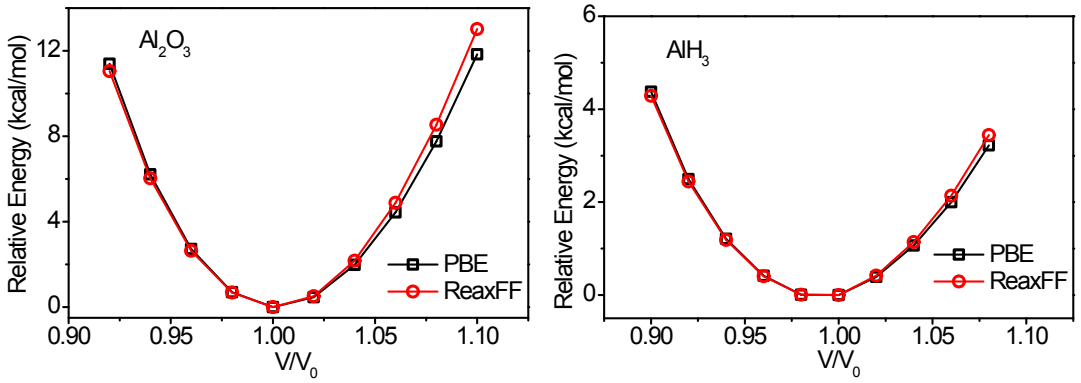
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A. Training set of Bond and bond angle parameters for Al-X(X=C/H/O/N).

The bond and bond angle parameters provides the most important energy terms. TABLE I lists the training set of Al-X(X=C/H/O/N) interactions. After the training, the parameters were tested and modified according to the energy-volume relationship as FIG. 1 shows.

TABLE I Profile of training set for Al-X (X=C/H/O/N) interactions. The bond lengths, bond angles and energies are in terms of angstrom, degree and kcal/mol, respectively.

	No.	Compound	Bond type	Bond length (Å)	Bond energy (kcal/mol)
Bond	1	AlH_2-CH_3	Al-C	1.9623	116.95
	2	AlH_3	Al-H	1.5837	126.54
	3	AlH_2-OH	Al-O	1.7179	166.62
	4	AlH_2-NH_2	Al-N	1.7842	147.35
	5	AlH_2-AlH_2	Al-Al	2.6182	80.08
	No.	Compound	Angle type	Bond angle (°)	Angle energy (kcal/mol)
Bond angle	1	AlH_2-OH	H-Al-O	115.54	34.12
	2	AlH_3	H-Al-H	120.00	44.47
	3	AlH_2-CH_3	H-Al-C	119.86	28.64
	4	CH_3-AlH-AlH_2	C-Al-Al	126.65	15.43
	5	CH_3-AlH-CH_3	C-Al-C	120.48	26.72
	6	CH_3-AlH-NH_2	C-Al-N	120.14	31.55
	7	CH_3-AlH-OH	C-Al-O	116.59	34.24
	8	NH_2-AlH-NH_2	N-Al-N	120.28	35.27
	9	OH-AlH-OH	O-Al-O	115.38	37.92



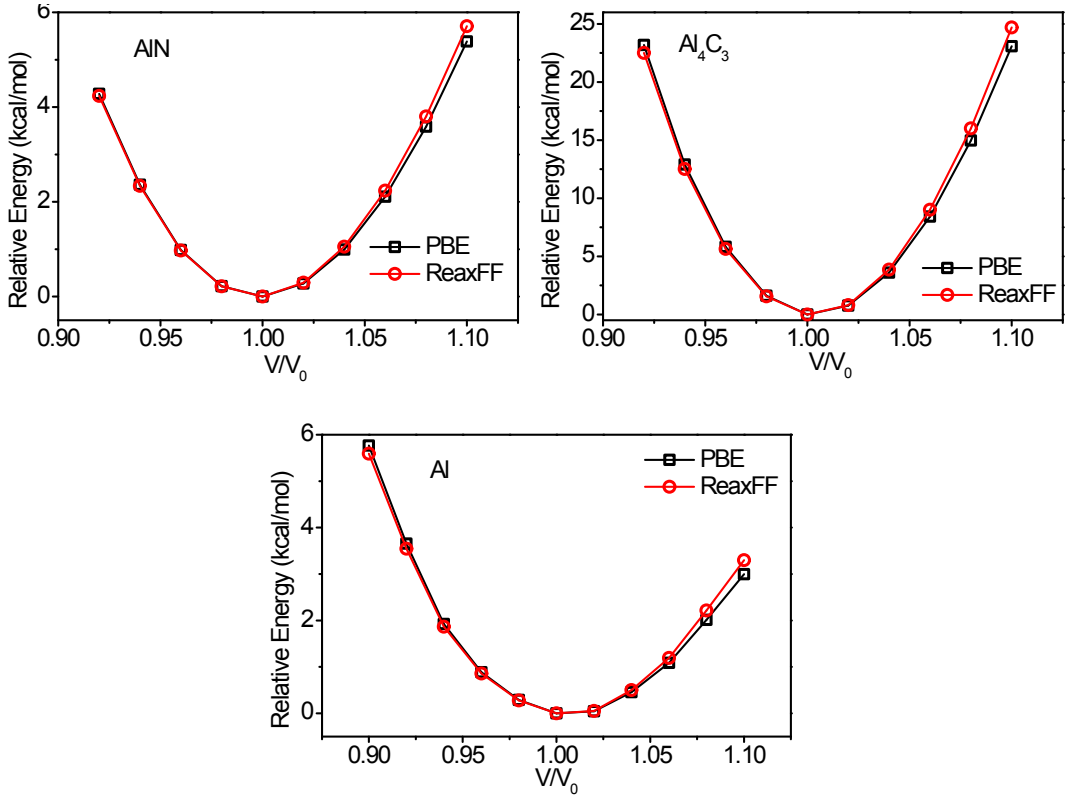


FIG. I The energy-volume relationships for the Al-X (X=C/H/O/N) crystals.

B. Training of low gradient (lg) dispersion correction parameters for Al-X.

In the ReaxFF-*lg*, the total energy of the system can be expressed as

$$E_{Reax\text{-}lg} = E_{Reax} + E_{lg} \tag{1}$$

where E_{Reax} is the energy evaluated from the previous ReaxFF force field, and E_{lg} is the long-range-correction terms using the low-gradient model:

$$E_{lg} = -\sum_{ij,i<j}^{N} \frac{C_{lg,ij}}{r_{ij}^{6} + d \cdot R_{eij}^{6}} \tag{2}$$

Here r_{ij} is the distance between atom *i* and atom *j*, R_{eij} is the equilibrium vdW distance between atom *i* and *j*, and $C_{lg,ij}$ is the dispersion energy correction parameter, *d* is a scaling factor. The R_e of C/H/O/N/Al is taken from Universal force field that accurately describes the vdW radii. Thus, the C_{lg} for Al-X are all terms need to trained for the lg parameters.

In order to obtain the lg parameters, supercells combine $A_{l2}O_3$ layers with H_2, O_2, N_2, CO_2 molecules were built respectively to calculate the adsorption energies (FIG. 2). The adsorption energies were calculated using ReaxFF and DFT-D method (GGA/PBE functional with Grimme's dispersion correction) and listed in TABLE II. From TABLE II, the ReaxFF underestimates the adsorption energies comparing with DFT-D method. However, When the lg parameter C_{lg} increase, the accuracy of adsorption energies reach the DFT-D level (FIG. 3). The trained C_{lg} parameters (cross points in FIG. 3) are listed in TABLE III.

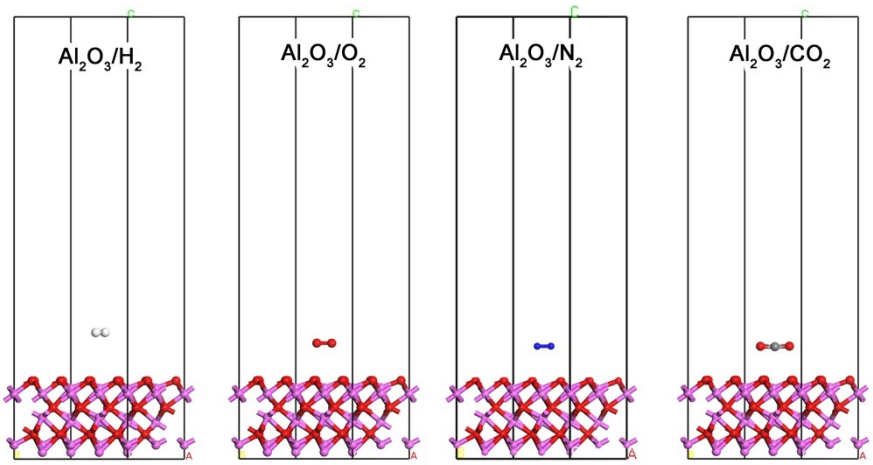


FIG. 2 Adsorption models for Al2O3 layers and H_2, O_2, N_2, CO_2 molecules.

TABLE II Calculated adsorption energies for Al2O3 layers and H_2, O_2, N_2, CO_2 molecules by DFT-D and ReaxFF methods.

	Adsorption energy (kcal/mol)	
	DFT-D	ReaxFF
Al_2O_3/H_2	-1.92	-0.10
Al_2O_3/O_2	-3.49	-3.31
Al_2O_3/N_2	-3.48	-3.19
Al_2O_3/CO_2	-8.49	-4.73

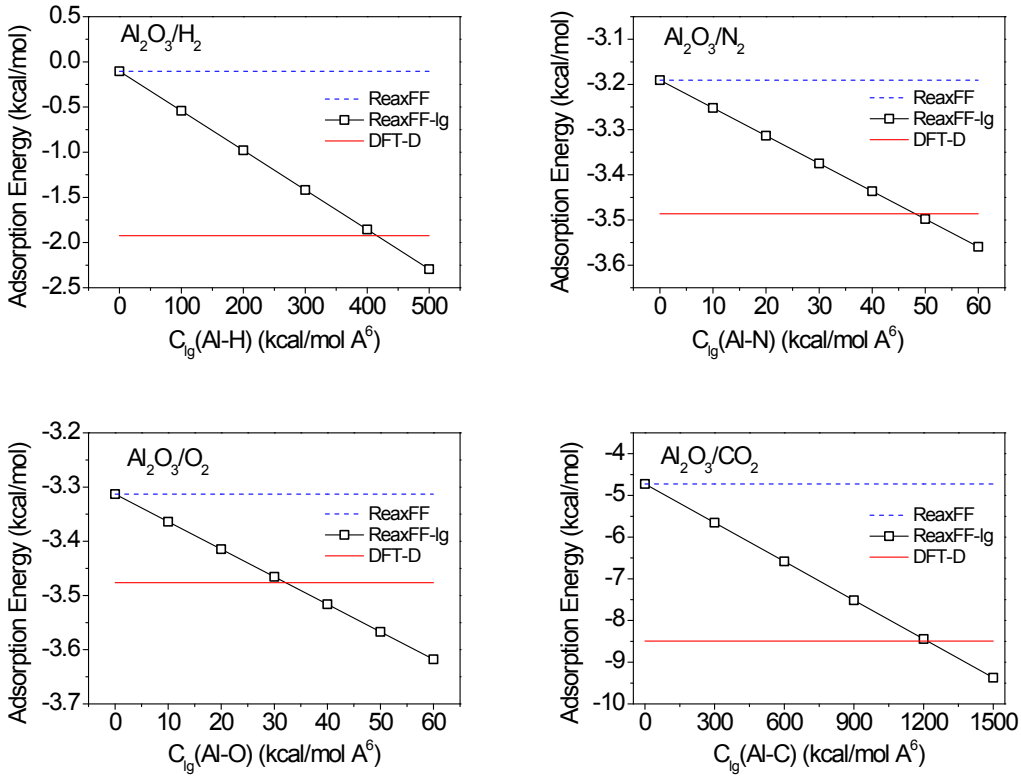


FIG. 3 Training of C_{lg} parameters using the adsorption energies calculated by DFT-D method.

TABLE III ReaxFF-lg dispersion correction parameters.

R_e (Å)		C_{lg} (kcal/mol Å^6)	
C	1.9255	C-Al	1215.91
H	1.8300	H-Al	415.68
N	1.7500	N-Al	862.40
O	1.4430	O-Al	34.08
Al	2.2450		

C. ReaxFF-lg parameters for C/H/O/N/Al aluminized explosives.

```
!ReaxFF-lg force field for Al/C/H/O/N atoms
39          ! Number of general parameters
    50.0000 !Overcoordination parameter
     9.4514 !Overcoordination parameter
    30.0000 !Valency angle conjugation parameter
   216.4305 !Triple bond stabilisation parameter
    12.4838 !Triple bond stabilisation parameter
     0.0000 !C2-correction
     1.0701 !Undercoordination parameter
     7.5000 !Triple bond stabilisation parameter
    11.9083 !Undercoordination parameter
    13.3822 !Undercoordination parameter
   -10.4637 !Triple bond stabilization energy
     0.0000 !Lower Taper-radius
    10.0000 !Upper Taper-radius
     2.8793 !Not used
    33.8667 !Valency undercoordination
     3.5895 !Valency angle/lone pair parameter
     1.0563 !Valency angle
     2.0384 !Valency angle parameter
     6.1431 !Not used
     6.9290 !Double bond/angle parameter
     0.0283 !Double bond/angle parameter: overcoord
     0.0570 !Double bond/angle parameter: overcoord
    -2.4837 !Not used
     5.8374 !Torsion/BO parameter
    10.0000 !Torsion overcoordination
     1.8820 !Torsion overcoordination
    -1.2327 !Conjugation 0 (not used)
     2.1861 !Conjugation
     1.5591 !vdWaals shielding
     0.0100 !Cutoff for bond order (*100)
     5.2216 !Valency angle conjugation parameter
```

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   3.4021 !Overcoordination parameter
  38.5241 !Overcoordination parameter
   2.1533 !Valency/lone pair parameter
   0.5000 !Not used
   1.0000 !Scale factor (d) in dispersion
   5.0000 !Molecular energy (not used)
   2.0000 !Version number
   6.5560 !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       1.3742    4.0000   12.0000    1.9684    0.1723    0.8712    1.2385    4.0000
        9.4606    2.1346    4.0000   31.0823   79.5548    5.7254    6.9235    0.0000
        1.2104    0.0000  183.7012    5.7419   33.3951   11.9957    0.8563    0.0000
       -2.8983    2.5000    1.0564    4.0000    2.9663    1.6737    0.1421   14.0707
        0.0001    1.9255
H       0.6867    1.0000    1.0080    1.3525    0.0616    0.8910   -0.1000    1.0000
        9.3858    5.0013    1.0000    0.0000  121.1250    3.8446   10.0839    1.0000
       -0.1000    0.0000   58.4228    3.8461    3.2540    1.0000    1.0698    0.0000
      -15.7683    2.1504    1.0338    1.0000    2.8793    1.2669    0.0139   12.4538
        0.0001    1.4430
O       1.3142    2.0000   15.9990    1.9741    0.0880    0.8712    1.1139    6.0000
       10.2186    7.7719    4.0000   29.5271  116.0768    8.5000    7.1412    2.0000
        0.9909   14.9473   69.2812    9.1371    1.6258    0.1863    0.9745    0.0000
       -3.5965    2.5000    1.0493    4.0000    2.9225    1.7221    0.1670   13.9991
      624.0000    1.7500
N       1.2450    3.0000   14.0000    1.9951    0.1088    1.0512    1.1911    5.0000
        9.9303    7.8431    4.0000   32.4758  100.0000    6.7768    6.8035    2.0000
        1.0636    0.1045  128.0119    2.1604    2.9464    2.5181    0.9745    0.0000
       -4.0959    2.0047    1.0183    4.0000    2.8793    1.5967    0.1649   13.9888
     1239.000    1.8300
Al      2.4443    3.0000   26.9820    2.0089    0.2161    0.5675   -1.6836    3.0000
       11.8538   16.3962    3.0000    0.0076   16.5151   -0.2451    6.3319    0.0000
       -1.0000    0.0000   67.5458  137.9671    0.2042    0.0000    0.8563    0.0000
      -14.9162    3.0000    1.0338    3.0000    2.5791    1.9989    0.0121   14.1618
        0.0001    2.2450
15        ! Nr of bonds; Edis1;LPpen;n.u.;pbe1;pbo5;13corr;pbo6
                                pbe2;pbo3;pbo4;Etrip;pbo1;pbo2;ovcorr
 1   1 141.9346 113.4487   67.6027    0.1554   -0.3045    1.0000   30.4515    0.4283
          0.0801   -0.2113    8.5395    1.0000   -0.0933    6.6967    1.0000    0.0000
 1   2 163.6889    0.0000    0.0000   -0.4525    0.0000    1.0000    6.0000    0.5921
         12.1053    1.0000    0.0000    1.0000   -0.0097    8.6351    0.0000    0.0000
 2   2 169.8421    0.0000    0.0000   -0.3591    0.0000    1.0000    6.0000    0.7503
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         9.3119    1.0000    0.0000    1.0000   -0.0169    5.9406    0.0000    0.0000
 1   3 164.0476  117.4881   72.1261   -0.6031   -0.1795    1.0000   14.9755    0.5413
         1.2626   -0.3063    7.0000    1.0000   -0.1588    4.5000    0.0000    0.0000
 3   3 110.4748  155.6441   40.0000    0.1150   -0.1054    1.0000   28.5221    0.2000
         0.9590   -0.2635    8.5715    1.0000   -0.1007    6.8548    1.0000    0.0000
 1   4 130.7147  175.2276   97.2523   -0.0368   -0.4942    1.0000   26.7545    0.5133
         0.3296   -0.3653    7.0000    1.0000   -0.1171    5.1025    1.0000    0.0000
 3   4  85.4950  114.0081   70.1453    0.5778   -0.1070    1.0000   16.6611    0.2339
         0.3474   -0.1948    8.3762    1.0000   -0.1089    5.8148    1.0000    0.0000
 4   4 157.7518   67.1322  160.9732   -0.5869   -0.1824    1.0000   12.0000    0.7136
         0.8204   -0.1657   10.6490    1.0000   -0.0967    4.5976    1.0000    0.0000
 2   3 224.3076    0.0000    0.0000   -0.6280    0.0000    1.0000    6.0000    1.0000
         5.0050    1.0000    0.0000    1.0000   -0.0512    5.1982    0.0000    0.0000
 2   4 212.1772    0.0000    0.0000   -0.3585    0.0000    1.0000    6.0000    0.3316
        10.4316    1.0000    0.0000    1.0000   -0.0658    6.4545    0.0000    0.0000
 1   5 106.1950    0.0000    0.0000    0.6481   -0.3000    0.0000   36.0000    0.0100
         3.5736   -0.3500   25.0000    1.0000   -0.1947    4.8726    0.0000    0.0000
 2   5  78.5674    0.0000    0.0000   -0.5170   -0.3000    0.0000   36.0000    0.0100
        13.0000   -0.3500   25.0000    1.0000   -0.1044    5.6108    0.0000    0.0000
 3   5 175.2517    0.0000    0.0000   -0.8707   -0.3000    0.0000   36.0000    0.0100
         0.9278   -0.3500   25.0000    1.0000   -0.1183    4.6533    0.0000    0.0000
 5   4 153.0801    0.0000    0.0000    0.3006   -0.2197    0.9846   22.9338    0.2078
         2.8313   -0.3555   11.9007    0.9831   -0.1709    6.8863    1.0000    0.0000
 5   5  65.7742    0.0000    0.0000   -0.4111   -0.3000    0.0000   16.0000    0.2955
         2.8637   -0.4197   14.3085    1.0000   -0.1993    4.8757    0.0000    0.0000
10      ! Nr of off-diagonal terms; Ediss;Ro;gamma;rsigma;rpi;rpi2
 1   2    0.0464    1.8296   10.1311    1.0029   -1.0000   -1.0000    0.0000
 2   3    0.0375    1.7275   10.8037    0.8813   -1.0000   -1.0000    0.0000
 2   4    0.0509    1.7672   10.4261    0.9990   -1.0000   -1.0000  295.0000
 1   3    0.1036    1.8869    9.5668    1.3590    1.1099    1.1534  632.0000
 1   4    0.1971    1.7356   10.0734    1.2754    1.2113    1.1172  650.0000
 3   4    0.0535    1.6709   10.8180    1.2968    1.1416    1.0167  880.0000
 1   5    0.3468    1.4007   12.8976    1.5468   -1.0000   -1.0000 1215.910
 2   5    0.1549    1.3617   12.7585    1.5010   -1.0000   -1.0000  415.680
 3   5    0.3745    1.8871    9.7359    1.4857   -1.0000   -1.0000   34.080
 4   5    0.1793    1.7164   11.2736    0.9450    1.3360   -0.9502  862.400
64      ! Nr of angles;at1;at2;at3;Thetao,o;ka;kb;pv1;pv2
 1   1   1   74.0317   32.2712    0.9501    0.0000    0.1780   10.5736    1.0400
 1   1   2   70.6558   14.3658    5.3224    0.0000    0.0058    0.0000    1.0400
 2   1   2   76.7339   14.4217    3.3631    0.0000    0.0127    0.0000    1.0400
 1   2   2    0.0000    0.0000    6.0000    0.0000    0.0000    0.0000    1.0400
 1   2   1    0.0000    3.4110    7.7350    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   65.3104    6.3897    7.5000    0.0000    0.2000   10.0000    1.8525
```

3	1	3	71.9855	28.5708	6.4252	0.0000	0.2000	0.0000	1.8525
1	1	4	65.8892	45.0000	1.6598	0.0000	0.2000	10.0000	1.8525
3	1	4	73.1057	25.8227	4.2145	0.0000	0.2000	0.0000	1.8525
4	1	4	65.8759	40.9838	2.4369	0.0000	0.2000	0.0000	1.8525
2	1	3	56.3039	17.3681	5.3095	0.0000	0.9110	0.0000	1.0400
2	1	4	71.5505	11.1820	3.7129	0.0000	0.9110	0.0000	1.0400
1	2	4	0.0000	0.0019	6.3000	0.0000	0.0000	0.0000	1.0400
1	3	1	72.3642	37.8942	1.1566	0.0000	0.7472	0.0000	1.2639
1	3	3	90.0000	45.0000	0.5719	0.0000	0.7472	0.0000	1.2639
1	3	4	70.4313	14.4055	7.1593	0.0000	0.7472	0.0000	1.2639
3	3	3	83.8833	23.3345	2.3433	-10.0000	0.7472	0.0000	1.2639
3	3	4	84.0407	45.0000	1.0695	0.0000	0.7472	0.0000	1.2639
4	3	4	73.9966	24.4410	5.2760	0.0000	0.7472	0.0000	1.2639
1	3	2	89.1394	37.0874	0.3849	0.0000	3.0000	0.0000	1.2618
2	3	3	80.7068	5.0854	5.7151	0.0000	3.0000	0.0000	1.2618
2	3	4	76.0238	45.0000	0.8637	0.0000	3.0000	0.0000	1.2618
2	3	2	82.3474	13.5165	3.4896	0.0000	0.3596	0.0000	1.3307
1	4	1	68.4330	19.3525	2.1625	0.0000	1.7325	0.0000	1.0440
1	4	3	86.2893	37.5587	1.2660	0.0000	1.7325	0.0000	1.0440
1	4	4	74.2404	12.0547	7.5000	0.0000	1.7325	0.0000	1.0440
3	4	3	78.5566	43.8492	1.3351	-26.1471	1.7325	40.0000	1.0440
3	4	4	77.4239	33.7297	1.7944	-0.9193	1.7325	0.0000	1.0440
4	4	4	64.9107	17.5558	7.5000	0.0000	1.7325	0.0000	1.0440
1	4	2	90.0000	32.0540	0.7195	0.0000	0.5355	0.0000	2.5279
2	4	3	84.1185	45.0000	1.3826	0.0000	0.5355	0.0000	2.5279
2	4	4	78.7133	24.6250	3.8202	0.0000	0.5355	0.0000	2.5279
2	4	2	56.3036	14.1532	3.3914	0.0000	0.2000	0.0000	2.1689
1	2	3	0.0000	0.0019	6.0000	0.0000	0.0000	0.0000	1.0400
1	2	4	0.0000	0.0019	6.0000	0.0000	0.0000	0.0000	1.0400
1	2	5	0.0000	0.0019	6.0000	0.0000	0.0000	0.0000	1.0400
3	2	3	0.0000	0.0019	6.0000	0.0000	0.0000	0.0000	1.0400
3	2	4	0.0000	0.0019	6.0000	0.0000	0.0000	0.0000	1.0400
4	2	4	0.0000	0.0019	6.0000	0.0000	0.0000	0.0000	1.0400
2	2	3	0.0000	0.0019	6.0000	0.0000	0.0000	0.0000	1.0400
2	2	4	0.0000	0.0019	6.0000	0.0000	0.0000	0.0000	1.0400
1	3	5	90.0000	5.0000	3.0000	0.0000	1.0000	0.0000	1.1000
2	3	5	90.0000	11.1212	4.3379	0.0000	3.0000	0.0000	3.0000
3	3	5	43.6280	11.0750	6.6200	0.0000	3.0000	0.0000	1.0100
5	3	5	64.5513	10.5987	1.0471	0.0000	3.0000	0.0000	1.6045
3	5	3	84.7469	7.3926	2.9453	0.0000	0.1000	0.0000	1.2535
3	5	5	27.4957	14.3276	0.2771	0.0000	2.3158	0.0000	2.2134
1	5	1	71.5643	40.0000	0.7916	0.0000	0.0230	0.0000	1.0011
5	1	5	1.0000	39.3256	10.0000	0.0000	0.4988	0.0000	1.3731
2	1	5	77.3364	13.9658	9.8503	0.0000	0.1352	0.0000	1.0000

```
 1   5   3   74.5260   40.0000    2.4295    0.0000    1.8739    0.0000    1.0010
 1   1   5   26.5597    9.1438    8.4576    0.0000    2.3277    0.0000    1.4756
 1   5   5   39.5036    6.3913    0.9117    0.0000    2.6905    0.0000    3.0000
 2   5   2  100.0000    5.9042    0.0871    0.0000    3.0000    0.0000    1.0100
 2   5   5   10.0000    4.2493    0.4967    0.0000    0.1000    0.0000    1.9554
 2   5   5  180.0000  -22.9923    5.1657    0.0000    0.8783    0.0000    2.3156
 5   2   5    0.0000   10.9458    0.1218    0.0000    0.1000    0.0000    1.0588
 2   2   5    0.0000    2.0796    1.0424    0.0000    1.5070    0.0000    1.2393
 1   5   2   79.1340    0.2838    3.8832    0.0000    0.1001    0.0000    3.0000
 1   2   5    0.0000    0.0100    0.0100    0.0000    0.7901    0.0000    2.9774
 5   4   5   64.5513   10.5987    1.0471    0.0000    3.0000    0.0000    1.6045
 4   5   4   84.7469    7.3926    2.9453    0.0000    0.1000    0.0000    1.2535
 1   2   5    0.0000    0.0100    0.0100    0.0000    0.7901    0.0000    2.9774
17       ! Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;V2(BO);vconj;n.u;n
 1   1   1   1    0.0000   48.4194    0.3163   -8.6506   -1.7255    0.0000    0.0000
 1   1   1   2    0.0000   63.3484    0.2210   -8.8401   -1.8081    0.0000    0.0000
 2   1   1   2    0.0000   45.2741    0.4171   -6.9800   -1.2359    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   1   3   0   -0.0002   85.8794    0.3236   -3.8134   -2.0000    0.0000    0.0000
 0   2   3   0    0.0000    0.1000    0.0200   -2.5415    0.0000    0.0000    0.0000
 0   3   3   0   -0.9667  116.4743    0.0002   -4.9422    0.0000    0.0000    0.0000
 0   1   4   0   -0.0069  150.0000    0.4891   -7.4921   -2.0000    0.0000    0.0000
 0   2   4   0    0.0000    0.1000    0.0200   -2.5415    0.0000    0.0000    0.0000
 0   3   4   0    1.6745   56.6301   -0.0008   -4.5064   -2.0000    0.0000    0.0000
 0   4   4   0    1.1253   75.3447    0.0080   -9.0000   -2.0000    0.0000    0.0000
 0   1   1   0    0.0930   18.5962    0.0002   -9.0000   -1.0000    0.0000    0.0000
 4   1   4   4   -2.0000   20.8732   -1.5000   -9.0000   -2.0000    0.0000    0.0000
 1   1   3   3   -0.0002   21.5452    0.1727   -9.0000   -2.0000    0.0000    0.0000
 1   3   3   1    0.0002   79.3777   -1.5000   -5.2139   -2.0000    0.0000    0.0000
 3   1   3   3   -1.3476   22.4932    1.5000   -9.0000   -2.0000    0.0000    0.0000
 4       ! Nr of hydrogen bonds;at1;at2;at3;Rhb;Dehb;vhb1
 3   2   3    2.0000   -5.0000    3.0000    3.0000
 3   2   4    1.7753   -5.0000    3.0000    3.0000
 4   2   3    1.3884   -5.0000    3.0000    3.0000
 4   2   4    1.6953   -4.0695    3.0000    3.0000
```