Retinal Isomerization

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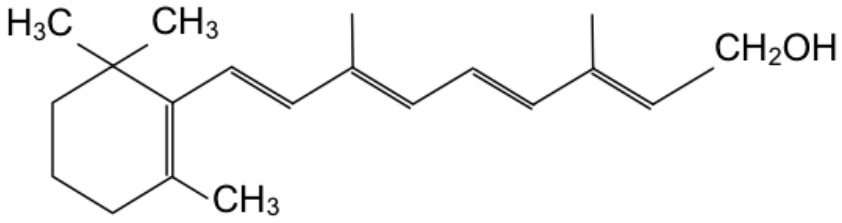
Isomerization reactions are very important in vision, as well as in many other chemical processes. When light is adsorbed, the double bond at carbon 11 in retinal (which is bonded to the protein opsin, forming rhodopsin) undergoes a conversion from the cis to the trans configuration. In this project you will use **QC-Lab** to examine the isomerization thermodynamics for a number of electronic structure methods and basis sets.

1

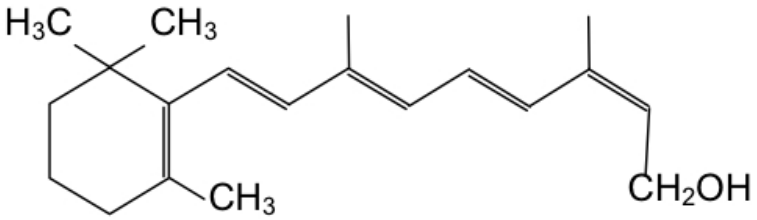
Using RHF/STO-3G, RHF/TZVP, B3LYP/TZVP, and MP2/TZVP, calculate the energy difference between the cis and trans isomers of 1,2-difluoroethylene in kcal/mol (1 a.u.=627.51 kcal/mol). Repeat this calculation using the semi-empirical methods AM1 and PM3 (see the Basis Set box). To what extent do different basis sets change the optimized geometries? First compare the structural parameters (bond lengths and angles) for the PM3, AM1, and MP2/TZVP optimized geometries. Then select the geometry optimized coordinates for the AM1 and PM3 structures and run single point energy minimization calculations using the MP2/TZVP level of theory. Compare the energies obtained from the single point calculations with the energies obtained from the MP2/TZVP geometry optimization. How do the values obtained from the different methods compare to the experimental enthalpy difference of 0.928 kcal/mol? (*N. C. Craig and E. A. Entemann J. Am. Chem. Soc.* 83, 3047, 1961) What is the effect of increasing the size of the basis set? How much of an effect does incorporating correlation energy (through density functional theory or second-order perturbation theory) have on the relative energies?

2

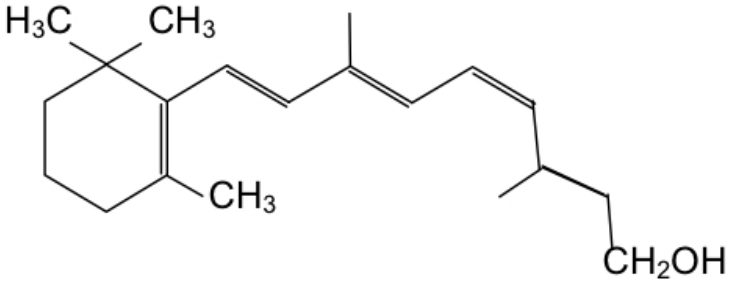
Vitamin A (retinol) is the immediate precursor to two important active metabolites including retinal, which plays a vital role in vision, and retinoic acid, which acts as an intracellular messenger for gene transcription. Due to the large number of double bonds in the molecule, a variety of isomers could exist; some of these are shown below. Using PM3, optimize the geometries and calculate relative energies of the three compounds. (Initial structures are provided on the course webpage. You will need to upload the coordinates to **QC-Lab**.) Which one is the most stable at this level of theory? What is the relative energy ordering (kcal/mol)? Briefly explain why you think we chose this method.



all-*trans*-retinol



13-*cis*-retinol



11-*cis*-retinol

Trans-retinol

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O   8.0    7.3762752835   1.4191718443   0.2369464157
C   6.0   -5.2494573328  -1.3227711266   0.2906000816
C   6.0   -4.7888408781  -0.0918791215   1.0702207928
C   6.0   -6.1978196396  -0.8994132346  -0.8352952318
C   6.0   -6.0101345630  -2.2519851984   1.2517332664
C   6.0   -6.2743698823  -3.5860914096   0.5811552277
C   6.0   -4.9592710136  -4.2870169351   0.2978444099
C   6.0   -3.9442225599  -3.3821807275  -0.3261330028
C   6.0   -2.7994091280  -4.1020147653  -0.9472269610
C   6.0   -4.0583496509  -2.0403230733  -0.3160529643
C   6.0   -3.0608889951  -1.1655178835  -0.9456626730
C   6.0   -1.8112348502  -1.0393968205  -0.4812683105
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C	6.0	-0.7870103202	-0.1812589213	-1.0727594150
C	6.0	-1.1528736482	0.6647296099	-2.2387117683
C	6.0	0.4545592420	-0.1951298834	-0.5404389804
C	6.0	1.5594676049	0.5948727948	-1.0450407560
C	6.0	2.7840147561	0.5248841636	-0.4998074602
C	6.0	3.9459146850	1.2817575356	-0.9628505513
C	6.0	3.7807669154	2.1763834935	-2.1388511541
C	6.0	5.1111384952	1.1322267702	-0.3061654589
C	6.0	6.3757800110	1.8366909076	-0.6668322668
H	1.0	8.1671323772	1.8787405194	-0.0093198017
H	1.0	-4.0628540793	-0.3611407946	1.8486065676
H	1.0	-5.6354491913	0.4046832847	1.5623748159
H	1.0	-4.3084951332	0.6440527744	0.4111046078
H	1.0	-6.6837437452	-1.7867342941	-1.2745386261
H	1.0	-5.6704853205	-0.3680930102	-1.6374582745
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H	1.0	-6.9611437006	-1.7752667773	1.5602286384
H	1.0	-5.4265216462	-2.3980560631	2.1821585050
H	1.0	-6.8266085162	-3.4048807814	-0.3691024006
H	1.0	-6.9260110380	-4.2227330799	1.2072838389
H	1.0	-5.1310204313	-5.1647746104	-0.3566993170
H	1.0	-4.5270033104	-4.6891284852	1.2373136225
H	1.0	-2.0548580718	-3.4230647816	-1.3851811959
H	1.0	-3.1505475783	-4.7693552466	-1.7464230223
H	1.0	-2.2839674921	-4.7213041792	-0.2004408376
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H	1.0	-1.5046824158	-1.6141739486	0.4045208411
H	1.0	-0.3063156921	1.2833503742	-2.5799623755
H	1.0	-1.9797958454	1.3435043550	-1.9889312678
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H	1.0	0.6662261081	-0.8402735666	0.3242649539
H	1.0	1.3380292705	1.2514628377	-1.9031258650
H	1.0	2.9594241326	-0.1416978270	0.3577540717
H	1.0	4.7098048725	2.6906921886	-2.4191584598
H	1.0	3.0282874468	2.9514748711	-1.9369460772
H	1.0	3.4462736245	1.6076862146	-3.0177632466
H	1.0	5.1655266761	0.4528752469	0.5575579517
H	1.0	6.6779736855	1.5929507389	-1.7061110521
H	1.0	6.2422284615	2.9362542264	-0.6046459793

11-cis-retinol

C	6.0	-4.1315508896	1.1082367442	-0.2245460399

C	6.0	1.7417146524	1.1859815107	0.5990806805
C	6.0	2.9414204210	1.8306563875	1.0898649157
C	6.0	4.1999654983	1.3868669967	0.9593582155
C	6.0	4.6732365127	0.1630628813	0.3195816530
C	6.0	4.1163066905	-0.3396239796	-0.7950527938
C	6.0	4.6313010292	-1.5567708629	-1.4841438597
C	6.0	-2.0461494448	-2.0528168468	0.7289892952
C	6.0	-4.9720092767	1.5570964704	0.9750859352
C	6.0	-3.5489284134	2.3330408847	-0.9294035986
C	6.0	0.2201071220	2.7115542877	1.8544411940
C	6.0	-5.0398634116	0.3599020627	-1.2141353742
C	6.0	5.8566192709	-0.4754629664	0.9610717013
C	6.0	-5.4667393639	-0.9699040316	-0.6230878966
C	6.0	-4.2546881967	-1.8603135775	-0.4249342501
C	6.0	-3.0998470835	-1.1442736404	0.2010711777
C	6.0	-3.0225428256	0.1983279016	0.2693809175
C	6.0	-1.8833438584	0.8941605208	0.8791719491
C	6.0	-0.6464314350	0.8580678869	0.3680153285
C	6.0	0.4938970084	1.5748989684	0.9367554665
H	1.0	-4.3492379134	1.9619903322	1.7827306342
H	1.0	1.8833940926	0.3416154661	-0.0962146925
H	1.0	2.7720267681	2.7772614050	1.6325453234
H	1.0	5.0046257156	1.9957650998	1.3964908894
H	1.0	3.2296832499	0.1479452222	-1.2325863502
H	1.0	5.6887849446	-1.4096734762	-1.7885716129
H	1.0	-2.9472747720	2.9431632991	-0.2411812838
H	1.0	-4.3454778086	2.9732604787	-1.3313135629
H	1.0	-2.8998520284	2.0433029181	-1.7658920600
H	1.0	-5.9246187398	0.9816765736	-1.4536931991
H	1.0	-5.6909968024	2.3353077993	0.6874370916
H	1.0	-5.9692180055	-0.7826175046	0.3531461236
H	1.0	-6.2124395790	-1.4688418652	-1.2692239769
H	1.0	-4.5286561854	-2.7394110653	0.1919734067
H	1.0	-3.9129414683	-2.2678777081	-1.3988900972
H	1.0	-2.4548738490	-2.6982634995	1.5188096153
H	1.0	-1.6638952350	-2.7047042592	-0.0684452593
H	1.0	-1.1893469461	-1.5122354027	1.1541687744
H	1.0	-2.1213708600	1.4800395519	1.7785934648
H	1.0	-0.4407418288	0.2598441950	-0.5308586132
H	1.0	-0.1645321876	2.3517922863	2.8189564950
H	1.0	-0.5300362281	3.3911559194	1.4275437903
H	1.0	1.1296297536	3.2997771723	2.0603346792
O	8.0	3.8200109478	-1.7942115508	-2.6135848515
H	1.0	5.6539065705	-1.5300655814	1.1974055216
H	1.0	6.1471539765	0.0193186725	1.8971321975
H	1.0	6.7278966109	-0.4511349465	0.2907149492

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H  1.0   4.1802859562  -2.5558881599  -3.0462831635
H  1.0   4.6044043672  -2.4319330301  -0.8012553220
H  1.0  -5.5451895762   0.7055184664   1.3781365536
H  1.0  -4.5092339462   0.2020665930  -2.1737010810
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13-cis retinol

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C  6.0  -4.5711867046   0.6965063385  -1.5319502705
C  6.0  -5.8877507019  -0.0127328159  -1.8923764181
C  6.0  -5.8103739780  -1.4782737166  -1.5081700734
C  6.0  -4.7405662682  -2.1720591702  -2.3309970719
C  6.0  -3.4680921669  -1.3902069105  -2.4003318736
C  6.0  -3.3860754997  -0.0941850208  -2.0486706531
C  6.0  -2.1208094798   0.6470995000  -2.1498989581
C  6.0  -1.2038914239   0.6391607546  -1.1753810559
C  6.0   0.0585651412   1.3741976448  -1.2275499714
C  6.0   1.0376643551   1.0471212709  -0.3570944207
C  6.0   2.3271858764   1.7066407784  -0.3136090283
C  6.0   3.3096706927   1.2886277346   0.4998278237
C  6.0   4.6278074905   1.9068000871   0.5872138528
C  6.0   5.5767034162   1.4627209899   1.4316391318
C  6.0   5.4104879412   0.3115586678   2.3665599975
C  6.0  -4.5861380895   2.0974692524  -2.1432948131
C  6.0  -4.4643667737   0.7985239511  -0.0078301197
C  6.0  -2.3019379861  -2.1615715779  -2.9093946689
C  6.0   0.2048555963   2.4556269449  -2.2365070593
C  6.0   4.9223864956   3.0697552239  -0.2972099840
O  8.0   6.6220788343   0.1542721490   3.0735682566
H  1.0   4.5784709042   0.4986312074   3.0759916779
H  1.0   6.4979961940  -0.5814727002   3.6569797819
H  1.0  -6.7328877985   0.4815290934  -1.3745130997
H  1.0  -6.0923785083   0.0898280699  -2.9763914537
H  1.0  -5.5699769978  -1.5506314913  -0.4228830514
H  1.0  -6.7876518448  -1.9766763003  -1.6451500597
H  1.0  -4.5334732691  -3.1783406301  -1.9153378332
H  1.0  -5.0999199926  -2.3399468408  -3.3671416185
H  1.0  -1.9870283164   1.2202870116  -3.0777129407
H  1.0  -1.3768250206   0.0435878114  -0.2676248730
H  1.0   0.8719201891   0.2372373196   0.3672349942
H  1.0   2.4542723798   2.5700049493  -0.9884876741
H  1.0   3.1351546033   0.4221232744   1.1533933223
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H  1.0   5.1720776655  -0.6173672538   1.8092007887
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H  1.0  -3.7032185453   2.6765409427  -1.8397976542
H  1.0  -3.4640232193   1.1238564537   0.3063620887
H  1.0  -5.1926674316   1.5124555038   0.3977763758
H  1.0  -4.6648927185  -0.1830980956   0.4532543841
H  1.0  -1.9877074518  -2.9132631357  -2.1723509332
H  1.0  -2.5606912519  -2.6922360469  -3.8357206732
H  1.0  -1.4334762800  -1.5234426310  -3.1224791215
H  1.0   1.1307092163   3.0347933030  -2.0853144568
H  1.0  -0.6402117826   3.1557760755  -2.1897806374
H  1.0   0.2397965651   2.0407529053  -3.2535040127
H  1.0   5.9407890995   3.4562100551  -0.1554477586
H  1.0   4.2278817431   3.8983643150  -0.1010238168
H  1.0   4.8220145772   2.7931247582  -1.3558827067
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