Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information

Determining the structure of α-phenylethyl isocyanide in chloroform by VCD spectroscopy and DFT calculations – Simple case or challenge?

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Content:

1. Comment about the extraction of the dipole strength, rotational strength and the angle ξ

For the PENC dimer and solvated dimer, the log file of the corresponding Gaussian 03 calculations yielded two entries for each vibrational mode with almost identical wavenumber, reduced masses, and force constants. To illustrate this, an example is given:

```
                     103                    104
                       B                      A
 Frequencies --   1403.3076              1403.4991
 Red. masses --      1.2204                 1.2198
 Frc consts  --      1.4159                 1.4157
 IR Inten    --     11.5932                 2.9941
 Dip. str.   --     32.9578                 8.5106
 Rot. str.   --     -3.0431                 1.5239
```

The slight difference in the wavenumbers, here 1403.3076 and 1403.4991, was attributed to numerical issues arising from the calculation itself. Since the dimeric structures were C2-symmetric, the obtained values for the dipole strength or rotational strength should be summed up to obtain the correct values. Afterwards, these values had to be divided by a factor of 2 to normalize the value to one mol and hence to ensure unit consistency with the experimental data.

The cartesian coordinates of the electronic and magnetic dipole transition moment can be extracted from the Gaussian chk file by running a Gaussian job with the following input line:

```
#p geom=allcheck freq=(readfc) iop(7/33=1)
```

The output section will look like

```
Dipole derivatives wrt mode 103:  2.19013D-01 -3.39783D+00 -3.78301D-07
 Vibrational polarizability contributions from mode 103       0.0006555       0.1577724       0.0000000
 Vibrational hyperpolarizability contributions from mode 103       0.0000000       0.0000000       0.0000000
 Dipole transition moments wrt mode 103:
 Electric:  3.69272D-01 -5.72900D+00 -6.37845D-07
 Magnetic:  2.99407D+00  7.24164D-01  6.64485D-07
```

The last two lines correspond to the cartesian coordinates.

For the two dimeric structures, two angles ξ were obtained for each vibrational mode, like it has been shown for the dipole strength and rotational strength. One of the angles is always 0° or 180° while the other one has a value different from 0°/180°. This is attributed to the attempt of the calculation software to map the calculated physical values on the given molecular structure. Here, the easiest way is to give a value of 0° or 180° to one of the vibrational modes and to assign the residual value of the angle to the second vibrational mode. Table S1 shows a section of the listing extracted from a logfile. For the robust modes analysis only the values different from 0°/180° were considered.

mode	ν_{theo}	ex	ey	ez	mx	my	mz	R_{theo}	xi [deg]
103	1403	0.369	-5.729	0.000	2.994	0.724	0.000	-3.04	99.9
104	1403	0.000	0.000	-2.917	0.000	0.000	-0.522	1.52	0.0
105	1483	-4.468	3.064	0.000	4.965	1.632	0.000	-17.19	127.4
106	1483	0.000	0.000	1.406	0.000	0.000	8.346	11.73	0.0
109	1492	0.000	0.000	0.232	0.000	0.000	-12.193	-2.83	180.0
110	1492	-4.485	-0.254	0.000	-1.087	-12.519	0.000	8.06	81.8

Tab. S1. Section of the ξ-listing of the solvated PENC dimer.

2. Comparison of the VCD spectra of PENC in the isolated state and using the PCM

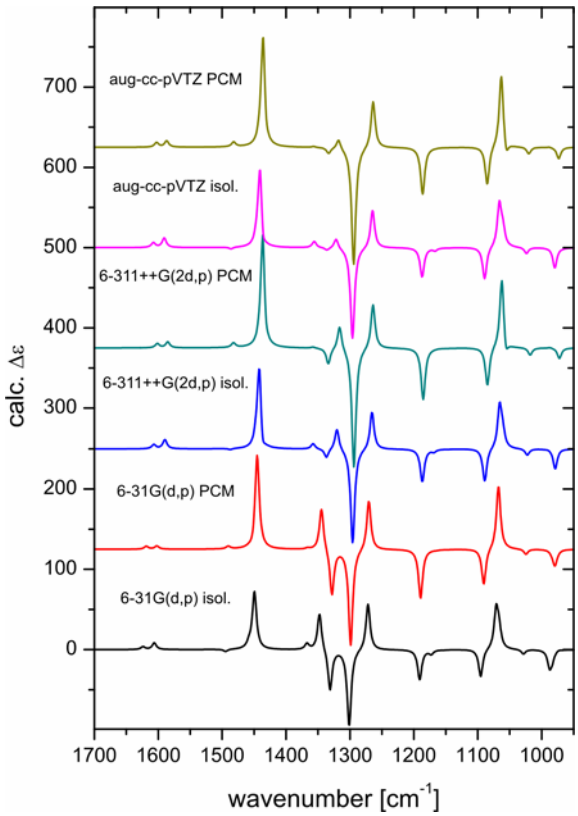


Fig. S1. VCD spectra of PENC calculated using the B3PW91 functional and the mentioned basis sets for the isolated state and within the PCM.

3. VCD spectra of the rotational isomers of isolated PENC

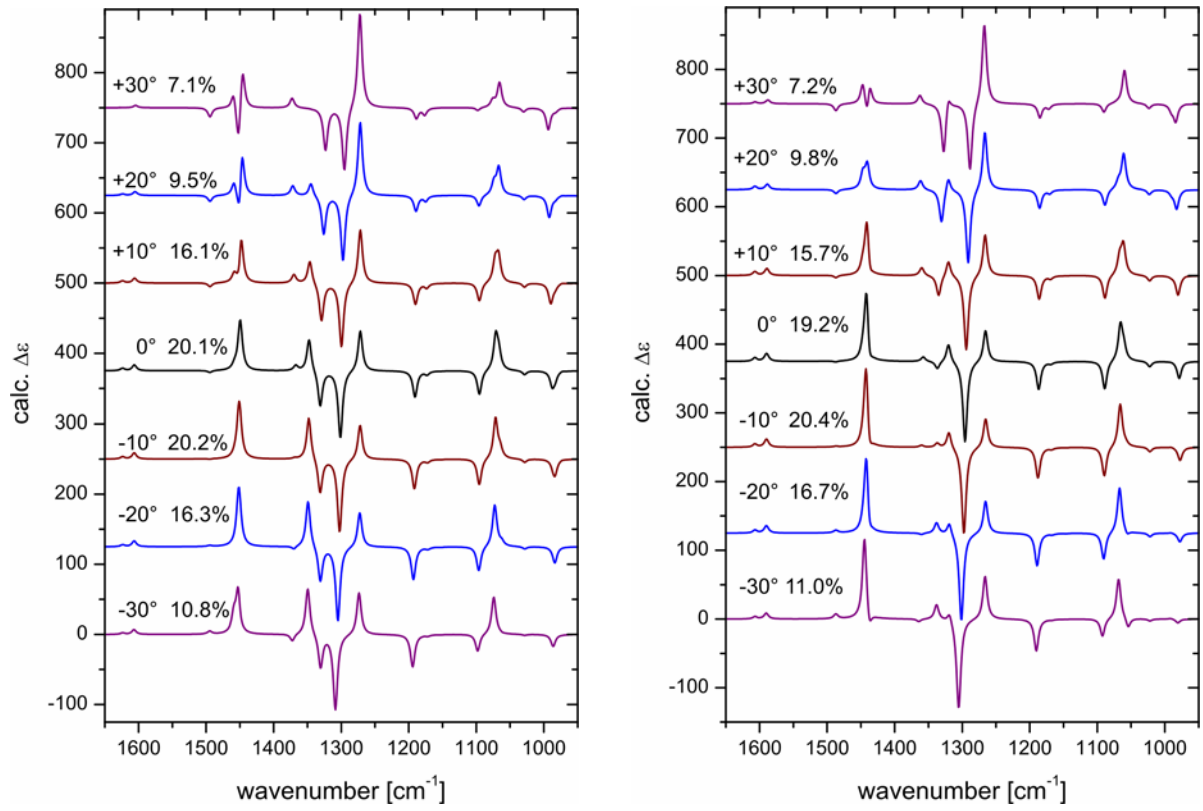


Fig. S2. VCD spectra of the rotational isomers of PENC calculated at the B3PW91/6-31G(d,p) (left) and B3PW91/6-311++G(2d,p) (right) level of theory. The corresponding amplitudes of the angles and populations for each conformer are shown next to the spectrum. Here, 0° corresponds to the energetically favoured conformers discussed in the main text.

4. Comparison of experimental and theoretical dipole and rotational strengths

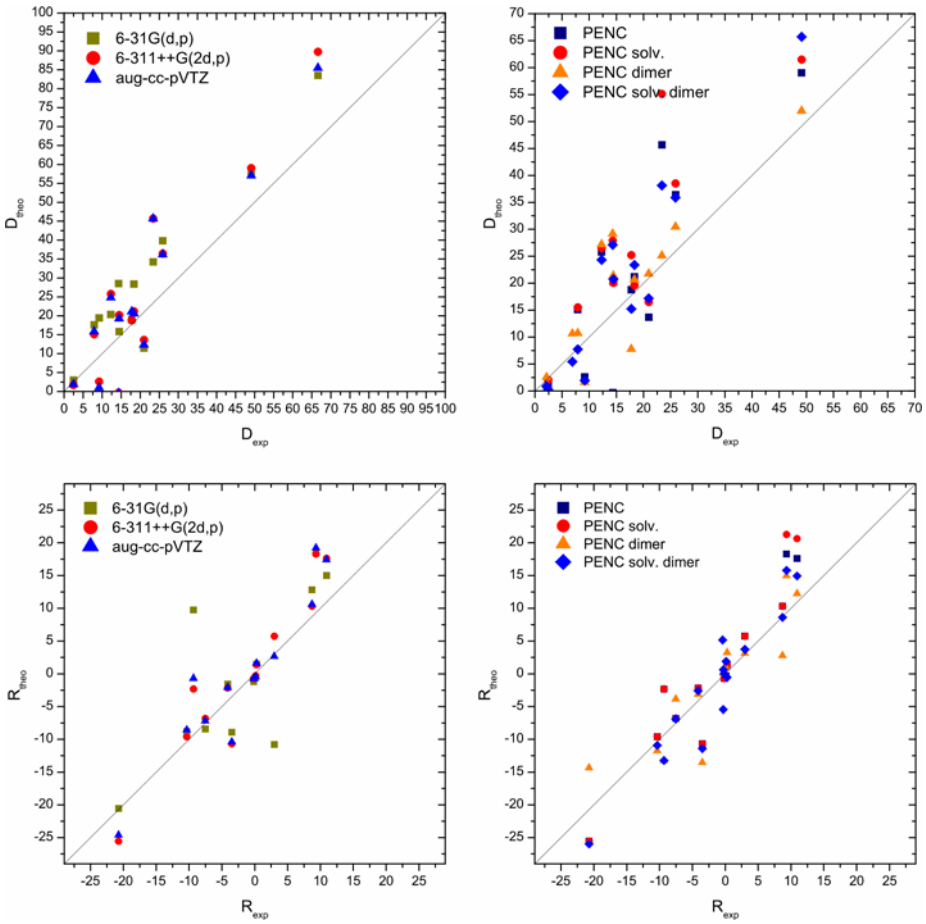


Fig. S3. Correlation between experimental and theoretical dipole strength D and rotational strength R for different basis sets and structures.

Experiment			6-31G(d,p) PENC iso						6-311++G(2d,p) PENC iso						aug-cc-pVTZ PENC iso					
ν_{exp}	D_{exp}	R_{exp}	ν_{theo}	ν_{scaled}	D_{theo}	***D_{theo}***	R_{theo}	***R_{theo}***	ν_{theo}	ν_{scaled}	D_{theo}	***D_{theo}***	R_{theo}	***R_{theo}***	ν_{theo}	ν_{scaled}	D_{theo}	***D_{theo}***	R_{theo}	**R_{theo}**
994	**25.91**	**-7.52**	1003	973	0.7	**39.83**	*0.4*	**-8.40**	1000	970	0.7	**36.43**	*0.13*	**-6.80**	997	967	0.2038	**36.22**	*-0.06*	**-7.19**
			1014	983	25.8		*-2.9*		1009	979	34.0		*-7.15*		1010	979	33.803		*-7.29*	
			1018	988	13.4		*-5.9*		1020	990	1.7		*0.21*		1017	986	0.5079		*0.18*	
															1021	990	1.7067		*-0.03*	
1005	**5.64**	**-0.27**																		
1030	**12.29**	**-4.12**	1060	1029	20.4	**20.37**	-1.6	**-1.56**	1054	1022	25.8	**25.79**	-2.16	**-2.16**	1055	1024	24.858	**24.86**	-2.07	**-2.07**
1076	**66.61**	**9.32**	1100	1067	30.7	**83.52**	*5.8*	**18.45**	1094	1061	34.9	**89.76**	*4.58*	**18.31**	1093	1061	32.538	**85.51**	*5.27*	**19.22**
			1104	1071	52.8		*12.7*		1099	1066	54.8		*13.73*		1099	1066	52.973		*13.94*	
1096	**7.88**	**-3.50**	1129	1095	17.6	**17.61**	-8.9	**-8.91**	1123	1089	15.1	**15.11**	-10.68	**-10.68**	1123	1089	15.87	**15.87**	-10.39	**-10.39**
1120	**5.21**	**-0.26**																		
1156	**2.45**	**-0.15**	1209	1173	3.0	**3.00**	-1.2	**-1.18**	1205	1169	1.7	**1.73**	-0.70	**-0.70**	1203	1167	1.9441	**1.94**	-0.76	**-0.76**
1182	**2.14**	**-0.27**																		
1203	**20.97**	**-10.34**	1228	1191	11.4	**11.42**	-8.8	**-8.79**	1223	1187	13.7	**13.68**	-9.60	**-9.60**	1224	1187	12.363	12.3631	-8.56	**-8.56**
1251	**6.59**	**-0.40**																		
1266	**4.33**	**-0.31**																		
1280	**18.35**	**8.73**	1311	1272	28.4	**28.36**	12.8	**12.83**	1305	1266	21.2	**21.20**	10.33	**10.33**	1304	1265	20.597	**20.60**	10.61	**10.61**
1313	**17.76**	**-20.72**	1341	1301	19.0	**19.00**	-20.5	**-20.55**	1336	1296	18.8	**18.78**	-25.53	**-25.53**	1336	1296	21.125	**21.12**	-24.59	**-24.59**
1333	**9.19**	**2.99**	1372	1331	19.4	**19.41**	-10.8	**-10.80**	1361	1320	2.6	**2.62**	5.74	**5.74**	1363	1322	0.9964	**1.00**	2.69	**2.69**
1350	**23.41**	**-9.32**	1389	1348	34.3	**34.25**	9.7	**9.74**	1378	1337	45.7	**45.68**	-2.32	**-2.32**	1377	1336	45.703	**45.70**	-0.69	**-0.69**
1380	**14.45**	**0.27**	1410	1367	15.8	**15.84**	1.5	**1.51**	1400	1358	20.2	**20.23**	1.39	**1.39**	1398	1356	19.293	**19.29**	1.63	**1.63**
1407	**4.19**	**0.10**																		
1453	**49.13**	**10.94**	1494	1449	11.3	**57.32**	*13.6*	**15.01**	1482	1437	12.2	**59.04**	*-5.30*	**17.62**	1481	1437	12.846	**57.07**	*-5.15*	**17.42**
			1496	1451	45.7		*0.3*		1486	1442	42.7		*20.97*		1485	1441	40.264		*20.88*	
			1503	1458	0.3		*1.1*		1492	1447	4.1		*1.96*		1491	1446	3.9617		*1.69*	
1497	**14.32**	**0.14**	1541	1495	28.5	**28.54**	-0.6	**-0.56**	1533	1487	29.1	**-0.28**	-0.28	**-0.28**	1532	1486	28.955	**-0.42**	-0.42	**-0.42**

Tab. S2. Dipole strength and rotational strength of the isolated α-phenylethyl isocyanide obtained from the calculations applying the B3PW91 functional and different basis sets.

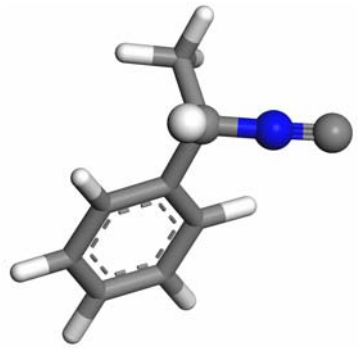
Experiment			**Solv. PENC**						**PENC dimer**						**Solv. PENC dimer**					
ν_{exp}	$\mathbf{D_{exp}}$	$\mathbf{R_{exp}}$	ν_{theo}	ν_{scaled}	D_{theo}	$\boldsymbol{D_{theo}}$	R_{theo}	$\boldsymbol{R_{theo}}$	ν_{theo}	ν_{scaled}	D_{theo}	$\boldsymbol{D_{theo}}$	R_{theo}	$\boldsymbol{R_{theo}}$	ν_{theo}	ν_{scaled}	D_{theo}	$\boldsymbol{D_{theo}}$	R_{theo}	$\mathbf{R_{theo}}$
994	**25.91**	**-7.52**	1000	970	1.2	38.5	*-0.1*	**-6.82**	1009	979	28.7	**30.5**	-7.51	**-7.32**	1007	977	34.4	**35.9**	-8.2	**-7.99**
			1007	977	34.9		*-7.2*		1021	990	1.8		0.19		1021	990	1.5		0.2	
			1021	990	2.4		*0.5*													
1005	**5.64**	**-0.27**																		
1030	**12.29**	**-4.12**	1054	1022	26.5	26.5	-1.8	**-2.16**	1054	1022	27.2	**27.2**	-6.76	**-6.76**	1055	1023	24.3	**24.3**	-2.6	**1.69**
1076	**66.61**	**9.32**	1093	1060	41.9	110.3	*6.1*	**21.28**	1092	1060	68.4	**125.8**	8.19	**29.46**	1093	1060	52.5	**121.8**	4.3	**17.01**
			1099	1066	68.5		*15.2*		1098	1065	57.5		21.27		1098	1065	69.4		12.7	
1096	**7.88**	**-3.50**	1123	1089	15.5	15.5	-13.0	**-10.68**	1122	1088	10.7	**10.7**	-27.98	**-27.98**	1122	1089	7.7	**7.7**	-11.5	**-11.52**
1120	**5.21**	**-0.26**																		
1156	**2.45**	**-0.15**	1204	1168	2.0	2.0	-0.5	**-0.70**	1181	1146	0.1	**0.1**	-0.06	**-0.06**	1182	1146	0.3	**0.3**	0.0	**0.00**
1182	**2.14**	**-0.27**							1204	1168	2.6	**2.6**	0.32	**0.32**	1205	1169	0.9	**0.9**	0.6	**0.63**
1203	**20.97**	**-10.34**	1224	1187	16.5	16.5	-11.8	**-9.60**	1227	1190	21.8	**21.8**	-23.35	**-23.35**	1225	1188	17.2	**17.2**	-10.9	**-10.85**
1251	**6.59**	**-0.40**																		
1266	**4.33**	**-0.31**																		
1280	**18.35**	**8.73**	1305	1266	19.6	19.6	10.3	**10.33**	1309	1270	20.7	**20.7**	4.29	**4.29**	1307	1268	23.4	**23.4**	10.3	**10.32**
1313	**17.76**	**-20.72**	1336	1296	25.2	25.2	-28.9	**-25.53**	1343	1302	7.8	**7.8**	-28.50	**-28.50**	1341	1300	15.2	**15.2**	-27.0	**-26.99**
1333	**9.19**	**2.99**	1361	1320	1.9	1.9	5.1	**5.74**	1361	1320	1.6	**1.6**	6.37	**6.37**	1361	1321	2.0	**2.0**	3.8	**3.84**
1350	**23.41**	**-9.32**	1378	1337	55.1	55.1	1.8	**-2.32**	1384	1342	25.1	**25.1**	-26.12	**-26.12**	1380	1339	38.1	**38.1**	-13.2	**-13.20**
1380	**14.45**	**0.27**	1402	1360	20.1	20.1	0.4	**1.39**	1401	1359	21.4	**21.4**	6.03	**6.03**	1403	1361	20.7	**20.7**	-0.8	**-0.76**
1407	**4.19**	**0.10**																		
1453	**49.13**	**10.94**	1482	1438	14.4	61.5	-5.7	**20.63**	1482	1438	8.7	**52.0**	-5.43	**-5.43**	1483	1439	15.7	**65.7**	-2.7	**15.10**
			1486	1442	39.0		24.2		1486	1442	38.2				1486	1442	39.9		15.2	
			1492	1447	8.0		2.2		1492	1447	5.1				1492	1447	10.1		2.6	
1497	**14.32**	**0.14**	1534	1488	27.9	27.9	0.0	**0.01**	1533	1487	29.2	**29.2**	1.89	**1.89**	1534	1488	27.1	**27.1**	1.9	**1.89**

Tab. S3. Dipole strength and rotational strength of solvated PENC, the PENC dimer, and the solvated PENC dimer obtained from the calculations applying the B3PW91 functional and the 6-311++G(2d,p) basis set.

5. Cartesian coordinates of PENC, solv. PENC, PENC dimer, and solv. PENC dimer (B3PW91/6-311++G(2d,p))

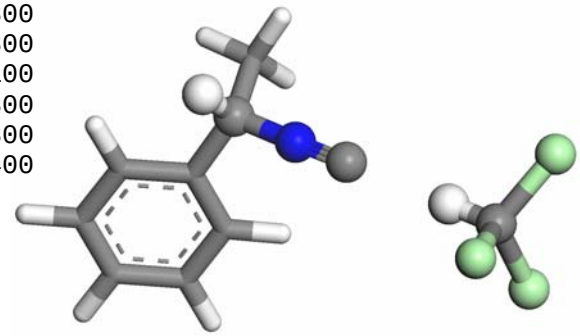
Isolated PENC

C	-2.36488900	-0.85132400	-0.42128100
C	-2.77835000	0.37177300	0.09086100
C	-1.83041400	1.30862300	0.48082000
C	-0.47573400	1.02517800	0.36492700
C	-0.05642500	-0.19984300	-0.14266200
C	-1.01079500	-1.13329700	-0.53850600
C	1.41169900	-0.57487500	-0.22413000
N	2.23785700	0.56723200	-0.45238800
C	2.93354000	1.49049300	-0.60841000
H	-3.09750100	-1.58541500	-0.73862800
H	-3.83561500	0.59668500	0.17795800
H	-2.14523500	2.26955600	0.87302000
H	0.25933800	1.76710600	0.65703800
H	-0.69439700	-2.08808900	-0.94887800
H	1.54886600	-1.23119200	-1.08919400
C	1.88805400	-1.30837400	1.03315000
H	1.28750600	-2.20732600	1.18021900
H	1.77472300	-0.66865700	1.90994100
H	2.93720600	-1.59340900	0.93662300



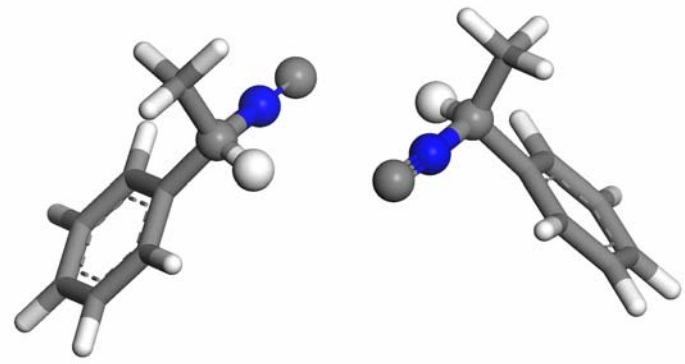
Solvated PENC

C	-5.46131000	-0.65279700	0.71387600
C	-5.15564300	-1.76579400	-0.05825100
C	-3.93636200	-1.82976300	-0.72026200
C	-3.02786300	-0.78478900	-0.61667100
C	-3.33117200	0.33408700	0.15208600
C	-4.55156100	0.39059300	0.81925100
C	-2.39599000	1.52542300	0.23464600
N	-1.02475100	1.12061700	0.21064000
C	0.09707400	0.81477300	0.16878800
H	-6.40650300	-0.59892300	1.24287000
H	-5.86226100	-2.58450700	-0.13740700
H	-3.68687200	-2.69992500	-1.31749500
H	-2.07191300	-0.84842400	-1.12519300
H	-4.79271000	1.25427000	1.43226300
H	-2.55012400	2.01683500	1.20005100
C	-2.64908300	2.53895500	-0.88467800
H	-3.68387900	2.88095100	-0.83508900
H	-2.48363900	2.07689200	-1.85927600
H	-1.98506200	3.39914300	-0.78279800
C	3.40511800	-0.14557900	0.05372800
H	2.36471200	0.16645300	0.10268100
Cl	3.51541600	-1.49993700	-1.08846800
Cl	4.36595200	1.23672600	-0.50808800
Cl	3.90523500	-0.64606800	1.68066400



PENC dimer

C	-1.17603200	4.09652000	-1.90674000
C	0.02543200	4.56720800	-2.41931600
C	1.20939700	4.31680900	-1.73680000
C	1.19213200	3.60437900	-0.54546600
C	-0.00985000	3.13425400	-0.02512000
C	-1.19213200	3.38114100	-0.71641500
C	-0.07273700	2.40814000	1.30435400
N	1.03529900	1.51632000	1.46538800
C	1.91862100	0.77221600	1.61810900
H	-2.10374600	4.27716200	-2.43877100
H	0.04055800	5.12100200	-3.35164800
H	2.15280900	4.67335900	-2.13597100
H	2.12170100	3.39869200	-0.02521300
H	-2.13224600	3.00270700	-0.32642800
H	-0.96712900	1.77810400	1.31485800
C	-0.13210400	3.37451100	2.48969600
H	-1.00745600	4.01749300	2.38609600
H	0.75911600	4.00411100	2.51647800
H	-0.20741600	2.82407100	3.42907700
C	1.17603200	-4.09652000	-1.90674000
C	-0.02543200	-4.56720800	-2.41931600
C	-1.20939700	-4.31680900	-1.73680000
C	-1.19213200	-3.60437900	-0.54546600
C	0.00985000	-3.13425400	-0.02512000
C	1.19213200	-3.38114100	-0.71641500
C	0.07273700	-2.40814000	1.30435400
N	-1.03529900	-1.51632000	1.46538800
C	-1.91862100	-0.77221600	1.61810900
H	2.10374600	-4.27716200	-2.43877100
H	-0.04055800	-5.12100200	-3.35164800
H	-2.15280900	-4.67335900	-2.13597100
H	-2.12170100	-3.39869200	-0.02521300
H	2.13224600	-3.00270700	-0.32642800
H	0.96712900	-1.77810400	1.31485800
C	0.13210400	-3.37451100	2.48969600
H	1.00745600	-4.01749300	2.38609600
H	-0.75911600	-4.00411100	2.51647800
H	0.20741600	-2.82407100	3.42907700



Solvated PENC dimer

C	0.98089700	3.99255600	3.25114200
C	-0.23574500	4.45941300	3.72991600
C	-1.39021300	4.26572200	2.98156300
C	-1.32822000	3.61335700	1.75783800
C	-0.11033400	3.14681900	1.27230600
C	1.04219600	3.33666700	2.02843500
C	0.00469500	2.48792000	-0.08839200
N	-1.09877200	1.60729600	-0.33499900
C	-1.98911500	0.89468800	-0.56023200
H	1.88532900	4.13060000	3.83342700
H	-0.28605700	4.96691500	4.68695600
H	-2.34524900	4.62058800	3.35338200
H	-2.23574200	3.45482200	1.18468500
H	1.99401800	2.96369300	1.66282700
H	0.89711000	1.85601600	-0.09321800
C	0.11033400	3.50731000	-1.22467500
H	0.98584000	4.13637200	-1.05934900
H	-0.77565500	4.14398600	-1.25118400
H	0.21612100	3.00243200	-2.18634800
C	-4.77091600	-0.93975500	-1.38082000
H	-3.91274100	-0.32972500	-1.10796800
Cl	-6.24273700	-0.03074600	-0.99777600
Cl	-4.66775700	-1.28714900	-3.11669000
Cl	-4.69180900	-2.44303500	-0.43145900
C	-0.98089700	-3.99255600	3.25114200
C	0.23574500	-4.45941300	3.72991600
C	1.39021300	-4.26572200	2.98156300
C	1.32822000	-3.61335700	1.75783800
C	0.11033400	-3.14681900	1.27230600
C	-1.04219600	-3.33666700	2.02843500
C	-0.00469500	-2.48792000	-0.08839200
N	1.09877200	-1.60729600	-0.33499900
C	1.98911500	-0.89468800	-0.56023200
H	-1.88532900	-4.13060000	3.83342700
H	0.28605700	-4.96691500	4.68695600
H	2.34524900	-4.62058800	3.35338200
H	2.23574200	-3.45482200	1.18468500
H	-1.99401800	-2.96369300	1.66282700
H	-0.89711000	-1.85601600	-0.09321800
C	-0.11033400	-3.50731000	-1.22467500
H	-0.98584000	-4.13637200	-1.05934900
H	0.77565500	-4.14398600	-1.25118400
H	-0.21612100	-3.00243200	-2.18634800
C	4.77091600	0.93975500	-1.38082000
H	3.91274100	0.32972500	-1.10796800
Cl	6.24273700	0.03074600	-0.99777600
Cl	4.66775700	1.28714900	-3.11669000
Cl	4.69180900	2.44303500	-0.43145900