Chlorophyll excitation energies and structural stability of the CP47 antenna of Photosystem II: a case study in the first-principles simulation of light-harvesting complexes

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Electronic Supplementary Information

Table S1. Computed site energies (in eV) of CP47 chromophores using the *ω*B97X-V functional with the Def2-TZVP basis set. Comparison of first excitation energies obtained *in vacuo*, in the electrostatic field of a PSII monomer, and in the electrostatic field of the PSII dimer. The pigment geometries in all cases are derived from QM/MM optimisations inside the complete PSII dimer. Parentheses indicate oscillator strengths.

Site	Q_y (Vacuum)	Q_y (Monomer)	Q_y (Dimer)
B1	1.941(0.22)	1.893 (0.24)	1.899 (0.25)
B2	1.928 (0.22)	1.948 (0.16)	1.953 (0.17)
B3	1.888 (0.23)	1.888 (0.19)	1.884 (0.19)
B4	1.935 (0.23)	1.928 (0.22)	1.947 (0.21)
B5	1.909 (0.22)	1.923 (0.17)	1.921 (0.17)
B6	1.924 (0.21)	1.923 (0.20)	1.933 (0.19)
B7	1.925 (0.23)	1.923 (0.19)	1.915 (0.21)
B8	1.951 (0.21)	1.998 (0.23)	1.967 (0.23)
B9	1.981 (0.22)	2.091 (0.20)	2.102 (0.20)
B10	1.965 (0.21)	1.974 (0.18)	1.966 (0.20)
B11	1.967 (0.23)	1.999 (0.24)	1.996 (0.24)
B12	1.939 (0.21)	1.944 (0.19)	1.941 (0.20)
B13	1.917 (0.23)	1.946 (0.25)	1.921 (0.27)
B14	1.942 (0.22)	1.957 (0.24)	1.956 (0.24)
B15	1.933 (0.22)	1.938 (0.20)	1.930 (0.21)
B16	1.945 (0.22)	2.009 (0.23)	2.050 (0.22)

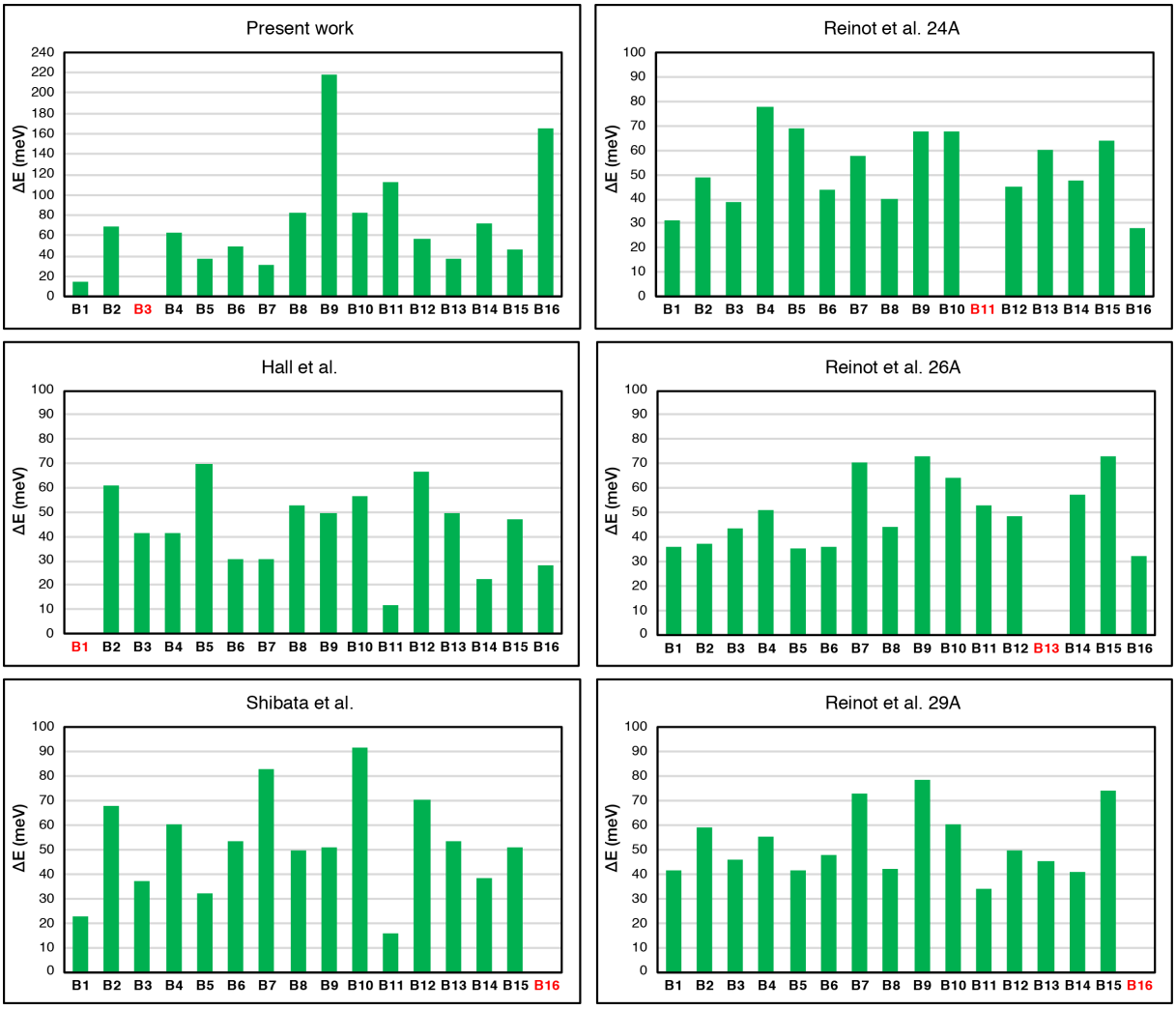

Figure S1. Comparison of vertical excitation energies for the CP47 chlorophylls computed in the present work with fitted site energies reported in selected past papers by Hall et al.,[1] Shibata et al.,[2] and Reinot et al.[3]

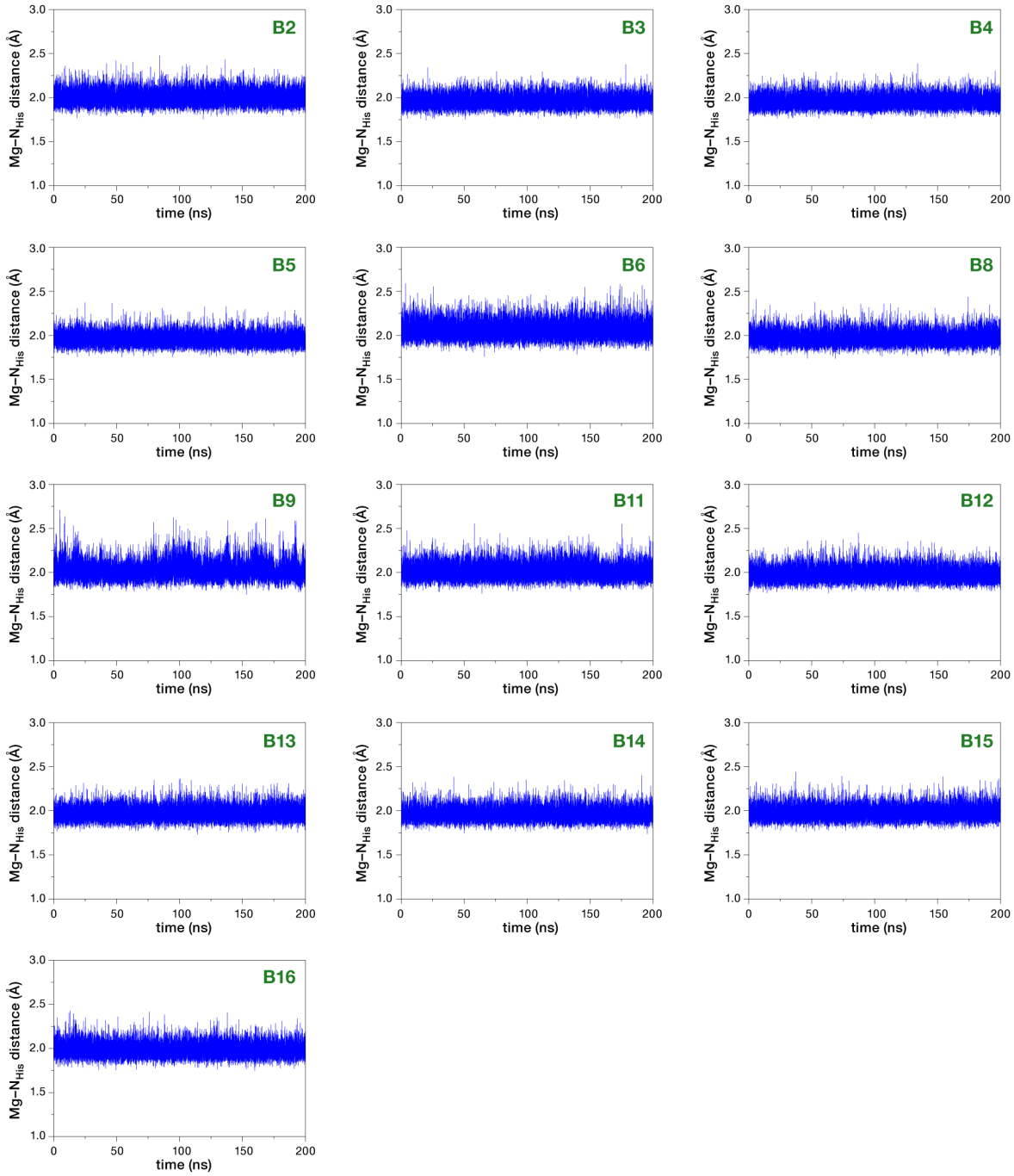

Figure S2. Distances between the Mg ion and the imidazole N atom for all CP47 chlorophylls that are formally coordinated by a histidine residue, from MD simulations carried out without specifying the presence of a Mg–N_{His} bond.

COFACTOR FORCE FIELD PARAMETERS

Definition of atoms types, bond connectivity and RESP charges for Chlorophyll *a*

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No Charge or Current Charge


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Bonded and LJ parameters for Chlorophyll *a*

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Force Field modification file for CLA
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csb 12.01         0.360              Inner Sp2 carbons in conjugated systems
cab 12.01         0.360              Inner Sp2 carbons in conjugated systems
ccs 12.01         0.360              Inner Sp2 carbons in conjugated systems
ct1 12.01         0.878              Sp3 C
ct2 12.01         0.878              Sp3 C
ct3 12.01         0.878              Sp3 C
crb 12.01         0.360              Sp2 carbons in non-pure aromatic systems
cbb 12.01         0.360              Sp2 carbons in non-pure aromatic systems
cnb 12.01         0.360              Sp2 carbons in non-pure aromatic systems
cpb 12.01         0.360              Sp2 carbons in non-pure aromatic systems
cqb 12.01         0.360              Sp2 carbons in non-pure aromatic systems
c2k 12.01         0.616              Sp2 C carbonyl group
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c2a 12.01          0.616              Sp2 C carbonyl group
nmh 14.01          0.530              Inner Sp2 N in conjugated systems
ns  14.01          0.530              Inner Sp2 N in conjugated systems
o2c 16.00          0.434              Oxygen with one connected atom
o1c 16.00          0.465              Ether and ester oxygen

BOND
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ns     mgc     50.00    2.150
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nmh    crb    316.00    1.380
ns     cnb    316.00    1.375
ns     crb    316.00    1.380
nmh    cpb    316.00    1.393
nmh    cqb    316.00    1.348
cnb    cbb    263.00    1.456
crb    cbb    263.00    1.439
cpb    cbb    263.00    1.441
cqb    cbb    283.00    1.421
cbb    cbb    340.00    1.402
cbb    ct2    323.50    1.513              # Same with c3-ca
cbb    ct3    200.00    1.497
cbb    c2e    190.00    1.479
ct3    c2e    170.00    1.522
ns     ccs    296.00    1.362
ccs    ct1    250.00    1.527
ct1    ct1    250.00    1.552
ct1    ct2    250.00    1.541
ct1    ct3    250.00    1.541
ct1    hc     358.00    1.090
c2k    o2c    700.00    1.226
c2k    cbb    263.00    1.455
c2k    ct1    170.00    1.604
csb    ct1    250.00    1.525
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cnb    cab    350.00    1.404
crb    cab    350.00    1.406
cpb    cab    350.00    1.407
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ccs    csb    370.00    1.370
cab    ha     376.00    1.092
ct3    hc     358.00    1.090
c2a    o2c    700.00    1.222
c2a    o1c    380.00    1.363
o1c    ct2    358.00    1.457
o1c    ct3    358.00    1.457
o1c    c3     358.00    1.457
c2a    ct1    250.00    1.522
c2a    ct2    250.00    1.522
ct2    ct2    260.00    1.526
ct2    ct3    260.00    1.526
ct2    hc     358.00    1.090
ct3    hc     358.00    1.090
ct3    h1     358.00    1.090
c2e    o2c    650.00    1.229
cbb    cf     562.40    1.338 # same as ce - cf.

ANGLE
nmh    mgc    ns         50.0      87.0
nmh    mgc    nmh        50.0     158.39
ns     mgc    ns         50.0     158.06
mgc    nmh    cnb        70.0     125.45
mgc    nmh    cpb        70.0     130.82
mgc    nmh    cqb        70.0     122.4
mgc    nmh    crb        70.0     126.83
mgc    ns     cnb        70.0     128.15   # Same with mgc-nmh-cnb
mgc    ns     crb        70.0     126.4    # Same with mgc-nmh-crb
mgc    ns     ccs        70.0     125.8
cnb    nmh    crb       100.0     107.18
cnb    ns     crb       100.0     106.62   # Same with cnb-nmh-crb
cpb    nmh    cqb       100.0     106.17
nmh    cnb    cbb        70.0     109.5
nmh    crb    cbb        70.0     110.28
ns     cnb    cbb        70.0     109.72   # Same with nmh-cnb-cbb
ns     crb    cbb        70.0     110.28    # Same with nmh-crb-cbb
nmh    cpb    cbb        70.0     109.75
nmh    cqb    cbb        70.0     112.23
cnb    cbb    cbb        63.0     106.19
crb    cbb    cbb        63.0     106.41
cpb    cbb    cbb        63.0     104.92
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cqb   cbb   cbb       63.0    106.92
nmh   cnb   cab       70.0    124.65
nmh   crb   cab       70.0    124.5
ns    cnb   cab       70.0    123.87   # Same with nmh-cnb-cab
ns    crb   cab       70.0    124.78   # Same with nmh-crb-cab
nmh   cpb   cab       70.0    122.04
nmh   cqb   csb       70.0    133.38
cbb   cbb   c2k       63.0    142.98
cbb   cbb   ct2       63.0    129.0
cbb   cbb   ct3       63.0    129.0
crb   cbb   ct3       63.0    123.5
cpb   cbb   ct3       63.0    127.11
cnb   cbb   c2e       63.0    124.4
cnb   cbb   ct2       63.0    124.4             # Same with cnb-cbb-c2e
cbb   cbb   c2e       63.0    128.5
cbb   cnb   cab       63.0    126.26
cbb   crb   cab       63.0    126.5
cbb   cpb   cab       63.0    128.14
ccs   ns    ccs      120.0    109.95
ns    ccs   ct1       70.0    110.59
ccs   ct1   ct1       63.0    101.61
ns    ccs   cab       70.0    125.5
ns    ccs   csb       70.0    123.21
ccs   ct1   ct2       63.0    112.1
ccs   ct1   ct3       63.0    112.1
ct1   ct1   ct2       63.0    114.0
ct1   ct1   ct3       63.0    114.0
ct1   ct2   ct2       63.0    114.0
ct1   ct2   ct3       63.0    114.0
cbb   ct2   ct3       63.250  112.090           # Same with c3-c3-ca
ccs   ct1   hc        35.0    109.5
ct1   ct1   hc        35.0    109.5
ct1   ct2   hc        35.0    109.5
cbb   ct2   hc        46.960  110.15            # Same with ca-c3-hc
ct2   ct1   hc        35.0    109.5
cbb   c2k   ct1       63.0    105.16
cbb   c2k   o2c       80.0    130.7
ct1   c2k   o2c       80.0    124.0
c2k   ct1   csb       63.0    104.67
cqb   csb   ct1       63.0    106.69
cqb   cbb   c2k       63.0    109.41
ct1   csb   ccs       63.0    128.26
c2k   ct1   c2a       63.0    111.0
csb   ct1   c2a       63.0    112.5
csb   ct1   hc        35.0    109.5
c2k   ct1   hc        35.0    109.5
csb   cqb   cbb       63.0    114.03
cnb   cab   cpb       63.0    126.9             # Same with csb-cqb-ccs
cnb   cab    ccs      63.0    129.9
crb   cab    ccs      63.0    127.92
crb   cab    cnb      63.0    128.48
cqb   csb    ccs      63.0    123.92
cnb   cab    ha       25.0    116.33
crb   cab    ha       25.0    115.48
cpb   cab    ha       25.0    116.72
ccs   cab    ha       25.0    115.98
cab   ccs    ct1      63.0    122.0
csb   ccs    ct1      63.0    125.8
c2a   o1c   ct2       45.0    106.0
c2a   o1c   ct3       45.0    106.0
c2a   o1c   c3        45.0    106.0
o1c   c2a   ct1       70.0    111.5
o1c   c2a   ct2       70.0    111.5
o2c   c2a   ct1       90.0    126.5
o2c   c2a   ct2       90.0    126.5
o2c   c2a   o1c      100.0    122.0
c2a   ct1   hc        35.0    109.5
c2a   ct2   hc        35.0    109.5
o1c   ct2   hc        35.0    109.5
o1c   ct2   h1        35.0    109.5
o1c   ct3   hc        35.0    109.5
o1c   ct3   h1        35.0    109.5
o1c   c3    h1        35.0    109.5
c2a   ct2   ct2       63.0    116.6
cbb   ct3    hc       35.0    109.5
cbb   c2e    o2c      80.0    121.9
cbb   c2e    ct3      63.0    118.0
ct1   ct3    ct3      40.0    114.2
ct1   ct3    hc       35.0    109.5
ct3   ct1    hc       35.0    109.5
```

```
ct3   c2e   o2c       80.0    122.4
c2e   ct3   hc        35.0    109.5
ct2   ct2   hc        35.0    109.5
ct2   ct3   hc        35.0    109.5
ct3   ct2   hc        35.0    109.5
ct3   ct3   hc        35.0    109.5
hc    ct2   hc        35.0    109.5
hc    ct3   hc        35.0    109.5
h1    ct3   h1        35.0    109.5
o2c   cqo   cq2       60.0    120.0
o1c   cq2   cqo       60.0    120.0
o1c   cq2   cq2       60.0    120.0
cq2   o1c   ct3       60.0    112.0
cqo   cq2   cq2       30.0    120.0
cq2   cqo   cq2       30.0    120.0
cqo   cq2   ct2       50.0    115.7
cq2   cq2   ct2       50.0    124.1
cqo   cq2   ct3       50.0    115.2
cq2   cq2   ct3       50.0    124.9
cq2   ct2   cqq       50.0    112.0
ct2   ct2   cqq       50.0    112.0
o1c   ct2   cqq       50.0    109.6
cq2   cqq   ct2       50.0    125.9
cqq   cq2   ct2       50.0    120.2
cqq   cq2   ct3       50.0    123.7
ct2   cq2   ct3       50.0    116.0
ct3   cq2   ct3       50.0    116.0
cq2   ct2   ct2       50.0    114.5
cq2   ct2   ct3       50.0    114.5
hc    ct2   cq2       35.0    109.5
hc    ct3   cq2       35.0    109.5
hc    ct2   cqq       35.0    109.5
on    no    ct2       80.0    109.5
on    no    ct3       80.0    109.5
ct3   no    ct2       60.0    109.5
ct3   no    ct3       60.0    109.5
no    ct2   ct2       67.7    115.0
no    ct2   hc        40.0    109.5
no    ct3   hc        40.0    109.5
ct2   ct2   ct2       58.0    109.5
ct2   ct2   ct3       58.0    109.5
ct2   ct1   ct3       58.0    111.5
ct2   ct1   ct2       58.0    111.5
ct3   ct1   ct2       58.0    111.5
ct3   ct1   ct3       58.0    111.5
o1c   c3    c2        50.0    109.6 # Same as o1c - ct2 - cqq
cbb   cbb   cf        65.490  124.050 # Same as     ce - ce - cf
cnb   cbb   cf        65.490  124.050 # Same as     ce - ce - cf
cbb   cf    c2        65.420  124.330 # Same as ce - cf - cf
cbb   cf    ha        50.240  117.980 # Same as ce - cf - ha

DIHE
X    nmh  mgc  X   1    0.000       180.000          2.000
X    ns   mgc  X   1    0.000       180.000          2.000
X    nmh  cnb  X   1    2.500       180.000          2.000
X    nmh  crb  X   1    2.500       180.000          2.000
X    ns   ccs  X   1    2.500       180.000          2.000
X    ns   cnb  X   1    2.500       180.000          2.000  # Same with X-nmh-cnb-X
X    ns   crb  X   1    2.500       180.000          2.000  # Same with X-nmh-crb-X
X    nmh  cpb  X   1    0.000       180.000          2.000
X    nmh  cqb  X   1    2.500       180.000          2.000
X    cnb  cbb  X   1    3.50        180.000          2.000
X    crb  cbb  X   1    3.50        180.000          2.000
X    cpb  cbb  X   1    3.50        180.000          2.000
X    cqb  cbb  X   1    3.50        180.000          2.000
X    cbb  cbb  X   1    5.00        180.000          2.000
ct1  ct1  ccs  X   1    1.575       180.000          2.000
hc   ct1  ccs  X   1    0.00        180.000          2.000
ct2  ct1  ccs  X   1    0.00        180.000          2.000
ct3  ct1  ccs  X   1    0.00        180.000          2.000
X    ct1  ct1  X   1    0.00        180.000          3.000
X    cbb  c2k  X   1    5.000       180.000          2.000
csb  ct1  c2k  X   1    1.575       180.000          2.000
hc   ct1  c2k  X   1    0.000       180.000          2.000
c2a  ct1  c2k  X   1    0.000       180.000          2.000
c2k  ct1  csb  X   1    1.575       180.000          2.000
hc   ct1  csb  X   1    0.000       180.000          2.000
c2a  ct1  csb  X   1    0.000       180.000          2.000
X    cab  ccs  X   1    3.500       180.000          2.000
X    csb  ccs  X   1    3.500       180.000          2.000
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X    cab  cnb  X   1    3.500       180.000          2.000
X    cab  crb  X   1    3.500       180.000          2.000
X    cab  cpb  X   1    3.500       180.000          2.000
X    csb  cqb  X   1    3.500       180.000          2.000
o2c  c2a  o1c  X   1    1.000       180.000          1.000
o2c  c2a  o1c  c3  1    1.000       180.000          1.000
o2c  c2a  o1c  ct3 1    1.000       180.000          1.000
o2c  c2a  o1c  c3  1    6.000       180.000          2.000
o2c  c2a  o1c  X   1    6.000       180.000          2.000
ct1  c2a  o1c  X   1    1.500       180.000          2.000
ct1  c2a  o1c  ct3 1    1.500       180.000          2.000
ct2  c2a  o1c  X   1    1.500       180.000          2.000
ct2  c2a  o1c  c3  1    1.500       180.000          2.000
o1c  c2a  ct2  X   1    0.030         0.000          3.000
o1c  c2a  ct2  hc  1    0.030         0.000          3.000
o1c  c2a  ct2  ct2 1    0.030         0.000          3.000
o2c  c2a  ct2  hc  1    0.030       180.000          3.000
o2c  c2a  ct2  ct2 1    0.030       180.000          3.000
X    c2a  ct1  X   1    0.000       180.000          3.000
X    o1c  ct2  X   1    0.180         0.000          3.000
c2a  o1c  c3   c2  1    0.180         0.000          3.000
X    o1c  ct3  hc  1    0.180         0.000          3.000
c2a  o1c  c3   h1  1    0.180         0.000          3.000
c2a  o1c  ct3  h1  1    0.180         0.000          3.000
X    cbb  c2e  X   1    5.000       180.000          2.000
X    cbb  ct3  X   1    0.000       180.000          2.000
X    ct1  ct2  X   1    0.156         0.000          3.000
X    ct1  ct3  X   1    0.156         0.000          3.000
X    ct2  ct2  X   1    0.156         0.000          3.000
X    ct2  ct3  X   1    0.156         0.000          3.000
X    ct3  ct3  X   1    0.156         0.000          3.000
X    c2e  ct3  X   1    0.000       180.000          2.000
X    cbb  cf   X   4   26.600       180.000          2.000 # Same with X-ce-cf-X
X    cbb  ct2  X   2    0.000       180.000          2.000 # Same with X-c3-ca-X

IMPROPER
X X csb X        1.100 180.0    2.0
X X ns  X        1.100 180.0    2.0
X X nmh X        1.100 180.0    2.0
X X cab X        1.100 180.0    2.0
X X cbb X        1.100 180.0    2.0
X X ccs X        1.100 180.0    2.0
X X cnb X        1.100 180.0    2.0
X X crb X        1.100 180.0    2.0
X X ccs X        1.100 180.0    2.0
X X cpb X        1.100 180.0    2.0
X X cqb X        1.100 180.0    2.0
X X c2k o2c     10.500 180.0    2.0

NONBON
mgc     0.650   0.250
cab     1.908   0.086
csb     1.908   0.086
cbb     1.908   0.086
ccs     1.908   0.086
cnb     1.908   0.086
cpb     1.908   0.086
cqb     1.908   0.086
crb     1.908   0.086
c2k     1.908   0.086
c2a     1.908   0.086
o1c     1.6637  0.170
o2c     1.6612  0.210
nmh     1.824   0.170
ns      1.824   0.170
ct1     1.908   0.1094
ct2     1.908   0.1094
ct3     1.908   0.1094
```

Definition of the GAFF2 based atoms types, bond connectivity and RESP charges for β-carotene

```
@<TRIPOS>MOLECULE
BCR
   96    97     1     0     0
SMALL
No Charge or Current Charge


@<TRIPOS>ATOM
      1 C1          5.2430    34.2110     7.1440 c3      2741 BCR       0.520876
      2 C2          4.3100    34.8670     8.1640 c3      2741 BCR      -0.153725
      3 C3          4.2420    34.3760     9.5990 c3      2741 BCR       0.057544
      4 C4          4.2390    32.8230     9.7110 c3      2741 BCR      -0.129668
      5 C5          4.8880    32.1110     8.5550 c2      2741 BCR       0.189555
      6 C6          5.3500    32.7170     7.3970 ce      2741 BCR      -0.406682
      7 C7          5.9500    31.8730     6.3290 ce      2741 BCR       0.118700
      8 C8          7.0420    31.0820     6.5130 cf      2741 BCR      -0.350037
      9 C9          7.4690    30.2260     5.4030 cf      2741 BCR       0.188330
     10 C10         8.4190    29.3240     5.6480 ce      2741 BCR      -0.316233
     11 C11         8.8860    28.3120     4.6990 ce      2741 BCR      -0.008810
     12 C12         9.7950    27.4720     5.2180 cf      2741 BCR      -0.376308
     13 C13        10.3210    26.2840     4.4570 cf      2741 BCR       0.221509
     14 C14        11.1310    25.4070     5.1140 ce      2741 BCR      -0.341417
     15 C15        11.6470    24.1590     4.5150 ce      2741 BCR      -0.112451
     16 C16        12.3400    23.2780     5.2460 cf      2741 BCR      -0.126191
     17 C17        12.7450    21.9790     4.6920 cf      2741 BCR      -0.332899
     18 C18        13.2860    20.9250     5.3860 ce      2741 BCR       0.206356
     19 C19        13.5180    19.6680     4.6210 ce      2741 BCR      -0.365331
     20 C20        14.1140    18.5980     5.1740 cf      2741 BCR      -0.007725
     21 C21        14.1690    17.3900     4.3260 cf      2741 BCR      -0.336895
     22 C22        14.7030    16.1910     4.6980 ce      2741 BCR       0.170995
     23 C23        14.5980    15.0460     3.7480 ce      2741 BCR      -0.315312
     24 C24        14.6160    13.7720     4.2080 cf      2741 BCR       0.054632
     25 C25        14.3950    12.5470     3.3440 cf      2741 BCR      -0.300273
     26 C26        13.1670    12.3560     2.8240 c2      2741 BCR       0.178004
     27 C27        12.8460    11.1670     1.9330 c3      2741 BCR      -0.100874
     28 C28        14.0880    10.8480     1.1190 c3      2741 BCR       0.041870
     29 C29        15.0930    10.3820     2.1360 c3      2741 BCR      -0.174348
     30 C30        15.4560    11.5200     3.0820 c3      2741 BCR       0.517469
     31 C31         6.6780    34.7870     7.0350 c3      2741 BCR      -0.417696
     32 C32         4.5400    34.5790     5.8530 c3      2741 BCR      -0.456532
     33 C33         4.9680    30.5960     8.7790 c3      2741 BCR      -0.379835
     34 C34         6.8390    30.3420     4.0290 c3      2741 BCR      -0.258093
     35 C35         9.9310    26.0930     3.0060 c3      2741 BCR      -0.204429
     36 C36        13.6120    20.9330     6.8650 c3      2741 BCR      -0.168116
     37 C37        15.3170    16.0070     6.0540 c3      2741 BCR      -0.235548
     38 C38        12.0740    13.3510     3.0770 c3      2741 BCR      -0.415232
     39 C39        16.6330    12.2520     2.4630 c3      2741 BCR      -0.454504
     40 C40        15.6970    10.9170     4.4460 c3      2741 BCR      -0.431307
     41 HC21        3.3000    34.8060     7.7580 hc      2741 BCR       0.033746
     42 HC22        4.5730    35.9250     8.2030 hc      2741 BCR       0.033746
     43 HC31        3.3410    34.7700    10.0700 hc      2741 BCR      -0.005016
     44 HC32        5.0910    34.7730    10.1540 hc      2741 BCR      -0.005016
     45 HC41        3.2090    32.4800     9.8000 hc      2741 BCR       0.049649
     46 HC42        4.7510    32.5380    10.6300 hc      2741 BCR       0.049649
     47 HC7         5.4890    31.8890     5.3410 ha      2741 BCR       0.089803
     48 HC8         7.5830    31.0840     7.4600 ha      2741 BCR       0.196276
     49 H10C        8.8850    29.3400     6.6330 ha      2741 BCR       0.158878
     50 H11C        8.5300    28.2450     3.6710 ha      2741 BCR       0.163465
     51 H12C       10.1660    27.6560     6.2270 ha      2741 BCR       0.206724
     52 H14C       11.4150    25.6400     6.1410 ha      2741 BCR       0.159668
     53 H15C       11.4610    23.9520     3.4610 ha      2741 BCR       0.182949
     54 H16C       12.6090    23.5290     6.2720 ha      2741 BCR       0.182269
     55 H17C       12.6010    21.8380     3.6210 ha      2741 BCR       0.155445
     56 H19C       13.1950    19.6140     3.5820 ha      2741 BCR       0.202424
     57 H20C       14.5290    18.6200     6.1810 ha      2741 BCR       0.160907
     58 H21C       13.7500    17.4630     3.3230 ha      2741 BCR       0.170255
     59 H23C       14.5070    15.2350     2.6790 ha      2741 BCR       0.181715
     60 H24C       14.8020    13.6180     5.2710 ha      2741 BCR       0.106958
     61 H271       12.0080    11.3970     1.2760 hc      2741 BCR       0.037749
     62 H272       12.5530    10.3080     2.5350 hc      2741 BCR       0.037749
     63 H281       14.4460    11.7250     0.5800 hc      2741 BCR       0.000153
     64 H282       13.8880    10.0760     0.3760 hc      2741 BCR       0.000153
     65 H291       15.9900    10.0210     1.6310 hc      2741 BCR       0.040575
     66 H292       14.6860     9.5450     2.7020 hc      2741 BCR       0.040575
     67 H311        7.2350    34.2350     6.2790 hc      2741 BCR       0.094143
     68 H312        7.1800    34.6930     7.9980 hc      2741 BCR       0.094143
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      69 H313         6.6270    35.8390     6.7540 hc      2741 BCR       0.094143
      70 H321         5.0960    34.1720     5.0080 hc      2741 BCR       0.102362
      71 H322         4.4860    35.6630     5.7650 hc      2741 BCR       0.102362
      72 H323         3.5330    34.1630     5.8570 hc      2741 BCR       0.102362
      73 H331         5.4430    30.1270     7.9180 hc      2741 BCR       0.101612
      74 H332         3.9630    30.1950     8.9040 hc      2741 BCR       0.101612
      75 H333         5.5550    30.3920     9.6740 hc      2741 BCR       0.101612
      76 H341         7.2990    29.6190     3.3560 hc      2741 BCR       0.076108
      77 H342         6.9930    31.3490     3.6410 hc      2741 BCR       0.076108
      78 H343         5.7690    30.1410     4.1010 hc      2741 BCR       0.076108
      79 H351        10.4000    25.1890     2.6200 hc      2741 BCR       0.062642
      80 H352        10.2640    26.9520     2.4240 hc      2741 BCR       0.062642
      81 H353         8.8470    26.0010     2.9290 hc      2741 BCR       0.062642
      82 H361        14.0300    19.9680     7.1510 hc      2741 BCR       0.054733
      83 H362        12.7030    21.1180     7.4370 hc      2741 BCR       0.054733
      84 H363        14.3380    21.7190     7.0750 hc      2741 BCR       0.054733
      85 H371        15.6820    14.9840     6.1520 hc      2741 BCR       0.071622
      86 H372        14.5670    16.1990     6.8210 hc      2741 BCR       0.071622
      87 H373        16.1470    16.7030     6.1760 hc      2741 BCR       0.071622
      88 H381        11.1620    13.0250     2.5780 hc      2741 BCR       0.105731
      89 H382        12.3730    14.3250     2.6890 hc      2741 BCR       0.105731
      90 H383        11.8940    13.4290     4.1490 hc      2741 BCR       0.105731
      91 H391        17.4330    11.5420     2.2530 hc      2741 BCR       0.100119
      92 H392        16.9940    13.0120     3.1560 hc      2741 BCR       0.100119
      93 H393        16.3180    12.7270     1.5350 hc      2741 BCR       0.100119
      94 H401        16.4630    10.1450     4.3720 hc      2741 BCR       0.090657
      95 H402        14.7720    10.4750     4.8180 hc      2741 BCR       0.090657
      96 H403        16.0300    11.6940     5.1340 hc      2741 BCR       0.090657
@<TRIPOS>BOND
     1     1     2 1
     2     1     6 1
     3     1    31 1
     4     1    32 1
     5     2     3 1
     6     2    41 1
     7     2    42 1
     8     3     4 1
     9     3    43 1
    10     3    44 1
    11     4     5 1
    12     4    45 1
    13     4    46 1
    14     5     6 2
    15     5    33 1
    16     6     7 1
    17     7     8 2
    18     7    47 1
    19     8     9 1
    20     8    48 1
    21     9    10 2
    22     9    34 1
    23    10    11 1
    24    10    49 1
    25    11    12 2
    26    11    50 1
    27    12    13 1
    28    12    51 1
    29    13    14 2
    30    13    35 1
    31    14    15 1
    32    14    52 1
    33    15    16 2
    34    15    53 1
    35    16    17 1
    36    16    54 1
    37    17    18 2
    38    17    55 1
    39    18    19 1
    40    18    36 1
    41    19    20 2
    42    19    56 1
    43    20    21 1
    44    20    57 1
    45    21    22 2
    46    21    58 1
    47    22    23 1
    48    22    37 1
    49    23    24 2
    50    23    59 1
    51    24    25 1
```

```
    52    24    60 1
    53    25    26 2
    54    25    30 1
    55    26    27 1
    56    26    38 1
    57    27    28 1
    58    27    61 1
    59    27    62 1
    60    28    29 1
    61    28    63 1
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    89    38    88 1
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    91    38    90 1
    92    39    91 1
    93    39    92 1
    94    39    93 1
    95    40    94 1
    96    40    95 1
    97    40    96 1
@<TRIPOS>SUBSTRUCTURE
     1 BCR          1 TEMP              0 ****  ****    0 ROOT
```

GAFF2 based bonded and LJ parameters for β-carotene

```
Remark line goes here
MASS

BOND #Associated parameters for the bonded atoms can be found in the AMBER GAFF2 force-field
library.

ANGLE #Associated parameters for the angles can be found in the AMBER GAFF2 force-field
library.


DIHE
c3-c3-ce-c2   6    0.000         0.000          3.000      same as X -c3-cc-X
c3-c3-ce-ce   6    0.000         0.000          3.000      same as X -c3-cc-X
hc-c3-cf-cf   1    0.380       180.000         -3.000      same as hc-c3-c2-c2
hc-c3-cf-cf   1    0.000         0.000         -2.000      same as hc-c3-c2-c2
hc-c3-cf-cf   1    1.150         0.000          1.000      same as hc-c3-c2-c2
hc-c3-cf-ce   1    0.380       180.000         -3.000      same as hc-c3-c2-c2
hc-c3-cf-ce   1    0.000         0.000         -2.000      same as hc-c3-c2-c2
hc-c3-cf-ce   1    1.150         0.000          1.000      same as hc-c3-c2-c2
hc-c3-ce-cf   1    0.380       180.000         -3.000      same as hc-c3-c2-c2
hc-c3-ce-cf   1    0.000         0.000         -2.000      same as hc-c3-c2-c2
hc-c3-ce-cf   1    1.150         0.000          1.000      same as hc-c3-c2-c2
hc-c3-ce-ce   1    0.380       180.000         -3.000      same as hc-c3-c2-c2
```

```
hc-c3-ce-ce   1    0.000          0.000          -2.000      same as hc-c3-c2-c2
hc-c3-ce-ce   1    1.150          0.000           1.000      same as hc-c3-c2-c2
c3-c3-cf-cf   6    0.000          0.000           3.000      same as X -c3-cd-X
c3-c3-cf-c2   6    0.000          0.000           3.000      same as X -c3-cd-X

IMPROPER
c3-c3-c2-ce          1.1          180.0         2.0          Using the default value
c2-c3-ce-ce          1.1          180.0         2.0          Using the default value
ce-cf-ce-ha          1.1          180.0         2.0          Same as X -X -ca-ha
ce-cf-cf-ha          1.1          180.0         2.0          Same as X -X -ca-ha
c3-ce-cf-cf          1.1          180.0         2.0          Using the default value
c3-ce-ce-cf          1.1          180.0         2.0          Using the default value
c2-c3-cf-cf          1.1          180.0         2.0          Using the default value
c3-c3-c2-cf          1.1          180.0         2.0          Using the default value

NONBON
#LJ parameters for the assigned atom types can be found in the AMBER GAFF2 force-field
library.
```

References

1. J. Hall, T. Renger, F. Müh, R. Picorel and E. Krausz, *Biochim. Biophys. Acta Bioenerg.*, 2016, **1857**, 1580-1593.

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3. T. Reinot, J. Chen, A. Kell, M. Jassas, K. C. Robben, V. Zazubovich and R. Jankowiak, *Anal. Chem. Insights*, 2016, **11**, 35-48.