Supporting information for:

Solvation dynamics: Improved reproduction of the time-dependent Stokes shift with polarizable empirical force field chromophore models

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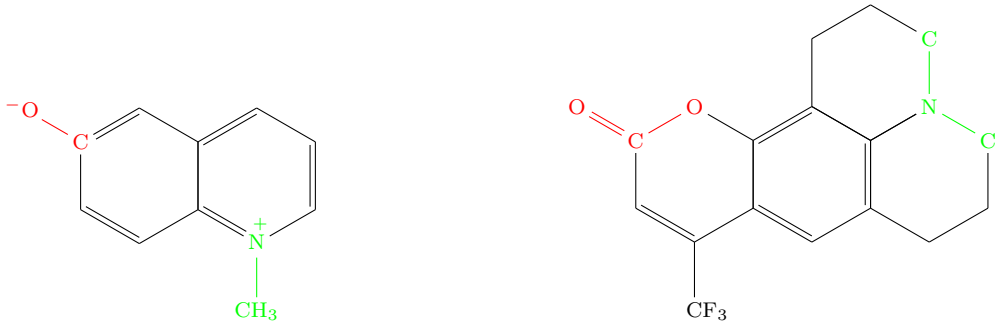
1 Solvent structure

Radial distribution functions around the whole solute, as well as the center of masses of the oxygen and nitrogen containing sites (colored in red and green in Fig. S1, respectively) were calculated for MQ and C153 in the ground and excited state. Fig. S2 depicts the radial distribution functions in water. Upon excitation, mainly the distribution around the oxygen site, which loses both electron densities and hydrogen bonds, changes. The polarizable and nonpolarizable force field produce nearly identical structures.



(a) N-methyl-6-oxyquinolinium betaine (MQ) (b) Coumarin 153 (C153)

Figure S1: Oxygen sites (red) and nitrogen sites (green) of MQ and C153 used in the analysis of radial distribution functions.

Fig. S3 depicts the radial distribution functions in methanol. The changes in solvent structure upon excitation are stronger for MQ than for C153. Again, mainly the structure around the oxygen site of MQ differs between the ground and excited state. The inclusion of polarizability to the force field does not change the solvent structure.

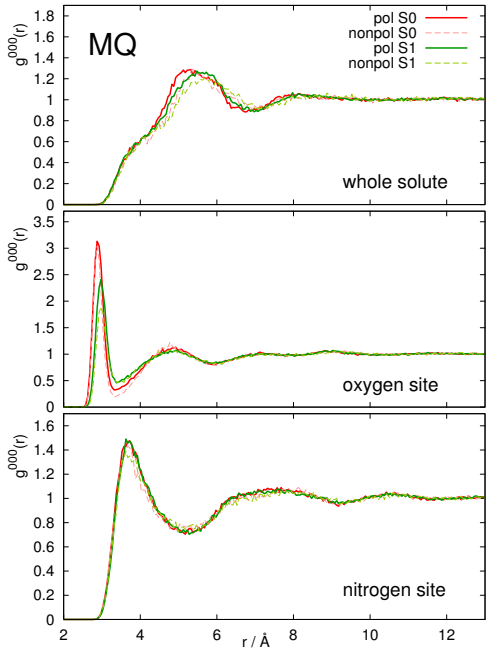


Figure S2: Radial distribution functions around the chromophore MQ (top) as well as around the oxygen (middle) and nitrogen containing sites (bottom) in water.

Fig. S4 depicts the radial distribution functions in EmimOTf. Since no hydrogen bonds occur between both chromophores and the solvent, no specific interactions or large changes were found for the oxygen site in MQ upon excitation. The solvent structure undergoes considerable changes upon inclusion of polarizability to the solvent models, especially at the oxygen sites of the two chromophores.

2 Mass of Drude particles

The masses of the Drude particles were set to 0.2 amu to be consistent with the Drude masses in the employed ionic liquid force field. To ensure that the choice of the mass does not affect any of our results we conducted additional simulations with a Drude mass of 0.4 amu for MQ in water and methanol, as well as C153 in methanol. The obtained dipole moment distributions, radial distribution functions and absolute time-dependent Stokes shifts are depicted in Fig. S5. The results from simulations with masses of 0.2 amu and 0.4 amu coincide apart from numerical errors.

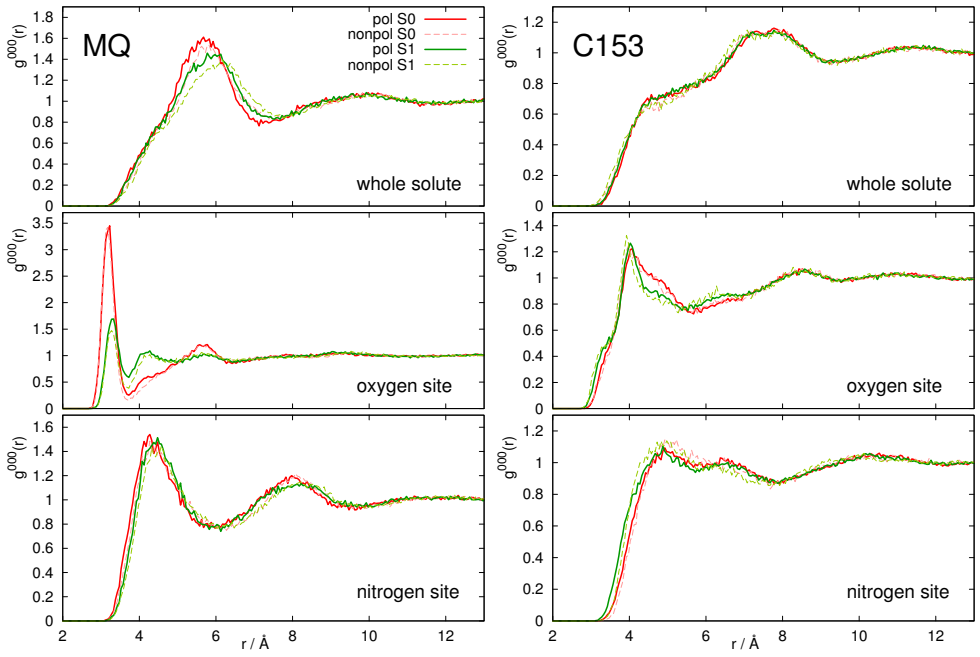


Figure S3: Radial distribution functions around the chromophores MQ and C153 (top) as well as around the oxygen (middle) and nitrogen containing sites (bottom) in methanol.

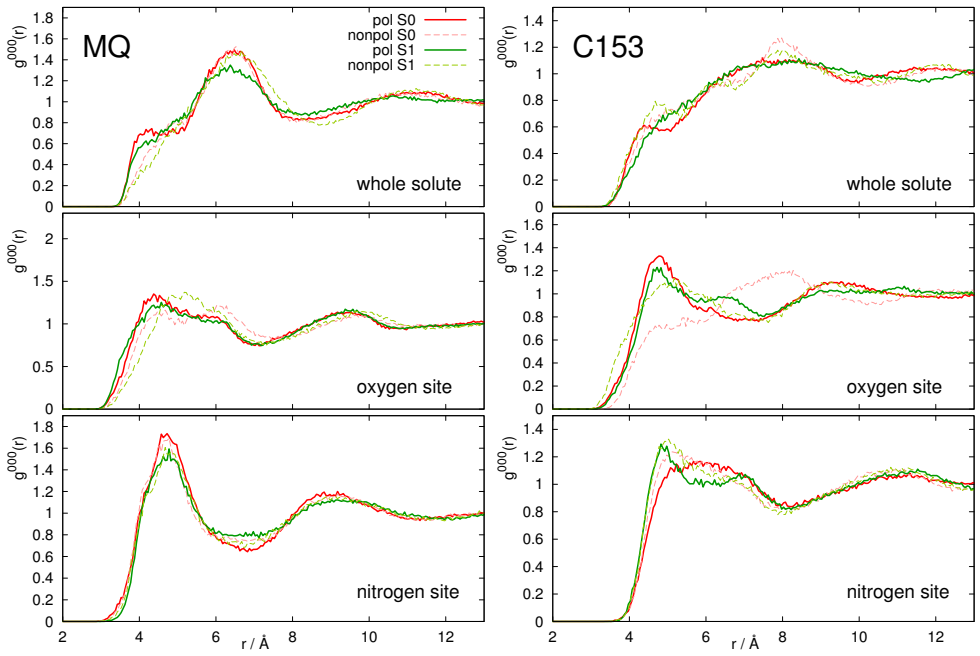


Figure S4: Radial distribution functions around the chromophores MQ and C153 (top) as well as around the oxygen (middle) and nitrogen containing sites (bottom) in EmimOTf.

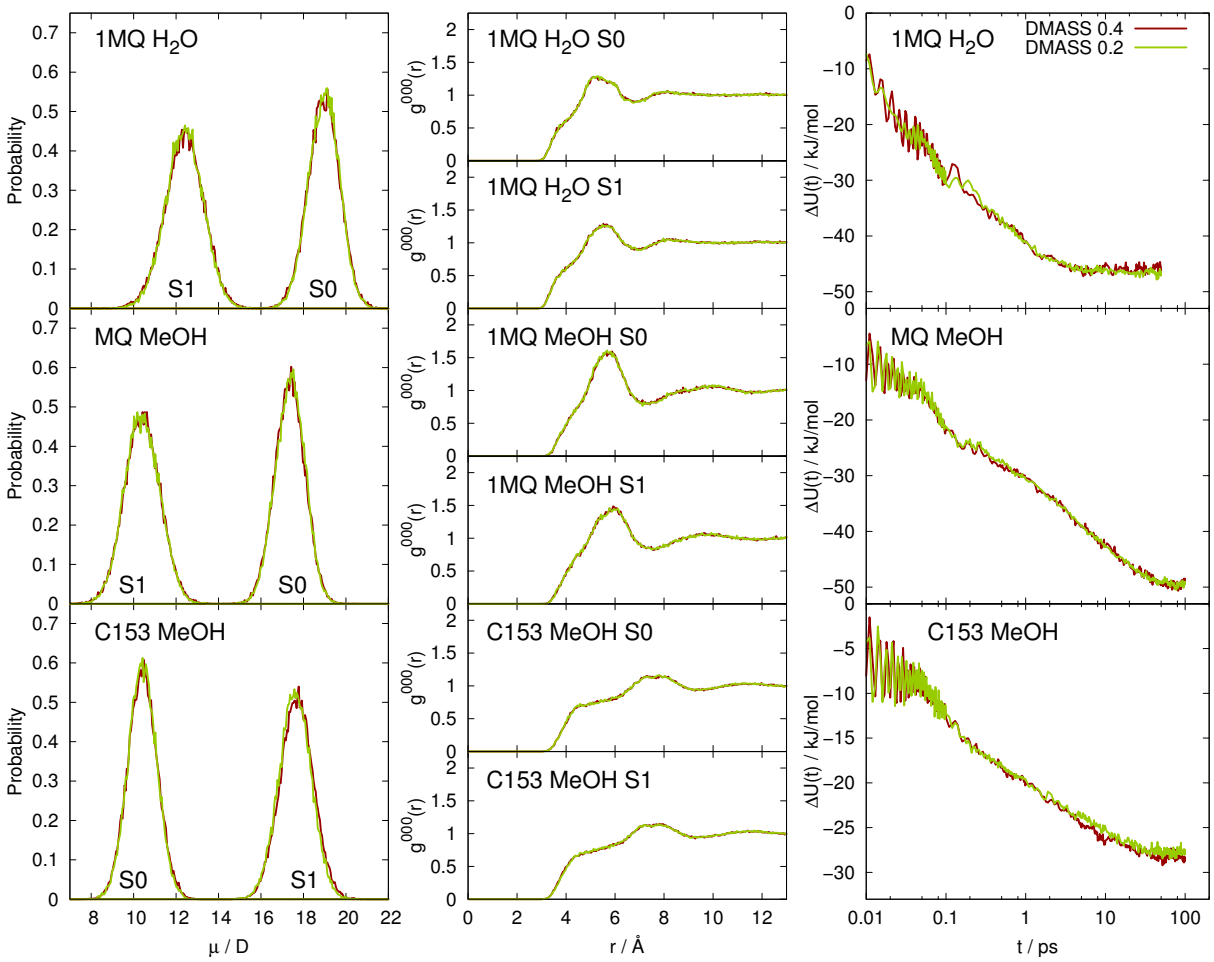


Figure S5: Dipole moments (left), radial distribution functions (middle) and time-dependent Stokes shift (right) of MQ in water (top), MQ in methanol (middle) and C153 in methanol (bottom).

3 TDSS fit parameters

Table S1 lists the fit parameters of the fit function

$$f(t) = a_0 + \sum_{i=1}^{3} a_i \cdot e^{-\frac{t}{\tau_i}} \tag{1}$$

as well as the magnitude of the overall shift in electrostatic energy ΔU.

Table S1: Fit parameters of the TDSS obtained from simulations with nonpolarizable solvent and chromophore (np/np), polarizable solvent and nonpolarizable chromophore (p/np) and polarizable solvent and chromophore force fields (p/p)

			a_0 [$\frac{\text{kJ}}{\text{mol}}$]	a_1 [$\frac{\text{kJ}}{\text{mol}}$]	a_2 [$\frac{\text{kJ}}{\text{mol}}$]	a_3 [$\frac{\text{kJ}}{\text{mol}}$]	τ_1 [ps]	τ_2 [ps]	τ_3 [ps]	ΔU [$\frac{\text{kJ}}{\text{mol}}$]
MQ	H_2O	p/np	58.5	27.7	8.7	7.3	0.023	0.263	1.32	43.7
		p/p	84.2	21.3	13.4	7.8	0.026	0.361	1.75	42.5
	MeOH	p/np	53.1	20.3	9.8	11.5	0.069	0.986	9.84	41.5
		p/p	53.0	16.6	7.4	16.6	0.072	0.879	7.78	40.5
	EmimOTf	p/np	41.5	19.8	6.7	7.9	0.077	10.4	658	34.4
		p/p	36.0	13.7	6.3	8.1	0.175	25.0	807	28.1
C153	MeOH	p/np	-67.0	14.1	6.6	5.4	0.110	1.17	13.0	26.1
		p/p	-52.7	11.1	5.3	6.0	0.117	1.29	11.	22.4
	EmimOTf	np/np	-64.0	17.5	6.1	8.5	0.245	21.7	863	32.0
		p/np	-64.0	15.9	5.3	8.2	0.095	10.9	886	29.4
		p/p	-49.5	13.3	5.3	7.1	0.083	9.18	986	25.8

4 Force field

Force field model of MQ. The masses of the Drude particles were set to 0.2 amu.

```
* DRUDE model compound topology file
*

READ RTF CARD
*============================================================
*.   T O P O L O G Y   O F   Q U I N O L O N E
*============================================================
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99
MASS     1 ND2R6C   14.00700
MASS     2 CD33A    12.01100
MASS     3 CD2R6B   12.01100
MASS     4 CD2R6A   12.01100
MASS     5 CD2R6I   12.01100
MASS     6 HDA3A     1.00800
MASS     7 HDR6B     1.00800
MASS     8 HDR6A     1.00800
MASS     9 OD30E    15.99900
MASS   199  DRUD     0.00000

AUTO DRUDE ANGL DIHE

RESI MQS0          0.000 !
GROUP
!
!            H2      H3
!             \     /
!      HN1     C2--C3
!        \    //    \\
!  HN2--CN--N1(+)   C4--H4
!        /    \     /
!      HN3    C8A==C4A
!             /     \
!        H8--C8     C5--H5
!             \\    //
!              C7--C6
!             /     \
!            H7     O6(-)
!
!charges: wB97xD/aug-cc-pVTZ CHelpG PCM scaled 0.88
!polarizability: MP2/Sadlej gas phase scaled 0.724
ATOM CN       CD33A    -0.0904     ALPHA   -1.302  THOLE 1.300
ATOM HN1      HDA3A     0.0876
ATOM HN2      HDA3A     0.0876
ATOM HN3      HDA3A     0.0876
ATOM N1       ND2R6C    0.0242     ALPHA   -1.218  THOLE 1.000
ATOM C2       CD2R6B    0.0203     ALPHA   -1.376  THOLE 1.100
ATOM H2       HDR6B     0.1296
ATOM C3       CD2R6A   -0.1573     ALPHA   -1.371  THOLE 1.300
ATOM H3       HDR6A     0.1330
ATOM C4       CD2R6A   -0.0759     ALPHA   -1.452  THOLE 1.300
ATOM H4       HDR6A     0.1261
ATOM C4A      CD2R6A    0.1667     ALPHA   -1.363  THOLE 1.300
ATOM C5       CD2R6A   -0.5181     ALPHA   -1.613  THOLE 1.300
ATOM H5       HDR6A     0.1536
ATOM C6       CD2R6I    0.6293     ALPHA   -1.271  THOLE 1.000
ATOM O6       OD30E    -0.7379     ALPHA   -1.173  THOLE 1.000
ATOM C7       CD2R6A   -0.2482     ALPHA   -1.363  THOLE 1.300
ATOM H7       HDR6A     0.1184
ATOM C8       CD2R6A   -0.1736     ALPHA   -1.432  THOLE 1.300
ATOM H8       HDR6A     0.1523
ATOM C8A      CD2R6B    0.0851     ALPHA   -1.333  THOLE 1.100
BOND C4   C4A
BOND C4   C3
BOND C4   H4
BOND C4A  C5
BOND C8A  N1
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BOND C8A  C8
BOND N1   CN
BOND C2   C3
BOND C2   H2
BOND C3   H3
BOND C8   H8
BOND C7   C6
BOND C7   H7
BOND C6   O6
BOND C5   H5
BOND CN   HN1
BOND CN   HN2
BOND CN   HN3
BOND N1   C2
BOND C8   C7
BOND C6   C5
BOND C4A  C8A

RESI MQS1          0.000 !
GROUP
!
!            H2       H3
!             \      /
!     HN1      C2--C3
!       \     //     \\
!  HN2--CN--N1(+)    C4--H4
!       /     \      /
!     HN3     C8A==C4A
!             /      \
!       H8--C8       C5--H5
!             \\     //
!              C7--C6
!             /      \
!            H7      O6(-)
!
!charges: wB97xD/aug-cc-pVTZ CHelpG PCM scaled 0.88
!polarizability: MP2/Sadlej gas phase scaled 0.724
ATOM CN       CD33A    -0.1575     ALPHA   -1.440  THOLE 1.300
ATOM HN1      HDA3A     0.0881
ATOM HN2      HDA3A     0.0881
ATOM HN3      HDA3A     0.0881
ATOM N1       ND2R6C    0.1221     ALPHA   -1.364  THOLE 1.000
ATOM C2       CD2R6B   -0.1629     ALPHA   -1.632  THOLE 1.100
ATOM H2       HDR6B     0.1390
ATOM C3       CD2R6A   -0.1057     ALPHA   -1.529  THOLE 1.300
ATOM H3       HDR6A     0.1114
ATOM C4       CD2R6A   -0.2116     ALPHA   -1.714  THOLE 1.300
ATOM H4       HDR6A     0.1124
ATOM C4A      CD2R6A    0.1646     ALPHA   -1.622  THOLE 1.300
ATOM C5       CD2R6A   -0.2937     ALPHA   -1.574  THOLE 1.300
ATOM H5       HDR6A     0.1341
ATOM C6       CD2R6I    0.6142     ALPHA   -1.271  THOLE 1.100
ATOM O6       OD30E    -0.5817     ALPHA   -1.032  THOLE 1.100
ATOM C7       CD2R6A   -0.3208     ALPHA   -1.688  THOLE 1.300
ATOM H7       HDR6A     0.1181
ATOM C8       CD2R6A   -0.1796     ALPHA   -1.565  THOLE 1.300
ATOM H8       HDR6A     0.1674
ATOM C8A      CD2R6B    0.0659     ALPHA   -1.493  THOLE 1.100
BOND C4   C4A
BOND C4   C3
BOND C4   H4
BOND C4A  C5
BOND C8A  N1
BOND C8A  C8
BOND N1   CN
BOND C2   C3
BOND C2   H2
BOND C3   H3
BOND C8   H8
BOND C7   C6
BOND C7   H7
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BOND C6   O6
BOND C5   H5
BOND CN   HN1
BOND CN   HN2
BOND CN   HN3
BOND N1   C2
BOND C8   C7
BOND C6   C5
BOND C4A  C8A

END


READ PARA CARD
*=============================================================
*.   P A R A M E T E R   O F   Q U I N O L O N E
*=============================================================
*

ATOMS
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
!      ID  NAME     MASS
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
MASS    1 ND2R6C   14.00700
MASS    2 CD33A    12.01100
MASS    3 CD2R6B   12.01100
MASS    4 CD2R6A   12.01100
MASS    5 CD2R6I   12.01100
MASS    6 HDA3A     1.00800
MASS    7 HDR6B     1.00800
MASS    8 HDR6A     1.00800
MASS    9 OD30E    15.99900
MASS  199  DRUD     0.00000

BONDS
!
! U_bond = k ( r - r0 )^2
!
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
!TYPE1    TYPE2    k [kcal/mol Angstroem^2]     r0 [Angstroem]
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
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CD33A    HDA3A    322.00       1.111
ND2R6C   CD33A    400.00       1.456
CD2R6A   CD2R6B   361.10       1.378
CD2R6A   CD2R6A   305.00       1.375
CD2R6A   HDR6A    340.00       1.080
CD2R6B   HDR6B    340.00       1.080
OD30E    CD2R6I   334.30       1.262
CD2R6I   CD2R6A   305.00       1.384
X        DRUD     500.0        0.000

ANGLES
!
! U_angle = k ( theta - theta0 )^2
!
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
!TYPE1    TYPE2     TYPE3     k [kcal/mol rad^2]     theta0 [deg]
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
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HDA3A    CD33A    HDA3A     35.50    108.40    5.40   1.802
CD2R6A   CD2R6B   HDR6B     43.40    120.00   18.60   2.1525
CD2R6B   CD2R6A   HDR6A     26.00    120.00   21.00   2.1525
CD2R6A   CD2R6A   HDR6A     30.00    120.00   22.00   2.1525
CD2R6A   CD2R6A   CD2R6B    46.10    120.00   29.80   2.4480
CD2R6A   CD2R6A   CD2R6A    40.00    120.00   35.00   2.4162
CD2R6A   CD2R6A   CD2R6I    50.00    118.20
CD2R6I   CD2R6A   HDR6A     30.00    116.55
CD2R6A   CD2R6I   OD30E     55.20    127.80
CD2R6A   CD2R6I   CD2R6A    50.00    111.50
CD2R6B   ND2R6C   CD2R6B    19.60    100.00   54.20   2.2850
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CD2R6B   ND2R6C   CD33A     40.00    118.40
CD2R6A   CD2R6B   CD2R6A    40.00    120.00   35.00   2.4162

DIHEDRALS
!
! U_dihedral = k ( 1 + Cos[n phi - delta] )
!
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
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!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
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CD2R6A   CD2R6A   CD2R6A   CD2R6B      5.350    2   180.00
HDR6A    CD2R6A   CD2R6B   HDR6B       2.400    2   180.00
CD2R6A   CD2R6A   CD2R6B   HDR6B       5.400    2   180.00
CD2R6A   CD2R6A   CD2R6A   CD2R6A      2.800    2   180.00
HDR6A    CD2R6A   CD2R6A   HDR6A       2.400    2   180.00
CD2R6A   CD2R6A   CD2R6A   HDR6A       4.200    2   180.00
CD2R6A  CD2R6A   CD2R6A   CD2R6I       2.800    2   180.00
CD2R6A  CD2R6A   CD2R6I   CD2R6A       2.800    2   180.00
CD2R6A  CD2R6I   CD2R6A   HDR6A       4.200    2   180.00
OD30E   CD2R6I   CD2R6A   CD2R6A       3.100    2   180.00
OD30E   CD2R6I   CD2R6A   HDR6A       4.200    2   180.00
CD2R6I  CD2R6A   CD2R6A   HDR6A       4.200    2   180.00
CD2R6A   CD2R6A   CD2R6B   CD2R6A      4.400    2   180.00
CD2R6B   ND2R6C   CD2R6B   CD2R6A      8.000    2   180.00
CD2R6B   ND2R6C   CD2R6B   HDR6B       0.138    2     0.00
CD2R6A   CD2R6A   CD2R6B   ND2R6C     10.147    2   180.00
HDR6A    CD2R6A   CD2R6B   ND2R6C      1.103    2   180.00
HDR6B  CD2R6B ND2R6C CD33A             0.300    2   180.00
CD2R6A CD2R6B ND2R6C CD33A             3.5000   2   180.00
HDA3A  CD33A  ND2R6C CD2R6B            0.0934   3     0.00
CD2R6A CD2R6B CD2R6A HDR6A             0.5272   2   180.00
CD2R6B CD2R6A CD2R6A CD2R6I            7.3361   2     0.00

NONBONDED nbxmod  5 atom vatom cdiel vdistance switch vswitch -
cutnb 16.0 ctofnb 12.0 ctonnb 10.0 eps 1.0 e14fac 1.0 wmin 1.5
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
!TYPE1          epsilon    rmin/2       epsilon14   rmin14/2
!           [kcal/mol] [Angstroem]    [kcal/mol] [Angstroem]
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
ND2R6C   0.0    -0.1180     1.8440
CD33A    0.0    -0.0780     2.0400  0.0 -0.01 1.9
CD2R6B   0.0    -0.1190     1.8700
CD2R6A   0.0    -0.0690     2.0900
CD2R6I   0.0    -0.7800     1.5500
OD30E    0.0    -0.8300     1.5200
HDA3A    0.0    -0.0240     1.3400
HDR6B    0.0    -0.0700     0.8000
HDR6A    0.0    -0.0300     1.0500
DRUD    0.00    -0.0000     0.0000


END
RETURN
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Force field model of C153. The masses of the Drude particles were set to 0.2 amu.

```
* DRUDE model compound topology file
*

READ RTF CARD
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*============================================================
*
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MASS     1  HDR6A      1.008
MASS     2  HDA2A      1.008
MASS     3  CD2R6A    12.011
MASS     4  CD2R6H    12.011
MASS     5  CD2O4A    12.011
MASS     6  CD32A     12.011
MASS     7  CD30A     12.011
MASS     8  ND3P2A    14.007
MASS     9  OD2C1B    16.000
MASS    10  OD306A    16.000
MASS    11  FDA3      18.99840
MASS   199  DRUD      0.0000

AUTO DRUDE ANGL DIHE

!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
RESI COS0       0.000
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
GROUP
!              H5    H6
!                \  /
!           H4    C11    H7
!             \  /   \  /
!          H3- C10    C12-H8
!               |     |
!  O1    O2    C9    N     H9
!   \\ /   \  /  \\ / \   /
!    C7     C8    C1   C13 -H10
!    |      ||    |     |
!    C6     C4    C2   C14 -H11
!    / \\  /  \  // \ /   \
!  H2    C5    C3   C15    H12
!        |      |   / \
!    F1-C16-F3  H1 H14 H13
!        |
!        F2
!charges: wB97xD/aug-cc-pVTZ CHelpG PCM scaled 0.9
!polarizability: MP2/Sadlej gas phase scaled 0.724
ATOM    C1      CD2R6A  0.1344  ALPHA   -1.030  THOLE   1.3
ATOM    C2      CD2R6A  -0.0164 ALPHA   -1.189  THOLE   1.3
ATOM    C3      CD2R6A  -0.2317 ALPHA   -1.288  THOLE   1.3
ATOM    H1      HDR6A   0.1621
ATOM    C4      CD2R6H  -0.0830 ALPHA   -1.314  THOLE   1.0
ATOM    C5      CD2R6H  0.0645  ALPHA   -1.211  THOLE   1.0
ATOM    C6      CD2R6H  -0.3691 ALPHA   -1.222  THOLE   1.0
ATOM    H2      HDR6A   0.1496
ATOM    C7      CD2O4A  0.7666  ALPHA   -1.057  THOLE   1.0
ATOM    O1      OD2C1B  -0.5947 ALPHA   -0.901  THOLE   1.2
ATOM    O2      OD306A  -0.3496 ALPHA   -0.981  THOLE   1.2
ATOM    C8      CD2R6H  0.2606  ALPHA   -1.235  THOLE   1.0
ATOM    C9      CD2R6A  -0.2093 ALPHA   -1.289  THOLE   1.3
ATOM    C10     CD32A   0.1748  ALPHA   -1.229  THOLE   1.3
ATOM    H3      HDA2A   -0.0115
ATOM    H4      HDA2A   -0.0115
ATOM    C11     CD32A   -0.0151 ALPHA   -1.360  THOLE   1.3
ATOM    H5      HDA2A   0.0097
ATOM    H6      HDA2A   0.0097
ATOM    C12     CD32A   0.0576  ALPHA   -1.332  THOLE   1.3
ATOM    H7      HDA2A   0.0324
ATOM    H8      HDA2A   0.0324
```

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ATOM     C13      CD32A    -0.0478 ALPHA    -1.364  THOLE   1.3
ATOM     H9       HDA2A    0.0626
ATOM     H10      HDA2A    0.0626
ATOM     C14      CD32A    -0.0031 ALPHA    -1.339  THOLE   1.3
ATOM     H11      HDA2A    0.0216
ATOM     H12      HDA2A    0.0216
ATOM     C15      CD32A    0.0149  ALPHA    -1.353  THOLE   1.3
ATOM     H13      HDA2A    0.0272
ATOM     H14      HDA2A    0.0272
ATOM     C16      CD30A    0.5635  ALPHA    -0.651  THOLE   0.9
ATOM     F1       FDA3     -0.1946 ALPHA    -0.428  THOLE   0.663
ATOM     F2       FDA3     -0.1946 ALPHA    -0.428  THOLE   0.663
ATOM     F3       FDA3     -0.1946 ALPHA    -0.428  THOLE   0.663

BOND C1   C2
BOND C1   C9
BOND C1   N
BOND C2   C3
BOND C2   C15
BOND C3   H1
BOND C3   C4
BOND C4   C5
BOND C4   C8
BOND C5   C6
BOND C5   C16
BOND C6   H2
BOND C6   C7
BOND C7   O1
BOND C7   O2
BOND O2   C8
BOND C8   C9
BOND C9   C10
BOND C10  H3
BOND C10  H4
BOND C10  C11
BOND C11  H5
BOND C11  H6
BOND C11  C12
BOND C12  H7
BOND C12  H8
BOND C12  N
BOND N    C13
BOND C13  H9
BOND C13  H10
BOND C13  C14
BOND C14  H11
BOND C14  H12
BOND C14  C15
BOND C15  H13
BOND C15  H14
BOND C16  F1
BOND C16  F2
BOND C16  F3
IMPR C7     C6     O1     O2

!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
RESI COS1       0.000
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
GROUP
!              H5    H6
!                \  /
!           H4    C11    H7
!             \  /   \  /
!          H3- C10    C12-H8
!               |     |
!  O1    O2    C9    N     H9
!   \\ /   \  /  \\ / \   /
!    C7     C8    C1   C13 -H10
!    |      ||    |     |
!    C6     C4    C2   C14 -H11
```

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!    / \\  /  \  // \ /   \
!  H2    C5    C3   C15    H12
!        |      |   / \
!    F1-C16-F3  H1 H14 H13
!        |
!        F2
!charges: wB97xD/aug-cc-pVTZ CHelpG PCM scaled 0.9
!polarizability: MP2/Sadlej gas phase scaled 0.724
ATOM    C1      CD2R6A  0.1348  ALPHA   -1.103  THOLE   1.3
ATOM    C2      CD2R6A  0.042   ALPHA   -1.236  THOLE   1.3
ATOM    C3      CD2R6A  -0.3109 ALPHA   -1.398  THOLE   1.3
ATOM    H1      HDR6A   0.1758
ATOM    C4      CD2R6H  0.0974  ALPHA   -1.274  THOLE   1.0
ATOM    C5      CD2R6H  -0.0743 ALPHA   -1.368  THOLE   1.0
ATOM    C6      CD2R6H  -0.406  ALPHA   -1.258  THOLE   1.0
ATOM    H2      HDR6A   0.1438
ATOM    C7      CD2O4A  0.673   ALPHA   -1.194  THOLE   1.0
ATOM    O1      OD2C1B  -0.634  ALPHA   -1.018  THOLE   1.2
ATOM    O2      OD306A  -0.3415 ALPHA   -1.040  THOLE   1.2
ATOM    C8      CD2R6H  0.2179  ALPHA   -1.457  THOLE   1.0
ATOM    C9      CD2R6A  -0.1666 ALPHA   -1.367  THOLE   1.3
ATOM    C10     CD32A   0.1453  ALPHA   -1.263  THOLE   1.3
ATOM    H3      HDA2A   -0.0013
ATOM    H4      HDA2A   -0.0013
ATOM    C11     CD32A   0.0182  ALPHA   -1.356  THOLE   1.3
ATOM    H5      HDA2A   0.0123
ATOM    H6      HDA2A   0.0123
ATOM    C12     CD32A   0.0321  ALPHA   -1.364  THOLE   1.3
ATOM    H7      HDA2A   0.05
ATOM    H8      HDA2A   0.05
ATOM    N       ND3P2A  -0.0449 ALPHA   -1.027  THOLE   1.0
ATOM    C13     CD32A   -0.0814 ALPHA   -1.401  THOLE   1.3
ATOM    H9      HDA2A   0.0852
ATOM    H10     HDA2A   0.0852
ATOM    C14     CD32A   0.0206  ALPHA   -1.382  THOLE   1.3
ATOM    H11     HDA2A   0.0279
ATOM    H12     HDA2A   0.0279
ATOM    C15     CD32A   -0.0279 ALPHA   -1.395  THOLE   1.3
ATOM    H13     HDA2A   0.0447
ATOM    H14     HDA2A   0.0447
ATOM    C16     CD30A   0.6138  ALPHA   -0.722  THOLE   0.9
ATOM    F1      FDA3    -0.2216 ALPHA   -0.452  THOLE   0.663
ATOM    F2      FDA3    -0.2216 ALPHA   -0.452  THOLE   0.663
ATOM    F3      FDA3    -0.2216 ALPHA   -0.452  THOLE   0.663

BOND C1   C2
BOND C1   C9
BOND C1   N
BOND C2   C3
BOND C2   C15
BOND C3   H1
BOND C3   C4
BOND C4   C5
BOND C4   C8
BOND C5   C6
BOND C5   C16
BOND C6   H2
BOND C6   C7
BOND C7   O1
BOND C7   O2
BOND O2   C8
BOND C8   C9
BOND C9   C10
BOND C10  H3
BOND C10  H4
BOND C10  C11
BOND C11  H5
BOND C11  H6
BOND C11  C12
BOND C12  H7
BOND C12  H8
```

```
BOND C12  N
BOND N    C13
BOND C13  H9
BOND C13  H10
BOND C13  C14
BOND C14  H11
BOND C14  H12
BOND C14  C15
BOND C15  H13
BOND C15  H14
BOND C16  F1
BOND C16  F2
BOND C16  F3
IMPR C7     C6     O1     O2

END


READ PARA CARD
*=============================================================
*.   P A R A M E T E R   O F   COUMARIN
*=============================================================
*

ATOMS
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
!      ID  NAME     MASS
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
MASS    1  HDR6A     1.008
MASS    2  HDA2A     1.008
MASS    3  CD2R6A   12.011
MASS    4  CD2R6H   12.011
MASS    5  CD2O4A   12.011
MASS    6  CD32A    12.011
MASS    7  CD30A    12.011
MASS    8  ND3P2A   14.007
MASS    9  OD2C1B   16.000
MASS   10  OD306A   16.000
MASS   11  FDA3     18.99840
MASS  199  DRUD     0.0000

BONDS
!
! U_bond = k ( r - r0 )^2
!
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
!TYPE1    TYPE2    k [kcal/mol Angstroem^2]     r0 [Angstroem]
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
OD306A   CD2R6H  330.00      1.37969
CD2O4A   OD306A  235.00      1.39145
CD2R6A   ND3P2A  330.00      1.38014
CD2R6H   CD2R6H  420.00      1.40119
CD2R6H   CD30A   198.00      1.50261
CD2R6H   CD2O4A  302.00      1.45473
CD2R6H   HDR6A   350.00      1.08324
CD2R6A   CD2R6A   305.00       1.375
CD2R6A   CD32A    230.00       1.490
CD2R6A   HDR6A    340.00       1.080
CD2R6A   CD2R6H   460.00       1.280
OD2C1B   CD2O4A   623.00       1.239
CD32A    HDA2A    309.00       1.111
CD32A    CD32A    222.50       1.530
ND3P2A   CD32A    215.00       1.510
CD30A    FDA3     473.00       1.360
X        DRUD     500.00       0.000

ANGLES
!
! U_angle = k ( theta - theta0 )^2
!
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
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!TYPE1    TYPE2     TYPE3     k [kcal/mol rad^2]     theta0 [deg]
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
CD2R6A    CD2R6A    CD2R6H  40.00     119.714   35.00   2.4162
CD2R6A    CD2R6H    CD2R6H  40.00     122.053
OD306A    CD2R6H    CD2R6A  40.00     115.158
CD2R6H    CD2O4A    OD306A  10.00     116.144
OD2C1B    CD2O4A    OD306A  20.00     118.203
CD2O4A    OD306A    CD2R6H 102.00     122.657
CD2R6A    CD2R6A    ND3P2A  40.00     120.098
CD2R6H    CD2R6H    CD2R6H  40.00     119.058
CD2R6H    CD2R6H    CD30A   45.80     119.366
CD2R6H    CD2R6H    HDR6A   42.00     122.322
CD2R6H    CD2R6H    CD2O4A 120.00     121.518
HDR6A     CD2R6H    CD2O4A  30.00     116.158
CD2R6H    CD2O4A    OD2C1B  10.00     125.653
CD2R6H    CD2R6H    OD306A  10.00     121.510
CD2R6H    CD2R6A    CD32A   45.80     121.064
CD2R6A    CD32A     CD32A   51.80     108.773
HDA2A     CD32A     ND3P2A  32.40     108.809   50.00   2.1300
CD2R6A    ND3P2A    CD32A   55.00     121.662
CD32A     ND3P2A    CD32A   53.00     114.275
CD2R6H    CD30A     FDA3    50.00     111.665   30.00   2.3570
CD2R6A    CD2R6A    CD2R6A  40.00     120.000   35.00   2.4162
CD2R6A    CD2R6A    CD32A   45.80     122.300
CD2R6A    CD2R6A    HDR6A   30.00     120.000   22.00   2.1525
CD2R6H    CD2R6A    HDR6A   30.00     117.500
CD2R6A    CD32A     HDA2A   49.30     107.500
HDA2A     CD32A     HDA2A   35.50     109.000    5.40   1.802
CD32A     CD32A     HDA2A   26.50     110.100   22.53   2.179
CD32A     CD32A     CD32A   58.35     113.600   11.16   2.561
ND3P2A    CD32A     CD32A   67.70     113.000
FDA3      CD30A     FDA3   125.00     106.500


DIHEDRALS
!
! U_dihedral = k ( 1 + Cos[n phi - delta] )
!
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
!TYPE1    TYPE2     TYPE3     TYPE4     k [kcal/mol]    n     delta [deg]
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
CD2R6A    CD2R6A    CD2R6A    CD2R6H  0.5000  2   180.00
CD2R6A    CD2R6A    CD2R6H    CD2R6H  0.5000  2   180.00
CD2R6A    CD2R6H    CD2R6H    CD2R6A  2.5000  2   180.00
HDR6A     CD2R6A    CD2R6H    CD2R6H  3.1000  2   180.00
CD2R6A    CD2R6A    CD2R6H    OD306A  3.1000  2   180.00
CD2R6A    CD2R6H    CD2R6H    CD2R6H  2.0000  2   180.00
CD2R6A    CD2R6H    CD2R6H    OD306A  3.9000  2   180.00
CD2R6H    CD2R6H    CD2R6H    OD306A  0.4000  2   180.00
CD2R6H    CD2R6H    CD2O4A    OD306A  0.4000  2   180.00
HDR6A     CD2R6H    CD2O4A    OD306A  2.4000  2   180.00
CD2O4A    OD306A    CD2R6H   CD2R6A   0.7600  2   180.00
CD2R6H    CD2R6H    OD306A    CD2O4A  0.9400  2   180.00
CD2R6H    CD2O4A    OD306A    CD2R6H  0.6000  2   180.00
OD2C1B    CD2O4A    OD306A    CD2R6H  0.7600  2   180.00
CD2R6A    CD2R6A    CD32A     CD32A   0.2300  2   180.00
CD2R6A    ND3P2A    CD32A     CD32A   2.5000  1   180.00
CD2R6A    ND3P2A    CD32A     HDA2A   0.0000  3   180.00
CD2R6A    CD2R6A    ND3P2A    CD32A   1.2000  2   180.00
CD2R6A    CD2R6A    ND3P2A    CD32A   0.3000  4     0.00
CD2R6A    CD32A     CD32A     CD32A   0.0400  3     0.00
CD2R6A    CD32A     CD32A     HDA2A   0.0400  3     0.00
CD2R6A    CD2R6A    CD2R6A    ND3P2A  3.1000  2   180.00
CD2R6A    CD2R6H    CD2R6H    CD30A   3.1000  2   180.00
CD2R6H    CD2R6A    CD2R6A    CD32A   3.1000  2   180.00
CD2R6H    CD2R6H    CD2R6H    HDR6A   1.0000  2   180.00
CD2R6H    CD2R6H    CD2R6H    CD2O4A  3.0000  2   180.00
CD2R6H    CD2R6H    CD30A     FDA3    0.3000  2     0.00
CD2R6H    CD2R6H    CD2R6A    CD32A   3.1000  2   180.00
CD2R6H    CD2R6H    CD2O4A    OD2C1B  1.0000  2   180.00
CD2R6H    CD2R6H    CD2R6H    CD2R6H  6.0000  2   180.00
```

```
HDR6A     CD2R6H    CD2R6H    CD30A    4.0000  2    180.00
HDR6A     CD2R6H    CD2O4A    OD2C1B   6.0000  2    180.00
CD2O4A    CD2R6H    CD2R6H    CD30A    3.1000  2    180.00
OD306A    CD2R6H    CD2R6A    CD32A    2.4000  2    180.00
CD2R6H    CD2R6H    CD2R6H    CD30A    3.1000  2    180.00
CD2R6H    CD2R6A    CD2R6A    ND3P2A   3.1000  2    180.00
CD2R6H    CD2R6A    CD32A     HDA2A    0.0020  6      0.00
CD2R6H    CD2R6A    CD32A     CD32A    0.2300  2    180.00
CD32A     CD2R6A    CD2R6A    ND3P2A   2.4000  2    180.00
CD32A     CD32A     ND3P2A    CD32A    2.5000  1    180.00
CD32A     CD32A     ND3P2A    CD32A    1.5000  2      0.00
CD32A     CD32A     ND3P2A    CD32A    0.5000  3      0.00
CD32A     ND3P2A    CD32A     HDA2A    0.0000  3    180.00
CD2R6A    CD2R6A    CD2R6A    HDR6A     4.200  2    180.00
CD2R6A    CD2R6A    CD32A     HDA2A     0.000  6      0.00
CD2R6A    CD2R6A    CD2R6A    CD32A     3.100  2    180.00
CD2R6A    CD2R6A    CD2R6A    CD2R6A    2.800  2    180.00
CD32A     CD2R6A    CD2R6A    HDR6A     4.200  2    180.00
CD32A     CD32A     CD32A     HDA2A     0.190  3      0.00
ND3P2A    CD32A     CD32A     CD32A     0.200  3      0.00
HDA2A     CD32A     CD32A     HDA2A     0.190  3      0.00
ND3P2A    CD32A     CD32A     HDA2A     0.190  3      0.00

IMPROPERS
! n > 0:
! U_improper = k ( 1 + Cos[n phi - delta] )
!
! n = 0:
! U_improper = k ( phi - delta )^2
!
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
!TYPE1     TYPE2      TYPE3      TYPE4     k [kcal/mol]     n      delta [deg]
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
CD2O4A    CD2R6H    OD2C1B    OD306A   51.0000  0      0.00

NONBONDED nbxmod  5 atom vatom cdiel vdistance switch vswitch -
cutnb 16.0 ctofnb 12.0 ctonnb 10.0 eps 1.0 e14fac 1.0 wmin 1.5
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
!TYPE1           epsilon     rmin/2        epsilon14    rmin14/2
!            [kcal/mol] [Angstroem]     [kcal/mol] [Angstroem]
!~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
HDR6A     0.0    -0.0300      1.0500
HDA2A     0.0    -0.0210      1.3400
CD2R6A    0.0    -0.0690      2.0900
CD2R6H    0.0    -0.1070      1.9700
CD2O4A    0.0    -0.0960      1.6730
CD32A     0.0    -0.0560      2.1000   0.0 -0.01 1.9
CD30A     0.0    -0.0200      2.2000   0.0 -0.01 1.9
ND3P2A    0.0    -0.3600      1.3800
OD2C1B    0.0    -0.2030      1.7740
OD306A    0.0    -0.0800      1.7400
FDA3      0.0    -0.0800      1.6200
DRUD      0.00   -0.0000      0.0000


END
RETURN
```