594  11.2599   0.1898   0.0000   0.1904   0.0000   1.4041
4  3  4  63.0740  14.8127   2.9929   0.0000   0.7552   0.0000   1.3634
3  3  4  73.6721  32.6330   1.7223   0.0000   1.0221   0.0000   1.4351
3  4  3  76.5431   0.0583   0.0500   0.0000   0.4968   0.0000   2.2792
3  4  4  69.4895   5.7742   8.0001   0.0000   1.7794   0.0000   2.7889
3  5  3  88.6293  18.2614   0.8145   0.0000  -0.1780   0.0000   2.3661
2  3  5  75.0000   7.8005   0.9394   0.0000   1.3523   0.0000   1.0400
3  3  5  60.0000  40.0000   4.0000   0.0000   1.0000   0.0000   1.0400
3  2  5   0.0000  10.0000   1.0000   0.0000   1.0000   0.0000   1.0400
3  5  4  71.5444  28.1377   3.5000   0.0000   0.2169   0.0000   1.1069
5  3  5  50.6740  13.3258   0.1000   0.0000   1.0718   0.0000   1.1254
1  3  5  76.8677   5.4250   3.1105   0.0000  -0.0827   0.0000   2.1396
2  5  3  75.0000  25.0000   2.0000   0.0000   1.0000   0.0000   1.2500
3  5  5  70.0000  25.0000   2.0000   0.0000   1.0000   0.0000   1.2500
4  3  5  72.6961  30.0000   0.7795   0.0000   2.0000   0.0000   1.0500
3  4  5  76.0866   0.2500   0.1116   0.0000   0.9966   0.0000   2.5091
4  5  4  38.1011  18.9494   3.0000   0.0000   1.2274   0.0000   1.0500
4  4  5  93.0539   6.1619   1.2781   0.0000   0.5598   0.0000   1.0500
38    ! Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;V2(BO);vconj;n.u;n
1  1  1  1  -0.2500  34.7453   0.0288  -6.3507  -1.6000   0.0000   0.0000
1  1  1  2  -0.2500  29.2131   0.2945  -4.9581  -2.1802   0.0000   0.0000
```

2	1	1	2	-0.2500	31.2081	0.4539	-4.8923	-2.2677	0.0000	0.0000
1	1	1	3	1.2799	20.7787	-0.5249	-2.5000	-1.0000	0.0000	0.0000
2	1	1	3	1.9159	19.8113	0.7914	-4.6995	-1.0000	0.0000	0.0000
3	1	1	3	-1.4477	16.6853	0.6461	-4.9622	-1.0000	0.0000	0.0000
1	1	3	1	0.4816	19.6316	-0.0057	-2.5000	-1.0000	0.0000	0.0000
1	1	3	2	1.2044	80.0000	-0.3139	-6.1481	-1.0000	0.0000	0.0000
2	1	3	1	-2.5000	31.0191	0.6165	-2.7733	-2.9807	0.0000	0.0000
2	1	3	2	-2.4875	70.8145	0.7582	-4.2274	-3.0000	0.0000	0.0000
2	1	3	3	-1.4383	80.0000	1.0000	-3.6877	-2.8000	0.0000	0.0000
3	1	3	1	-1.1390	78.0747	-0.0964	-4.5172	-3.0000	0.0000	0.0000
3	1	3	2	-2.5000	70.3345	-1.0000	-5.5315	-3.0000	0.0000	0.0000
3	1	3	3	-0.1583	20.0000	1.5000	-9.0000	-2.0000	0.0000	0.0000
1	3	3	1	0.0002	80.0000	-1.5000	-4.4848	-2.0000	0.0000	0.0000
1	3	3	2	-2.5000	0.1181	0.0268	-5.4085	-2.9498	0.0000	0.0000
2	3	3	2	0.1995	5.0000	0.2000	-2.6000	0.0000	0.0000	0.0000
1	3	3	3	0.4118	0.5219	0.9706	-2.5004	-0.9972	0.0000	0.0000
2	3	3	3	0.1000	43.1840	0.5000	-6.6539	0.0000	0.0000	0.0000
3	3	3	3	0.1000	1.0000	0.1000	-2.5000	-0.9000	0.0000	0.0000
0	1	2	0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0	2	2	0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0	2	3	0	0.0000	0.1000	0.0200	-2.5415	0.0000	0.0000	0.0000
0	1	1	0	0.0000	50.0000	0.3000	-4.0000	0.0000	0.0000	0.0000
0	3	3	0	0.5511	25.4150	1.1330	-5.1903	-1.0000	0.0000	0.0000
1	1	3	3	-0.0002	20.1851	0.1601	-9.0000	-2.0000	0.0000	0.0000
2	1	4	4	0.0000	0.0000	0.0000	-5.0000	0.0000	0.0000	0.0000
1	1	1	5	0.0000	19.3871	0.0103	-25.5765	-1.7255	0.0000	0.0000
5	1	1	5	0.0000	80.5586	0.1104	-8.0928	-1.7255	0.0000	0.0000
0	1	5	0	4.0000	45.8264	0.9000	-4.0000	0.0000	0.0000	0.0000
0	5	5	0	4.0000	45.8264	0.9000	-4.0000	0.0000	0.0000	0.0000
2	1	3	5	-1.5000	13.7486	0.1710	-3.7686	0.0000	0.0000	0.0000
2	3	5	3	-0.3120	-1.7990	0.2371	-3.2710	0.0000	0.0000	0.0000
1	3	5	3	-1.5000	-2.5000	0.6794	-2.5000	0.0000	0.0000	0.0000
5	3	5	3	-1.5000	7.4600	-0.9075	-9.0000	0.0000	0.0000	0.0000
2	1	5	1	0.5984	7.2907	0.1161	-5.1321	-2.1802	0.0000	0.0000

```
2  1  1  5   0.2704  32.0532   0.2173  -5.3228  -2.1802   0.0000   0.0000
1  1  5  1   0.5864  32.4198  -0.2514  -8.4627  -1.6000   0.0000   0.0000
1    ! Nr of hydrogen bonds;at1;at2;at3;Rhb;Dehb;vhb1
3  2  3   2.1200  -3.5800   1.4500  19.5000
```