Supporting Information

for

Relationship between the Excited State Relaxation Paths of Rhodopsin and Isorhodopsin

Angela Strambi, Pedro B. Coto, Luis Manuel Frutos, Nicolas Ferré and Massimo Olivucci

Contains: details of the QM/MM scheme (sections 1 and 2); protein models (section 3) and coordinates of all optimized structures (section 4); energies and electronic properties of each structure (section 5); structural and spectroscopic parameters compared to experimental data and other computed published data (section 6); CASSCF/AMBER energy profiles (section 7); CASPT2//CASSCF bare chromophore (PSB9) energy profile and analysis of the MM term effect (section 8); complete torsional motion data (section 9).

1. Methodology

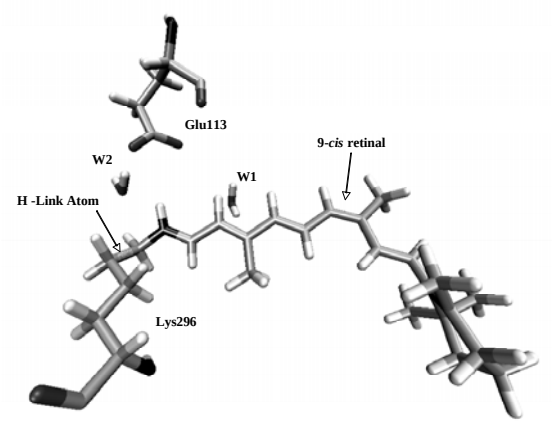
Our QM/MM scheme is fully described in ref.1[1]. Briefly, the method is based on a hydrogen link-atom scheme[2] with the frontier placed at the Cδ-Cε bond of the Lys296 side chain (see Scheme S1 and S2). The *ab initio* QM calculations are based on a CASSCF/6-31G* level. The active space comprises the full π-system of PSB9 (12 electrons in 12 π-orbitals). The MM (we use the AMBER force field) and QM segments interact in the following way: (i) all QM atoms feel the electrostatic potential of the MM point charges, (ii) stretching, bending and torsional potentials involving at least one MM atom are described by the MM potential (iii) QM and MM atom pairs separated by more then two bonds interact via either standard or re-parametrized [3,4] van der Waals potentials. CASSCF/6-31G*/AMBER geometry optimization is carried out with the GAUSSIAN03[5] and TINKER[6] programs. The ultimate goal was to obtain $\lambda^{a,f}{}_{max}$ and oscillator strengths for S_0->S_1 and S_0->S_2 transitions of PSB9 in the protein and solution environments. Although residue polarizability and dispersion force effects should, in principle, contribute to determine the excitation energy values of the chromophore these are not included in the model (i.e the change in electronic structure of the chromophore is assumed not to effect the protein charge distribution). This approximation is likely to contribute with an error of few kcal mol^{-1}.

2. The QM/MM Scheme

The QM/MM force-field is defined by the following Hamiltonian:

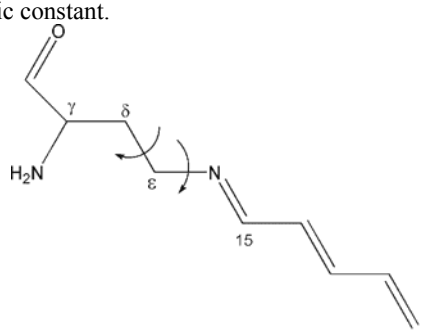
$$\hat{H} = \hat{H}_{QM} + \hat{H}_{MM} - \sum_A \sum_i \frac{Q_A}{\left|\bar{R}_A - \bar{r}_i\right|} + \sum_A \sum_j \frac{Q_A Z_j}{\left|\bar{R}_A - \bar{R}_j\right|} + E^{vdW}_{QM/MM} + E^{bonded}_{QM/MM}$$

where $\hat{H}_{QM}$ describes the QM segment in the vacuum, $\hat{H}_{MM}$ represents the MM segment and the remaining terms describe the interactions between the QM and MM segments. These include:
(i) the electrostatic interaction of QM electrons with the MM point charges (Q_A)
(ii)) the electrostatic interaction of QM nuclei (Z_j) with the MM point charges (Q_A)
(iii) the short-range van der Waals interactions (E^{vdW}) and
(iiii) additional parametrized potentials (E^{bonded}) required to correctly describe the QM/MM frontier geometry
(that has the same location in each system studied, see Scheme 1S).



Scheme 1S

Notice that the QM wavefunction is polarized by the MM point charges. In contrast, the MM point charges remain constant during the calculation. On the other hand, the charges of the chosen AMBER96 force-field[7 8] take into account the polarization effect in a mean-field way. Notice that the same charges are used for the excited state computations without introducing an *ad hoc* dielectric constant.



Scheme 2S

The QM/MM frontier is set at the Cε-Cδ bond of the Lys296 side-chain (see Schemes 1S and 2S). This choice ensures a QM segment (comprising the retinal chromophore and the last bond of the Lys296 side-chain) of a moderate size and far enough from the QM segment "reactive part" (i.e. the π-backbone). The simplest and more widely used Hydrogen Link Atom (HLA) scheme is used to cap the pending valence on the QM Cε atom. The link hydrogen atom is fixed at 1 Å from C∑ and kept along the C∑-C™ axis.

As documented elsewhere[3], to correctly describe the frontier, the HLA may interact with all the MM point charges, but cannot be involved in other MM potentials. Few MM potentials involving the frontier atoms have been re-parameterized. First the values of the point charges residing on the Lys296 atoms have been changed to reflect its QM/MM status. In fact, in AMBER96 any aminoacid residue has a net charge. The lysine residue has a net charge of +1 (i.e. protonated lysine). In our QM/MM framework, the MM part of Lys296 residue must have a null charge and this requires changes in the MM point charges of this residue (Table 1S).

Table 1S. The values of the re-parametrized QM/MM point charges for Lys296.

Atom	N	C_α	$C_{carbonyl}$	H_N	$O_{carbonyl}$	H_α
Charge	-0.3981	-0.2400	0.6840	0.2246	-0.6396	0.1426
Atom	C_β	H_β	C_γ	H_γ	C_δ	H_δ
Charge	-0.0094	0.0362	0.0187	0.0103	0.0000	0.0621

The charge of the frontier MM carbon atom C™ is set to 0 to ensure that the QM wavefunction is not over-polarized by the close HLA. This procedure is allowed by the little value of the original AMBER96 point charge and makes possible to use the standard MM bonded potentials (stretching, bending, etc.) for the description of the geometry of the frontier. Secondly, the van der Waals atomic parameters for retinal (i.e. for a conjugated hydrocarbon chain containing sp2 carbon atoms) are not defined in the AMBER96 force-field. Similarly, the C_{15}-N-C∑-C™ torsion potential does not exist in AMBER96.

These missing parameters have been determined in such a way to reproduce the ground state (S_0) and first excited state (S_1) CASSCF torsional energy profiles relative to the N-C∑-C™-C© and C_{15}-N-C∑-C™ dihedral angles of the model system given in Scheme 2S above[4]. The resulting van der Waals parameters are (R*=1.87 Å, ∑=0.0860 kcal.mol-1) for an sp2 carbon atom of the retinal π-system, (R*=1.87 Å, ∑=0.1094 kcal.mol-1) for a sp3 carbon atom of retinal (i.e. the methyl substituents in position 9 ad 13 see Scheme 1S) and (R*=0.92 Å, ∑=0.0157 kcal.mol-1) for the hydrogen atom of retinal. The C_{15}-N-C∑-C™ torsion potential is given by: 0.750 [1+cos(\−0)].

3. The protein model

3.1 Isorhodopsin (isoRh)

The refinement at 2.8 Å of the bovine rhodopsin crystal structure (1HZX in the PDB archive)[9] was used as a basis to build our **isoRh** model, replacing the native 11-*cis* retinal chromophore with its 9-*cis* isomer. In particular, we selected the higher resolution monomer A. In this monomer some residues located far from the retinal chromophore region are missing (236-240 and 331-333). Since we are interested in a correct description of the retinal region only we did not try to add these residues. For the same reason, the ionization status of the potentially charged carboxylic residues of the protein has been defined with a simple choice: since the majority of the carboxylic residues are located in the region near the cytoplasm side these are deprotonated (i.e. negatively charged) whenever a counterion is found in its vicinity. If not, we assume a protonated (i.e. neutral) state. The same strategy is used for the residues in the extracellular region.

Close to the retinal, there are few potentially charged ionic residues such as Glu113 (i.e. the retinal PSB counterion), Asp83 and Glu181. While Glu113 is defined as deprotonated and forming a salt bridge with the protonated Schiff base[10] the Asp83 and Glu181 residues are kept neutral since no counterion can be identified in their vicinity. Indeed, experimental evidence[11] has been reported indicating that these residues are both protonated (i.e neutral). In the retinal region the Glu122 residues could have His211 as counterion thus leading to an ion-pair. However, FTIR experiments suggest that Glu122 is protonated. Accordingly, His211 and Glu122 have been taken as protonated (i.e. neutral) in our model. Finally, all histidine residues have been defined as protonated residues with the only exception of His195 that is in close contact with Glu197.

Two water molecules have been introduced in the model. The first one, already present in the crystal structure, is located between the retinal and Glu181. The second one (W2 in Scheme 1S) has been placed between the retinal protonated Shiff base and its counterion Glu113, as suggested by Kandori et al.[12]. The other hetero atoms appearing in the crystal structure have been omitted because they are not in direct interaction with retinal. To get a globally neutral model, a chloride ion has been set close to Arg147.

3.2 Isorhodopsin-1U19 (isoRh-1U19)

The **isoRh-1U19** model is derived from the more recent crystallographic structure of bovine rhodopsin deposited in the Protein Data Bank with ID code 1U19[13] (refinement at 2.2 Å). This structure includes regions that were missing in the 1HZX structure (236-240 and 331-333), it reports a specific position of the W2 water molecule. The full procedure to build the model with the 9-*cis* retinal instead of 11-*cis* retinal matchs the one described above for **isoRh** model.

4. Optimized structures isoRh.

4.1 Excited state relaxed scan along the C_9-C_{10} torsional coordinate in Isorhodopsin

Cartesian coordinates (in Å) of optimized CASSCF(12,12)/6-31G*/AMBER structures, together with AMBER charges of the MM atoms. Atoms in bold font have been kept frozen during the geometry optimization. Atom HLA denotes the hydrogen link atom.

S_0-isoRh – Optimized without constraints at the CASSCF(12,12)/6-31G*/Amber single-root level of theory.

Atom	x	y	z	charge
N	1.115000	6.263000	-5.371000	-.51630
C	.802000	5.176000	-4.440000	.03970
C	1.939000	4.161000	-4.361000	.53660
O	2.403000	3.834000	-3.272000	-.58190
H	.490880	6.403990	-6.155220	.29360
H	.662240	5.589200	-3.441300	.11050

C	-.489000	4.470000	-4.871000	.05600
C	-1.315000	3.910000	-3.725000	.01360
C	-.537000	2.945000	-2.849000	.80540
O	.016000	1.956000	-3.391000	-.81880
O	-.487000	3.178000	-1.614000	-.81880
H	-.314450	3.720260	-5.641100	-.01730
H	-1.159730	5.222770	-5.250980	-.01730
H	-2.210400	3.426000	-4.109320	-.04250
H	-1.646270	4.758730	-3.123840	-.04250
N	1.945000	-1.516000	4.990000	-.39805
C	1.831000	-.073000	5.101000	-.24000
C	1.950000	.463000	6.511000	.68395
O	1.822000	1.662000	6.713000	-.63955
H	1.144121	-2.060535	4.703399	.22455
H	2.671565	.372660	4.569058	.14260
C	.541764	.476425	4.451902	-.00940
C	.521919	.168600	2.962524	.01870
C	-.803381	.499260	2.268429	.00000
C	-.920224	-.388496	1.019073	
N	.147516	-.095221	.049618	
H	.485256	1.551607	4.561953	.03620
H	-.338443	.091200	4.952056	.03620
H	.705223	-.890079	2.851257	.01030
H	1.335019	.708860	2.475565	.01030
H	-.844377	1.559941	2.005885	.06210
H	-1.636179	.272001	2.938377	.06210
H	-1.877945	-.241543	.551658	
H	-.812161	-1.422724	1.291774	
H	.001099	.686399	-.575757	
C	1.211197	-.815102	-.008477	
C	2.279240	-.675597	-.955264	
C	3.418925	-1.425600	-.855964	
C	4.404629	-1.325005	-1.926757	
C	5.605899	-1.955328	-1.922794	
C	6.488870	-1.959316	-3.072943	
C	7.748360	-2.470840	-3.134058	
C	8.479100	-2.969462	-1.960696	
C	9.713067	-3.514004	-2.018362	
C	10.520416	-3.935474	-.839902	
C	3.712694	-2.369904	.290639	
C	8.449288	-2.485682	-4.467002	
H	1.251181	-1.596830	.724638	
H	2.171204	.055837	-1.740500	
H	4.135278	-.724722	-2.780829	
H	5.906021	-2.515216	-1.058817	
H	6.096800	-1.491945	-3.959510	
H	8.033873	-2.825569	-.992070	
H	10.158292	-3.689927	-2.982504	
H	4.596188	-2.027320	.818727	
H	2.924253	-2.448411	1.022845	
H	3.920673	-3.366610	-.080890	
H	9.434267	-2.039922	-4.416040	
H	8.570930	-3.501794	-4.832630	
H	7.878874	-1.919936	-5.191492	
C	10.897339	-3.057342	.119483	
C	11.716291	-3.469144	1.324201	
C	10.512239	-1.590975	.144070	
C	12.385454	-4.832066	1.182029	
H	12.472095	-2.710291	1.509919	
H	11.061790	-3.463512	2.195994	
C	11.403767	-5.828967	.581737	
H	13.271820	-4.744644	.562707	

H	12.714691	-5.176459	2.159521	
C	10.935625	-5.420187	-.827416	
H	11.840115	-6.823456	.538537	
H	10.534591	-5.894228	1.235534	
C	12.059344	-5.666315	-1.856214	
C	9.728661	-6.303887	-1.194635	
H	11.740854	-5.404148	-2.861136	
H	12.951197	-5.092692	-1.632306	
H	12.331321	-6.718443	-1.869959	
H	9.398205	-6.151073	-2.216237	
H	9.989686	-7.353149	-1.090989	
H	8.887243	-6.100341	-.536317	
H	11.362382	-.988862	.459859	
H	10.166851	-1.214970	-.809310	
H	9.721290	-1.420497	.871192	
O	1.102552	-2.079476	-3.565572	-.83400
H	1.724360	-2.075647	-2.819048	.41700
H	1.365076	-1.235264	-3.984624	.41700
O	-2.107341	1.326155	-.872097	-.83400
H	-1.502340	2.082170	-1.108039	.41700
H	-2.869432	1.535803	-1.434171	.41700
HLA	-.844225	.189064	1.831876	

S_1-22°-isoRh - Excited-state (S_1) structure of isoRh obtained without enforcing any geometrical constraint in the QM system. CASSCF two-root state-average calculations with equal weights (0.5) for S_0 and S_1. Value of the C_8-C_9-C_{10}-C_{11} dihedral (in degrees) is reported in the name of each structures from now on.

Atom	x	y	z	charge
N	1.115000	6.263000	-5.371000	-.51630
C	0.802000	5.176000	-4.440000	.03970
C	1.939000	4.161000	-4.361000	.53660
O	2.403000	3.834000	-3.272000	-.58190
H	0.490880	6.403990	-6.155220	.29360
H	0.662240	5.589200	-3.441300	.11050
C	-0.489000	4.470000	-4.871000	.05600
C	-1.315000	3.910000	-3.725000	.01360
C	-0.537000	2.945000	-2.849000	.80540
O	0.016000	1.956000	-3.391000	-.81880
O	-0.487000	3.178000	-1.614000	-.81880
H	-0.314450	3.720260	-5.641100	-.01730
H	-1.159730	5.222770	-5.250980	-.01730
H	-2.210400	3.426000	-4.109320	-.04250
H	-1.646270	4.758730	-3.123840	-.04250
N	1.945000	-1.516000	4.990000	-.39805
C	1.831000	-0.073000	5.101000	-.24000
C	1.950000	0.463000	6.511000	.68395
O	1.822000	1.662000	6.713000	-.63955
H	1.145771	-2.057564	4.692794	.22455
H	2.673895	0.369835	4.570388	.14260
C	0.548679	0.473359	4.434600	-.00940
C	0.537398	0.163030	2.942734	.01870
C	-0.796877	0.469546	2.251388	.00000
C	-0.920995	-0.406177	0.995739	
N	0.128888	-0.107957	0.031989	
H	0.491257	1.548733	4.541842	.03620
H	-0.336194	0.089437	4.927046	.03620
H	0.743595	-0.890562	2.827581	.01030
H	1.339760	0.719025	2.455184	.01030
H	-0.852538	1.530023	1.991566	.06210
H	-1.625046	0.228462	2.920895	.06210
H	-1.885216	-0.254513	0.541856	

H	-0.818073	-1.443871	1.261447	
H	0.013346	0.697021	-0.556333	
C	1.211823	-0.860562	-0.060465	
C	2.239241	-0.674503	-0.952282	
C	3.463057	-1.487640	-0.939491	
C	4.342566	-1.323623	-1.956981	
C	5.650010	-1.979772	-2.025976	
C	6.516151	-1.821850	-3.055202	
C	7.859182	-2.410244	-3.111932	
C	8.544592	-2.813721	-1.973097	
C	9.762095	-3.517814	-2.014927	
C	10.549217	-3.928617	-0.853376	
C	3.732780	-2.439280	0.212572	
C	8.471070	-2.540621	-4.482067	
H	1.236598	-1.660339	0.648611	
H	2.167936	0.137779	-1.657270	
H	4.106779	-0.622390	-2.737290	
H	5.925675	-2.604730	-1.196269	
H	6.234268	-1.187251	-3.876492	
H	8.119184	-2.598248	-1.009187	
H	10.104906	-3.872286	-2.972532	
H	4.568994	-2.082970	0.804695	
H	2.900794	-2.536069	0.892364	
H	3.969822	-3.434108	-0.144035	
H	9.517462	-2.265811	-4.496155	
H	8.389099	-3.562095	-4.849622	
H	7.957681	-1.889432	-5.178131	
C	10.886781	-3.057974	0.140362	
C	11.703036	-3.481651	1.341193	
C	10.493602	-1.594556	0.181345	
C	12.411368	-4.821208	1.171157	
H	12.432804	-2.706820	1.560802	
H	11.031649	-3.517667	2.199710	
C	11.458988	-5.829883	0.546260	
H	13.299079	-4.695718	0.559848	
H	12.743729	-5.177925	2.142802	
C	10.989771	-5.410592	-0.859336	
H	11.921048	-6.811169	0.482880	
H	10.589976	-5.933656	1.195001	
C	12.118344	-5.645497	-1.882750	
C	9.790422	-6.305442	-1.230712	
H	11.809588	-5.387746	-2.892064	
H	13.010792	-5.075786	-1.650808	
H	12.387383	-6.698127	-1.891050	
H	9.459600	-6.161250	-2.254467	
H	10.066546	-7.350532	-1.128224	
H	8.945570	-6.118550	-0.571609	
H	11.342070	-0.996276	0.507544	
H	10.153559	-1.197320	-0.764920	
H	9.700965	-1.439548	0.910701	
O	1.074959	-2.099778	-3.542033	-.83400
H	1.513263	-2.012591	-2.676295	.41700
H	1.383567	-1.262909	-3.942360	.41700
O	-2.120275	1.332145	-0.873677	-.83400
H	-1.494300	2.069285	-1.112147	.41700
H	-2.868045	1.541348	-1.450632	.41700
HLA	-0.840200	0.164002	1.813277	

S_1-30°-isoRh – Excited-state (S_1) structure of isoRh obtained by constraining the C_8-C_9-C_{10}-C_{11} dihedral to -30°. CASSCF two-root state-average calculations with equal weights (0.5) for S_0 and S_1.

Atom	x	y	z	charge
N	1.115000	6.263000	-5.371000	-.51630
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H	-2.210400	3.426000	-4.109320	-.04250
H	-1.646270	4.758730	-3.123840	-.04250
N	1.945000	-1.516000	4.990000	-.39800
C	1.831000	-0.073000	5.101000	-.24000
C	1.950000	0.463000	6.511000	.68390
O	1.822000	1.662000	6.713000	-.63950
H	1.146906	-2.055827	4.686470	.22455
H	2.680643	0.365357	4.577452	.14260
C	0.562926	0.475538	4.408376	-.00940
C	0.592291	0.190979	2.907698	.01870
C	-0.744303	0.451091	2.200335	.00000
C	-0.845952	-0.454670	0.962721	
N	0.191345	-0.155665	-0.014736	
H	0.495628	1.548532	4.532630	.03620
H	-0.332292	0.079464	4.871105	.03620
H	0.851480	-0.850054	2.772960	.01030
H	1.375064	0.791570	2.441737	.01030
H	-0.830008	1.505281	1.923644	.06210
H	-1.569529	0.202006	2.870471	.06210
H	-1.817562	-0.339767	0.511722	
H	-0.713082	-1.481633	1.256495	
H	0.067234	0.649860	-0.597880	
C	1.255328	-0.932878	-0.150180	
C	2.267293	-0.776428	-1.068885	
C	3.467460	-1.613128	-1.092800	
C	4.412947	-1.351766	-2.032510	
C	5.720477	-2.021284	-2.112020	
C	6.632197	-1.764254	-3.073348	
C	7.980082	-2.367644	-3.130598	
C	8.658734	-2.740355	-1.986283	
C	9.838628	-3.515517	-2.003668	
C	10.624632	-3.927260	-0.865346	
C	3.657606	-2.704615	-0.055822	
C	8.531966	-2.559956	-4.515085	
H	1.280602	-1.733572	0.557714	
H	2.223688	0.067680	-1.737368	
H	4.235930	-0.554783	-2.732150	
H	5.954527	-2.738496	-1.346070	
H	6.401532	-1.046520	-3.840718	
H	8.233713	-2.472489	-1.036651	
H	10.121894	-3.947987	-2.947558	
H	4.342903	-2.378001	0.720347	
H	2.738537	-2.974718	0.440733	
H	4.050856	-3.608228	-0.501724	
H	9.595704	-2.741271	-4.555454	
H	8.027222	-3.401560	-4.988900	
H	8.330561	-1.671964	-5.107717	

C	10.888390	-3.089054	0.190577	
C	11.715268	-3.532124	1.375729	
C	10.425562	-1.650065	0.301371	
C	12.526458	-4.799091	1.131911	
H	12.376166	-2.718811	1.662984	
H	11.034241	-3.674192	2.216689	
C	11.656051	-5.836894	0.440265	
H	13.405637	-4.570206	0.538165	
H	12.879026	-5.186406	2.084705	
C	11.164302	-5.377930	-0.944799	
H	12.187587	-6.777358	0.328737	
H	10.791647	-6.040065	1.071346	
C	12.303328	-5.491642	-1.978123	
C	10.020735	-6.328272	-1.357466	
H	11.983136	-5.193263	-2.973013	
H	13.171612	-4.897940	-1.713850	
H	12.618470	-6.529173	-2.047385	
H	9.671715	-6.154134	-2.370249	
H	10.359789	-7.358836	-1.312031	
H	9.171861	-6.228718	-0.685110	
H	11.226675	-1.049742	0.725673	
H	10.138068	-1.198087	-0.637652	
H	9.579606	-1.574399	0.982913	
O	1.063186	-2.108054	-3.563175	-.83400
H	1.466543	-1.992167	-2.680932	.41700
H	1.390980	-1.280186	-3.967377	.41700
O	-2.101854	1.328166	-0.835115	-.83400
H	-1.465336	2.055924	-1.074496	.41700
H	-2.836992	1.537181	-1.427473	.41700
HLA	-0.779835	0.134633	1.767923	

S_1-40°-isoRh - Excited-state (S_1) structure of isoRh obtained by constraining the C_8-C_9-C_{10}-C_{11} dihedral to -40°. CASSCF two-root state-average calculations with equal weights (0.5) for S_0 and S_1.

Atom	x	y	z	charge
N	1.115000	6.263000	-5.371000	-.51630
C	0.802000	5.176000	-4.440000	.03970
C	1.939000	4.161000	-4.361000	.53660
O	2.403000	3.834000	-3.272000	-.58190
H	0.490880	6.403990	-6.155220	.29360
H	0.662240	5.589200	-3.441300	.11050
C	-0.489000	4.470000	-4.871000	.05600
C	-1.315000	3.910000	-3.725000	.01360
C	-0.537000	2.945000	-2.849000	.80540
O	0.016000	1.956000	-3.391000	-.81880
O	-0.487000	3.178000	-1.614000	-.81880
H	-0.314450	3.720260	-5.641100	-.01730
H	-1.159730	5.222770	-5.250980	-.01730
H	-2.210400	3.426000	-4.109320	-.04250
H	-1.646270	4.758730	-3.123840	-.04250
N	1.945000	-1.516000	4.990000	-.39800
C	1.831000	-0.073000	5.101000	-.24000
C	1.950000	0.463000	6.511000	.68390
O	1.822000	1.662000	6.713000	-.63950
H	1.150285	-2.055395	4.676988	.22455
H	2.678949	0.366612	4.575733	.14260
C	0.560024	0.474943	4.416736	-.00940
C	0.586269	0.186568	2.918578	.01870
C	-0.749069	0.458355	2.215999	.00000
C	-0.858588	-0.447122	0.979726	
N	0.181407	-0.158406	0.003615	

H	0.491709	1.548078	4.539928	.03620
H	-0.331904	0.077222	4.883927	.03620
H	0.835620	-0.857051	2.786876	.01030
H	1.373255	0.779276	2.449817	.01030
H	-0.821994	1.512700	1.936686	.06210
H	-1.575593	0.219102	2.888355	.06210
H	-1.827888	-0.321447	0.527239	
H	-0.736835	-1.475499	1.272598	
H	0.053086	0.635492	-0.592202	
C	1.249795	-0.931203	-0.119494	
C	2.258406	-0.783937	-1.040228	
C	3.451373	-1.625930	-1.064416	
C	4.374150	-1.400309	-2.035035	
C	5.674320	-2.075834	-2.124003	
C	6.627232	-1.739186	-3.017011	
C	7.949852	-2.390685	-3.097491	
C	8.644173	-2.739164	-1.954305	
C	9.811258	-3.529909	-1.979648	
C	10.610022	-3.940475	-0.850328	
C	3.671428	-2.676265	0.008044	
C	8.477592	-2.629349	-4.485633	
H	1.279832	-1.721211	0.599130	
H	2.206855	0.044249	-1.727047	
H	4.187154	-0.621195	-2.751107	
H	5.869990	-2.865695	-1.420702	
H	6.444971	-0.947327	-3.722390	
H	8.233409	-2.444672	-1.006101	
H	10.083706	-3.962595	-2.927743	
H	4.427979	-2.339148	0.707815	
H	2.788516	-2.883200	0.591259	
H	3.995638	-3.617296	-0.415342	
H	9.553773	-2.579710	-4.557324	
H	8.160126	-3.604891	-4.849694	
H	8.075180	-1.879052	-5.155216	
C	10.903267	-3.092254	0.188660	
C	11.749636	-3.529461	1.361840	
C	10.458781	-1.646640	0.284977	
C	12.538767	-4.811610	1.122592	
H	12.428284	-2.721931	1.622217	
H	11.084108	-3.649068	2.218452	
C	11.647038	-5.846280	0.453920	
H	13.414036	-4.602520	0.516398	
H	12.898578	-5.191627	2.075211	
C	11.143751	-5.392249	-0.928358	
H	12.167008	-6.793252	0.342617	
H	10.790104	-6.036544	1.099044	
C	12.276018	-5.499900	-1.968821	
C	9.999141	-6.344323	-1.332432	
H	11.947368	-5.194213	-2.958419	
H	13.142695	-4.904108	-1.705354	
H	12.597109	-6.534516	-2.049051	
H	9.658658	-6.189100	-2.351256	
H	10.336112	-7.374071	-1.264848	
H	9.144253	-6.231678	-0.669744	
H	11.270372	-1.049465	0.692008	
H	10.167351	-1.203912	-0.657142	
H	9.620513	-1.550955	0.972644	
O	1.052069	-2.095762	-3.563975	-.83400
H	1.511166	-2.004027	-2.705717	.41700
H	1.297353	-1.232084	-3.951966	.41700
O	-2.086344	1.333428	-0.835547	-.83400
H	-1.442303	2.059069	-1.065109	.41700

H	-2.802499	1.547286	-1.447887	.41700
HLA	-0.787318	0.142266	1.784426	

S_1-50°-isoRh - Excited-state (S_1) structure of isoRh obtained by constraining the C_8-C_9-C_{10}-C_{11} dihedral to -50°. CASSCF two-root state-average calculations with equal weights (0.5) for S_0 and S_1.

Atom	x	y	z	charge
N	1.115000	6.263000	-5.371000	-.51630
C	0.802000	5.176000	-4.440000	.03970
C	1.939000	4.161000	-4.361000	.53660
O	2.403000	3.834000	-3.272000	-.58190
H	0.490880	6.403990	-6.155220	.29360
H	0.662240	5.589200	-3.441300	.11050
C	-0.489000	4.470000	-4.871000	.05600
C	-1.315000	3.910000	-3.725000	.01360
C	-0.537000	2.945000	-2.849000	.80540
O	0.016000	1.956000	-3.391000	-.81880
O	-0.487000	3.178000	-1.614000	-.81880
H	-0.314450	3.720260	-5.641100	-.01730
H	-1.159730	5.222770	-5.250980	-.01730
H	-2.210400	3.426000	-4.109320	-.04250
H	-1.646270	4.758730	-3.123840	-.04250
N	1.945000	-1.516000	4.990000	-.39800
C	1.831000	-0.073000	5.101000	-.24000
C	1.950000	0.463000	6.511000	.68390
O	1.822000	1.662000	6.713000	-.63950
H	1.149938	-2.055008	4.677042	.22455
H	2.686916	0.362232	4.585021	.14260
C	0.576040	0.475264	4.388491	-.00940
C	0.656396	0.210430	2.884921	.01870
C	-0.667141	0.449718	2.147437	.00000
C	-0.750477	-0.493786	0.938236	
N	0.289505	-0.215151	-0.040430	
H	0.491749	1.545245	4.529130	.03620
H	-0.325782	0.059862	4.818396	.03620
H	0.949725	-0.821811	2.741277	.01030
H	1.434815	0.837116	2.447043	.01030
H	-0.741834	1.494202	1.834110	.06210
H	-1.506578	0.226724	2.809372	.06210
H	-1.718791	-0.399291	0.476853	
H	-0.613372	-1.509453	1.266229	
H	0.173716	0.583172	-0.632478	
C	1.343450	-1.006242	-0.174068	
C	2.348462	-0.881604	-1.104495	
C	3.511516	-1.753218	-1.139484	
C	4.482192	-1.492004	-2.058097	
C	5.762169	-2.196086	-2.171353	
C	6.757410	-1.771691	-2.973828	
C	8.077604	-2.436315	-3.095574	
C	8.806525	-2.758552	-1.972095	
C	10.002155	-3.509861	-2.029471	
C	10.877834	-3.908756	-0.970308	
C	3.647710	-2.875490	-0.128810	
C	8.517206	-2.703174	-4.507706	
H	1.370249	-1.798257	0.544037	
H	2.325344	-0.038652	-1.774673	
H	4.344656	-0.653480	-2.716892	
H	5.908398	-3.077732	-1.571241	
H	6.630177	-0.881522	-3.564664	
H	8.404006	-2.476412	-1.018844	
H	10.251954	-3.916277	-2.991536	

H	4.227442	-2.542761	0.726363	
H	2.692992	-3.209362	0.249604	
H	4.131841	-3.743753	-0.552435	
H	9.563643	-2.941986	-4.624034	
H	7.931108	-3.524412	-4.920288	
H	8.312732	-1.820729	-5.107288	
C	11.116256	-3.127825	0.141930	
C	12.090081	-3.553334	1.216735	
C	10.477890	-1.780592	0.415093	
C	13.006070	-4.708187	0.828642	
H	12.684626	-2.690813	1.505047	
H	11.497127	-3.815723	2.096253	
C	12.202247	-5.774922	0.103444	
H	13.827816	-4.353077	0.214966	
H	13.447654	-5.123575	1.731614	
C	11.596127	-5.261331	-1.211846	
H	12.815754	-6.643994	-0.113074	
H	11.400730	-6.120044	0.755840	
C	12.697334	-5.102146	-2.277708	
C	10.580729	-6.322500	-1.686310	
H	12.298264	-4.711326	-3.210597	
H	13.505270	-4.456288	-1.951348	
H	13.129390	-6.073449	-2.503072	
H	10.183092	-6.118517	-2.675445	
H	11.063036	-7.293998	-1.735155	
H	9.744044	-6.402843	-0.996078	
H	11.181405	-1.157903	0.958454	
H	10.183580	-1.242120	-0.475900	
H	9.598153	-1.890189	1.047612	
O	1.069798	-2.109302	-3.565304	-.83400
H	1.479147	-2.002366	-2.683042	.41700
H	1.404206	-1.280530	-3.962473	.41700
O	-2.062345	1.326173	-0.780232	-.83400
H	-1.419211	2.046476	-1.026995	.41700
H	-2.782190	1.522472	-1.393493	.41700
HLA	-0.696238	0.120478	1.725471	

S_1-60°-isoRh - Excited-state (S_1) structure of isoRh obtained by constraining the C_8-C_9-C_{10}-C_{11} dihedral to -60°. CASSCF two-root state-average calculations with equal weights (0.5) for S_0 and S_1.

Atom	x	y	z	charge
N	1.115000	6.263000	-5.371000	-.51630
C	0.802000	5.176000	-4.440000	.03970
C	1.939000	4.161000	-4.361000	.53660
O	2.403000	3.834000	-3.272000	-.58190
H	0.490880	6.403990	-6.155220	.29360
H	0.662240	5.589200	-3.441300	.11050
C	-0.489000	4.470000	-4.871000	.05600
C	-1.315000	3.910000	-3.725000	.01360
C	-0.537000	2.945000	-2.849000	.80540
O	0.016000	1.956000	-3.391000	-.81880
O	-0.487000	3.178000	-1.614000	-.81880
H	-0.314450	3.720260	-5.641100	-.01730
H	-1.159730	5.222770	-5.250980	-.01730
H	-2.210400	3.426000	-4.109320	-.04250
H	-1.646270	4.758730	-3.123840	-.04250
N	1.945000	-1.516000	4.990000	-.39800
C	1.831000	-0.073000	5.101000	-.24000
C	1.950000	0.463000	6.511000	.68390
O	1.822000	1.662000	6.713000	-.63950
H	1.151545	-2.055163	4.673237	.22455

H	2.674616	0.369080	4.570901	.14260
C	0.551688	0.473301	4.431302	-.00940
C	0.552747	0.169088	2.938244	.01870
C	-0.782698	0.466063	2.247667	.00000
C	-0.900474	-0.418264	0.997789	
N	0.138355	-0.122738	0.025182	
H	0.489730	1.547994	4.543150	.03620
H	-0.334573	0.083465	4.916006	.03620
H	0.772392	-0.881816	2.818233	.01030
H	1.348985	0.737029	2.455086	.01030
H	-0.846448	1.524542	1.983144	.06210
H	-1.608563	0.225067	2.920316	.06210
H	-1.871379	-0.281809	0.552480	
H	-0.785339	-1.452131	1.273150	
H	0.007521	0.668180	-0.570597	
C	1.215558	-0.884248	-0.096877	
C	2.217180	-0.733980	-1.020313	
C	3.412162	-1.562822	-1.041294	
C	4.300774	-1.388367	-2.054588	
C	5.584592	-2.085157	-2.152103	
C	6.620863	-1.626142	-2.879536	
C	7.895018	-2.356961	-3.033505	
C	8.658108	-2.660618	-1.920983	
C	9.789359	-3.492999	-1.969024	
C	10.585822	-3.912467	-0.840136	
C	3.695401	-2.544055	0.082878	
C	8.311809	-2.673675	-4.445042	
H	1.256172	-1.673307	0.622021	
H	2.149458	0.085687	-1.715137	
H	4.104401	-0.622756	-2.782188	
H	5.712363	-2.978388	-1.564211	
H	6.515517	-0.728448	-3.461991	
H	8.291291	-2.323524	-0.968265	
H	10.025096	-3.953815	-2.917217	
H	4.524710	-2.182686	0.682566	
H	2.864696	-2.671869	0.758213	
H	3.955748	-3.524867	-0.295092	
H	9.366143	-2.501239	-4.620183	
H	8.087388	-3.709291	-4.697652	
H	7.758079	-2.036051	-5.123839	
C	10.920937	-3.050114	0.173892	
C	11.738251	-3.495563	1.364693	
C	10.555753	-1.579419	0.224538	
C	12.453021	-4.827677	1.169574	
H	12.461560	-2.720237	1.602379	
H	11.062954	-3.551180	2.220897	
C	11.507011	-5.831586	0.528605	
H	13.340913	-4.687165	0.561630	
H	12.787397	-5.196442	2.135554	
C	11.035064	-5.394451	-0.871130	
H	11.977090	-6.807589	0.448835	
H	10.638188	-5.955143	1.174566	
C	12.160923	-5.600513	-1.902785	
C	9.838797	-6.291719	-1.250291	
H	11.847214	-5.320367	-2.904871	
H	13.054477	-5.035444	-1.662584	
H	12.431175	-6.652144	-1.938473	
H	9.511269	-6.152126	-2.275898	
H	10.118563	-7.335894	-1.148888	
H	8.989986	-6.111062	-0.594665	
H	11.398624	-1.014886	0.614649	
H	10.285294	-1.148047	-0.729577	

H	9.725157	-1.420518	0.910184	
O	1.076564	-2.089276	-3.531997	-.83400
H	1.453582	-1.977192	-2.636143	.41700
H	1.414865	-1.256240	-3.916958	.41700
O	-2.121591	1.331729	-0.861810	-.83400
H	-1.475842	2.053380	-1.093572	.41700
H	-2.848372	1.547654	-1.461170	.41700
HLA	-0.823794	0.157621	1.811716	

S_1-70°-isoRh - Excited-state (S_1) structure of isoRh obtained by constraining the C_8-C_9-C_{10}-C_{11} dihedral to -70°. CASSCF two-root state-average calculations with equal weights (0.5) for S_0 and S_1.

Atom	x	y	z	charge
N	1.115000	6.263000	-5.371000	-.51630
C	0.802000	5.176000	-4.440000	.03970
C	1.939000	4.161000	-4.361000	.53660
O	2.403000	3.834000	-3.272000	-.58190
H	0.490880	6.403990	-6.155220	.29360
H	0.662240	5.589200	-3.441300	.11050
C	-0.489000	4.470000	-4.871000	.05600
C	-1.315000	3.910000	-3.725000	.01360
C	-0.537000	2.945000	-2.849000	.80540
O	0.016000	1.956000	-3.391000	-.81880
O	-0.487000	3.178000	-1.614000	-.81880
H	-0.314450	3.720260	-5.641100	-.01730
H	-1.159730	5.222770	-5.250980	-.01730
H	-2.210400	3.426000	-4.109320	-.04250
H	-1.646270	4.758730	-3.123840	-.04250
N	1.945000	-1.516000	4.990000	-.39800
C	1.831000	-0.073000	5.101000	-.24000
C	1.950000	0.463000	6.511000	.68390
O	1.822000	1.662000	6.713000	-.63950
H	1.149726	-2.054635	4.676899	.22455
H	2.680940	0.364719	4.577376	.14260
C	0.565334	0.475153	4.407903	-.00940
C	0.596029	0.188816	2.908216	.01870
C	-0.742619	0.455819	2.210464	.00000
C	-0.869089	-0.467653	0.988704	
N	0.160739	-0.201812	-0.002674	
H	0.497281	1.548079	4.531309	.03620
H	-0.329015	0.077510	4.870494	.03620
H	0.852057	-0.853019	2.773678	.01030
H	1.377746	0.787414	2.437955	.01030
H	-0.811828	1.505808	1.914737	.06210
H	-1.565466	0.235852	2.894001	.06210
H	-1.844361	-0.344782	0.548171	
H	-0.753223	-1.491793	1.295190	
H	0.033214	0.592696	-0.593063	
C	1.210298	-0.994160	-0.158607	
C	2.195299	-0.872840	-1.110288	
C	3.371600	-1.719683	-1.157334	
C	4.331994	-1.472823	-2.097274	
C	5.611225	-2.168265	-2.197509	
C	6.662894	-1.691880	-2.898090	
C	7.943508	-2.429161	-3.051654	
C	8.772893	-2.575495	-1.957468	
C	9.861981	-3.469347	-1.952630	
C	10.659392	-3.894918	-0.839720	
C	3.553150	-2.827572	-0.135698	
C	8.264928	-2.900339	-4.446802	
H	1.243483	-1.783824	0.559797	

H	2.139934	-0.034945	-1.783482	
H	4.188973	-0.650518	-2.772471	
H	5.738498	-3.064704	-1.612443	
H	6.573726	-0.785529	-3.471887	
H	8.452301	-2.118272	-1.040613	
H	10.038800	-4.007764	-2.868675	
H	4.291038	-2.535516	0.603099	
H	2.648134	-3.051349	0.407165	
H	3.879571	-3.746544	-0.603657	
H	9.313022	-3.102239	-4.620482	
H	7.697450	-3.794947	-4.699683	
H	7.963622	-2.118714	-5.138842	
C	10.985174	-3.058780	0.205056	
C	11.823744	-3.530592	1.369225	
C	10.581010	-1.602039	0.306767	
C	12.563945	-4.839885	1.118936	
H	12.536381	-2.750098	1.622849	
H	11.159863	-3.622304	2.232268	
C	11.638565	-5.844256	0.450424	
H	13.437660	-4.654553	0.503000	
H	12.922511	-5.234202	2.066233	
C	11.146528	-5.364876	-0.928191	
H	12.132361	-6.804888	0.332979	
H	10.777060	-6.015877	1.095722	
C	12.267611	-5.479326	-1.980536	
C	9.972867	-6.282624	-1.333121	
H	11.931849	-5.142764	-2.957916	
H	13.147787	-4.903034	-1.716892	
H	12.568376	-6.517377	-2.090680	
H	9.635985	-6.122387	-2.352243	
H	10.279862	-7.321766	-1.266060	
H	9.121378	-6.146186	-0.670170	
H	11.388871	-1.034140	0.758685	
H	10.345259	-1.136059	-0.639945	
H	9.713715	-1.496357	0.957211	
O	1.047093	-2.128033	-3.568824	-.83400
H	1.387018	-1.996575	-2.658559	.41700
H	1.419101	-1.310650	-3.955717	.41700
O	-2.092680	1.330418	-0.816357	-.83400
H	-1.447460	2.051032	-1.055591	.41700
H	-2.813790	1.531309	-1.426651	.41700
HLA	-0.786807	0.133291	1.783748	

S_1-80°-isoRh - Excited-state (S_1) structure of isoRh obtained by constraining the C_8-C_9-C_{10}-C_{11} dihedral to -80°. CASSCF two-root state-average calculations with equal weights (0.5) for S_0 and S_1.

Atom	x	y	z	charge
N	1.115000	6.263000	-5.371000	-.51630
C	0.802000	5.176000	-4.440000	.03970
C	1.939000	4.161000	-4.361000	.53660
O	2.403000	3.834000	-3.272000	-.58190
H	0.490880	6.403990	-6.155220	.29360
H	0.662240	5.589200	-3.441300	.11050
C	-0.489000	4.470000	-4.871000	.05600
C	-1.315000	3.910000	-3.725000	.01360
C	-0.537000	2.945000	-2.849000	.80540
O	0.016000	1.956000	-3.391000	-.81880
O	-0.487000	3.178000	-1.614000	-.81880
H	-0.314450	3.720260	-5.641100	-.01730
H	-1.159730	5.222770	-5.250980	-.01730
H	-2.210400	3.426000	-4.109320	-.04250

H	-1.646270	4.758730	-3.123840	-.04250
N	1.945000	-1.516000	4.990000	-.39800
C	1.831000	-0.073000	5.101000	-.24000
C	1.950000	0.463000	6.511000	.68390
O	1.822000	1.662000	6.713000	-.63950
H	1.152769	-2.053330	4.666906	.22455
H	2.675945	0.367569	4.571730	.14260
C	0.556548	0.472771	4.422550	-.00940
C	0.576566	0.177565	2.926146	.01870
C	-0.766869	0.424499	2.231604	.00000
C	-0.860912	-0.474754	0.989267	
N	0.184828	-0.182123	0.028361	
H	0.489086	1.546466	4.541319	.03620
H	-0.332773	0.077836	4.896881	.03620
H	0.840897	-0.862415	2.795766	.01030
H	1.350488	0.780890	2.449556	.01030
H	-0.863301	1.478080	1.958363	.06210
H	-1.584988	0.164111	2.905511	.06210
H	-1.826781	-0.352381	0.530182	
H	-0.737394	-1.503787	1.277733	
H	0.080653	0.630553	-0.537012	
C	1.235439	-0.974202	-0.132442	
C	2.255012	-0.803861	-1.027939	
C	3.395672	-1.690720	-1.085471	
C	4.474082	-1.317216	-1.828639	
C	8.914258	-2.557465	-1.824390	
C	8.036215	-2.291596	-2.859162	
C	6.801645	-1.530749	-2.561075	
C	5.694757	-2.070592	-2.015355	
C	9.984962	-3.455089	-1.932563	
C	10.802501	-3.937724	-0.853458	
C	3.357501	-2.979752	-0.292787	
C	8.215786	-2.696872	-4.300709	
H	1.248664	-1.802920	0.543398	
H	2.276364	0.094265	-1.615757	
H	4.437733	-0.353962	-2.298236	
H	5.720985	-3.087010	-1.659992	
H	6.792367	-0.509360	-2.894775	
H	8.643807	-2.172078	-0.858482	
H	10.134115	-3.930264	-2.891385	
H	3.646317	-2.803501	0.738173	
H	2.358074	-3.396780	-0.284113	
H	4.004978	-3.738099	-0.703068	
H	9.228208	-2.956480	-4.578951	
H	7.564256	-3.540442	-4.529135	
H	7.902404	-1.863308	-4.923794	
C	11.182293	-3.128910	0.192937	
C	12.001937	-3.655340	1.346394	
C	10.875527	-1.647878	0.320886	
C	12.688218	-4.988289	1.085540	
H	12.740397	-2.907651	1.620700	
H	11.324653	-3.740813	2.199555	
C	11.723468	-5.939673	0.396890	
H	13.582363	-4.835106	0.489848	
H	13.008827	-5.409898	2.035023	
C	11.243760	-5.419954	-0.971397	
H	12.179453	-6.916016	0.258770	
H	10.859135	-6.089927	1.043779	
C	12.363496	-5.559851	-2.020850	
C	10.047406	-6.301120	-1.387984	
H	12.047266	-5.207615	-2.999252	
H	13.263094	-5.019856	-1.745207	

H	12.626238	-6.608786	-2.132926	
H	9.723797	-6.129806	-2.409946	
H	10.329245	-7.348148	-1.321283	
H	9.195567	-6.146350	-0.729181	
H	11.728358	-1.148444	0.771482	
H	10.656586	-1.145766	-0.612991	
H	10.031959	-1.488998	0.990300	
O	1.122971	-2.041404	-3.505880	-.83400
H	1.400396	-1.844077	-2.584599	.41700
H	1.527755	-1.248767	-3.913727	.41700
O	-2.091104	1.332659	-0.807717	-.83400
H	-1.430932	2.038573	-1.049036	.41700
H	-2.795079	1.531846	-1.437476	.41700
HLA	-0.799723	0.110503	1.797803	

S_1-90°-isoRh (isoRh-CI) - Excited-state (S_1) structure of isoRh obtained by constraining the C_8-C_9-C_{10}-C_{11} dihedral to -90°. CASSCF two-root state-average calculations with equal weights (0.5) for S_0 and S_1.

Atom	x	y	z	charge
N	1.115000	6.263000	-5.371000	-.51630
C	0.802000	5.176000	-4.440000	.03970
C	1.939000	4.161000	-4.361000	.53660
O	2.403000	3.834000	-3.272000	-.58190
H	0.490880	6.403990	-6.155220	.29360
H	0.662240	5.589200	-3.441300	.11050
C	-0.489000	4.470000	-4.871000	.05600
C	-1.315000	3.910000	-3.725000	.01360
C	-0.537000	2.945000	-2.849000	.80540
O	0.016000	1.956000	-3.391000	-.81880
O	-0.487000	3.178000	-1.614000	-.81880
H	-0.314450	3.720260	-5.641100	-.01730
H	-1.159730	5.222770	-5.250980	-.01730
H	-2.210400	3.426000	-4.109320	-.04250
H	-1.646270	4.758730	-3.123840	-.04250
N	1.945000	-1.516000	4.990000	-.39800
C	1.831000	-0.073000	5.101000	-.24000
C	1.950000	0.463000	6.511000	.68390
O	1.822000	1.662000	6.713000	-.63950
H	1.153005	-2.052729	4.665157	.22455
H	2.680800	0.364298	4.576879	.14260
C	0.565079	0.473598	4.401743	-.00940
C	0.602763	0.186133	2.900196	.01870
C	-0.730470	0.433480	2.182083	.00000
C	-0.826037	-0.492435	0.958858	
N	0.201389	-0.203639	-0.021514	
H	0.493777	1.546482	4.526344	.03620
H	-0.330986	0.074928	4.860133	.03620
H	0.871069	-0.852837	2.769249	.01030
H	1.383349	0.789786	2.434956	.01030
H	-0.811865	1.481915	1.884399	.06210
H	-1.560016	0.198714	2.851844	.06210
H	-1.800591	-0.394762	0.511250	
H	-0.682619	-1.511871	1.269450	
H	0.093925	0.609901	-0.580641	
C	1.214658	-1.027120	-0.248768	
C	2.173922	-0.892252	-1.211645	
C	3.340270	-1.749212	-1.259777	
C	4.381541	-1.406716	-2.067486	
C	8.911260	-2.537103	-1.811233	
C	8.018107	-2.331550	-2.849511	
C	6.784711	-1.555477	-2.593534	

C	5.630451	-2.125059	-2.188643	
C	9.964003	-3.452364	-1.917197	
C	10.810527	-3.938067	-0.869524	
C	3.368085	-2.957882	-0.349499	
C	8.201190	-2.800627	-4.271922	
H	1.246053	-1.852534	0.428487	
H	2.151748	-0.015524	-1.829148	
H	4.301445	-0.488551	-2.614626	
H	5.649755	-3.146968	-1.843477	
H	6.803869	-0.523206	-2.891192	
H	8.644813	-2.126899	-0.852772	
H	10.079584	-3.949294	-2.869718	
H	3.528852	-2.649990	0.677767	
H	2.419700	-3.480817	-0.380713	
H	4.130663	-3.671303	-0.612412	
H	9.187150	-3.170510	-4.513103	
H	7.472160	-3.578185	-4.498077	
H	7.992139	-1.956141	-4.924361	
C	11.201544	-3.138406	0.179980	
C	12.075141	-3.666273	1.292678	
C	10.854432	-1.669023	0.344409	
C	12.752647	-4.998993	1.000448	
H	12.823409	-2.916513	1.533912	
H	11.433943	-3.754986	2.173374	
C	11.777678	-5.946532	0.318633	
H	13.638673	-4.843002	0.393081	
H	13.086946	-5.431124	1.940370	
C	11.272711	-5.409098	-1.031917	
H	12.233915	-6.919802	0.161347	
H	10.925074	-6.108394	0.977920	
C	12.382410	-5.494786	-2.098349	
C	10.079601	-6.293504	-1.454317	
H	12.047602	-5.122412	-3.063465	
H	13.272125	-4.941139	-1.817153	
H	12.671334	-6.532402	-2.243718	
H	9.731428	-6.096095	-2.463438	
H	10.371010	-7.339162	-1.427638	
H	9.239341	-6.170469	-0.774222	
H	11.705800	-1.149670	0.775188	
H	10.590411	-1.158649	-0.572582	
H	10.025966	-1.550158	1.041981	
O	1.048111	-2.113679	-3.557084	-.83400
H	1.327658	-1.936659	-2.627976	.41700
H	1.448958	-1.303422	-3.931477	.41700
O	-2.094442	1.327835	-0.803698	-.83400
H	-1.436255	2.032530	-1.052071	.41700
H	-2.794741	1.508171	-1.442586	.41700
HLA	-0.763881	0.109940	1.754647	

S_0-I (BathoRh) – Optimized without constraints at the CASSCF(12,12)/6-31G*/Amber single-root level of theory.

Atom	x	y	z	charge
N	1.115000	6.263000	-5.371000	-.51630
C	0.802000	5.176000	-4.440000	.03970
C	1.939000	4.161000	-4.361000	.53660
O	2.403000	3.834000	-3.272000	-.58190
H	0.490880	6.403990	-6.155220	.29360
H	0.662240	5.589200	-3.441300	.11050
C	-0.489000	4.470000	-4.871000	.05600
C	-1.315000	3.910000	-3.725000	.01360
C	-0.537000	2.945000	-2.849000	.80540

O	0.016000	1.956000	-3.391000	-.81880
O	-0.487000	3.178000	-1.614000	-.81880
H	-0.314450	3.720260	-5.641100	-.01730
H	-1.159730	5.222770	-5.250980	-.01730
H	-2.210400	3.426000	-4.109320	-.04250
H	-1.646270	4.758730	-3.123840	-.04250
N	1.945000	-1.516000	4.990000	-.39800
C	1.831000	-0.073000	5.101000	-.24000
C	1.950000	0.463000	6.511000	.68390
O	1.822000	1.662000	6.713000	-.63950
H	1.158202	-2.061244	4.667790	.22455
H	2.682135	0.365308	4.579253	.14260
C	0.542843	0.475179	4.454407	-.00940
C	0.521195	0.188356	2.960517	.01870
C	-0.829403	0.503343	2.309750	.00000
C	-0.956037	-0.335348	1.031062	
N	0.075110	0.034456	0.053931	
H	0.477554	1.548164	4.579728	.03620
H	-0.334760	0.080877	4.951730	.03620
H	0.735666	-0.862245	2.818992	.01030
H	1.309139	0.765731	2.474786	.01030
H	-0.908173	1.572381	2.093381	.06210
H	-1.638627	0.224310	2.988825	.06210
H	-1.929406	-0.192630	0.591590	
H	-0.808651	-1.376289	1.263288	
H	-0.030286	0.923644	-0.419241	
C	1.024894	-0.761578	-0.272144	
C	2.105779	-0.436601	-1.163028	
C	3.057358	-1.377634	-1.431941	
C	4.398199	-0.960016	-1.822689	
C	5.382265	-1.824911	-2.156420	
C	6.801821	-1.625957	-1.884016	
C	7.826269	-2.307971	-2.451335	
C	9.015040	-2.519931	-1.620798	
C	10.174869	-3.101320	-1.984594	
C	11.156563	-3.633539	-1.005012	
C	2.831446	-2.850489	-1.149420	
C	7.723133	-2.975966	-3.799914	
H	1.029389	-1.698808	0.252504	
H	2.233773	0.590500	-1.461435	
H	4.651049	0.066920	-1.633824	
H	5.101240	-2.828431	-2.420457	
H	7.004402	-1.090437	-0.972782	
H	8.849917	-2.336925	-0.575717	
H	10.355201	-3.325875	-3.021229	
H	3.328618	-3.149377	-0.233135	
H	1.782473	-3.103311	-1.069548	
H	3.231598	-3.460971	-1.947435	
H	8.569539	-2.701554	-4.420038	
H	7.728080	-4.061084	-3.724742	
H	6.833981	-2.655224	-4.333014	
C	11.499866	-2.985765	0.135624	
C	12.397846	-3.605824	1.181480	
C	11.039085	-1.596080	0.524693	
C	13.154310	-4.838632	0.712398	
H	13.105721	-2.857142	1.526526	
H	11.771566	-3.853978	2.040425	
C	12.229764	-5.733217	-0.096592	
H	14.017377	-4.544495	0.125867	
H	13.526291	-5.375201	1.583407	
C	11.701226	-5.033542	-1.358312	
H	12.735013	-6.650415	-0.385954	

H	11.384046	-6.026484	0.524929	
C	12.825815	-4.889785	-2.398672	
C	10.591037	-5.929329	-1.943327	
H	12.459534	-4.399749	-3.298334	
H	13.667260	-4.322760	-2.018484	
H	13.192260	-5.870457	-2.691970	
H	10.251078	-5.591433	-2.916017	
H	10.966062	-6.940728	-2.067626	
H	9.729266	-5.971454	-1.281689	
H	11.865407	-1.063308	0.987813	
H	10.680514	-1.003372	-.307137	
H	10.244331	-1.644933	1.266040	
O	1.013843	-2.063357	-3.673685	-.83400
H	1.575052	-1.871772	-2.903195	.41700
H	1.225716	-1.247448	-4.172286	.41700
O	-2.163091	1.331212	-.914026	-.83400
H	-1.565613	2.082099	-1.176252	.41700
H	-2.942766	1.531699	-1.455646	.41700
HLA	-0.873493	0.211238	1.864386	

4.2 Optimized structures isoRh-1U19

Our goal with the computation of the full relaxed scan for Isorhodopsin lies on the chance to compare it with the one already computed for Rhodopsin. For this reason the scan we present here is based on the original model derived from the 1HZX crystallographic structure, consistently with the one published for Rhodopsin[14]. A more recent crystallographic structure for bovine rhodopsin has been released at 2.2 Å of resolution (1U19 in the PDB archive) and we recomputed the ground state equilibrium structure for Isorhodopsin and its spectroscopic properties using a new model based on the 1U19 crystallographic coordinates. The ground state structure corresponding to Bathorhodopsin has also been recomputed with the new model. The coherence of geometries and absorption characteristics with the new model is an element that can strengthen the validity of the information we get from the analysis of results obtained with the older model.

Cartesian coordinates (in Å) of optimized CASSCF(12,12)/6-31G*/AMBER structures, together with AMBER charges of the MM atoms. Atoms in bold font have been kept frozen during the geometry optimization. Atom HLA denotes the hydrogen link atom.

S_0-isoRh-1U19 – Optimized without constraints at the CASSCF(12,12)/6-31G*/Amber single-root level of theory.

Atom	x	y	z	charge
N	10.520000	10.363000	6.446000	-.51630
C	10.760000	9.255000	5.533000	.03970
C	9.522000	8.328000	5.504000	.53660
O	8.963000	8.099000	4.430000	-.58190
H	11.215060	10.546060	7.160530	.29360
H	10.920780	9.647430	4.527670	.11050
C	12.010000	8.491000	6.001000	.05600
C	12.924000	8.018000	4.897000	.01360
C	12.224000	7.104000	3.927000	.80540
O	11.573000	6.150000	4.405000	-.81880
O	12.324000	7.333000	2.696000	-.81880
H	11.749240	7.670970	6.655730	-.01730
H	12.642890	9.155690	6.553350	-.01730
H	13.783750	7.503090	5.321570	-.04250
H	13.302360	8.895670	4.366940	-.04250
N	9.288000	2.666000	-3.866000	-.39800
C	9.402000	4.127000	-3.979000	-.24000
C	9.263000	4.578000	-5.418000	.68390
O	9.260000	5.769000	-5.647000	-.63950

H	10.097746	2.107949	-3.630056	.22455
H	8.576920	4.596363	-3.441836	.14260
C	10.732950	4.620865	-3.353514	-.00940
C	10.849534	4.437496	-1.821765	.01870
C	12.000129	5.288204	-1.229028	.00000
C	12.446481	5.035849	0.236800	
N	11.339217	5.108479	1.209626	
H	10.834867	5.681610	-3.567017	.03620
H	11.571805	4.128360	-3.843737	.03620
H	11.020324	3.384786	-1.603039	.01030
H	9.911903	4.746762	-1.359238	.01030
H	11.733916	6.341679	-1.330385	.06210
H	12.880645	5.113231	-1.851750	.06210
H	13.150742	5.800061	0.525058	
H	12.929435	4.071437	0.311728	
H	11.403592	5.863658	1.898088	
C	0.461420	-1.316183	2.598878	
C	-0.156816	-2.005006	1.363479	
C	-1.080258	-1.095048	0.567487	
C	-0.311340	0.127134	0.080516	
C	0.623380	0.740941	1.106991	
C	1.005247	0.090027	2.234693	
C	1.897010	0.712741	3.262621	
C	3.119364	1.272587	3.085261	
C	3.883114	1.912402	4.176576	
C	5.080040	2.556613	4.051058	
C	5.969879	2.702089	2.909167	
C	7.190256	3.296851	3.037645	
C	8.213182	3.399102	1.993147	
C	9.350210	4.129219	2.237178	
C	10.414514	4.212172	1.267593	
C	-0.602015	-1.220532	3.715215	
C	1.600634	-2.224857	3.103147	
C	1.125301	2.106622	0.680519	
C	3.297272	1.834686	5.569917	
C	7.928182	2.696334	0.680830	
H	1.549489	2.685600	1.488837	
H	1.884120	2.000510	-0.092419	
H	0.311476	2.681502	0.244579	
H	0.280007	-0.128992	-0.799015	
H	-1.015804	0.888567	-0.244264	
H	-1.477302	-1.633851	-0.290530	
H	-1.933922	-0.792676	1.166538	
H	-0.694341	-2.891715	1.687601	
H	0.643032	-2.346203	0.706345	
H	-0.201963	-0.763464	4.615715	
H	-1.477988	-0.660260	3.407538	
H	-0.940744	-2.216425	3.988520	
H	2.025328	-1.879450	4.039576	
H	1.218399	-3.228539	3.270014	
H	2.407073	-2.293151	2.376980	
H	1.501725	0.689312	4.262816	
H	3.544526	1.275385	2.096264	
H	5.453539	3.020167	4.946802	
H	5.664798	2.304603	1.958271	
H	7.447903	3.729763	3.991183	
H	9.462686	4.714600	3.137331	
H	10.479077	3.453243	0.508613	
H	3.915509	2.379809	6.270674	
H	2.302259	2.259156	5.628665	
H	3.234203	0.801227	5.901093	
H	8.760558	2.661789	-0.005860	

H	7.617605	1.674379	0.855887	
H	7.110681	3.200029	0.174905	
O	10.498098	1.884926	4.801868	-.83400
O	10.067663	8.409507	1.889966	-.83400
H	9.575659	8.316393	2.728597	.41700
H	10.963873	8.134129	2.183461	.41700
H	9.914527	1.824261	4.030260	.41700
H	10.233043	2.768138	5.127249	.41700
HLA	12.159059	5.198369	-0.707116	

S_0-I-1U19 – Optimized without constraints at the CASSCF(12,12)/6-31G*/Amber single-root level of theory.

Atom	x	y	z	charge
N	10.520000	10.363000	6.446000	-.51630
C	10.760000	9.255000	5.533000	.03970
C	9.522000	8.328000	5.504000	.53660
O	8.963000	8.099000	4.430000	-.58190
H	11.213490	10.542950	7.161910	.29360
H	10.913560	9.641420	4.524180	.11050
C	12.010000	8.491000	6.001000	.05600
C	12.924000	8.018000	4.897000	.01360
C	12.224000	7.104000	3.927000	.80540
O	11.573000	6.150000	4.405000	-.81880
O	12.324000	7.333000	2.696000	-.81880
H	11.749680	7.671000	6.656020	-.01730
H	12.643020	9.155840	6.553110	-.01730
H	13.783650	7.502620	5.321500	-.04250
H	13.303450	8.895320	4.366820	-.04250
N	9.288000	2.666000	-3.866000	-.39800
C	9.402000	4.127000	-3.979000	-.24000
C	9.263000	4.578000	-5.418000	.68390
O	9.260000	5.769000	-5.647000	-.63950
H	10.096647	2.108731	-3.624904	.22455
H	8.576851	4.595815	-3.441564	.14260
C	10.731358	4.623752	-3.353293	-.00940
C	10.850677	4.431073	-1.822345	.01870
C	12.011912	5.264266	-1.226823	.00000
C	12.515173	4.872746	0.185995	
N	11.483320	5.041751	1.221658	
H	10.834118	5.684925	-3.565024	.03620
H	11.569989	4.133034	-3.845792	.03620
H	11.019255	3.375357	-1.618874	.01030
H	9.917752	4.736365	-1.346946	.01030
H	11.729969	6.318984	-1.226812	.06210
H	12.862336	5.158112	-1.902051	.06210
H	13.343965	5.506005	0.454143	
H	12.851141	3.845717	0.179503	
H	11.483290	5.922577	1.746640	
C	-0.039164	-0.781488	2.957853	
C	-0.563961	-1.609624	1.771244	
C	-1.456700	-0.801903	0.841266	
C	-0.682000	0.379642	0.270750	
C	0.185852	1.111276	1.276773	
C	0.525757	0.574507	2.475209	
C	1.532690	1.177030	3.399673	
C	2.728705	1.641569	2.980852	
C	3.932080	1.918985	3.781429	
C	4.986664	2.441102	3.106264	
C	6.412622	2.414912	3.439557	
C	7.270299	3.271880	2.837876	
C	8.700614	3.093371	2.542629	

C	9.523125	4.172552	2.380430	
C	10.677865	4.082990	1.524714	
C	-1.175605	-0.525148	3.961393	
C	1.055654	-1.618015	3.650415	
C	0.707453	2.426910	0.738972	
C	3.979673	1.546532	5.239873	
C	9.121390	1.681475	2.177677	
H	1.052449	3.105310	1.507673	
H	1.529086	2.258063	0.045672	
H	-0.078309	2.924856	0.177469	
H	-0.028389	0.046078	-0.536671	
H	-1.373312	1.088669	-0.177103	
H	-1.808172	-1.430372	0.025875	
H	-2.335696	-0.450477	1.370563	
H	-1.098791	-2.474571	2.153885	
H	0.286300	-1.990514	1.205818	
H	-0.847075	0.138787	4.757886	
H	-2.062759	-0.107934	3.498208	
H	-1.486950	-1.454200	4.430209	
H	1.367771	-1.192407	4.597492	
H	0.679286	-2.616197	3.854341	
H	1.935658	-1.713652	3.019556	
H	1.340776	1.081165	4.454889	
H	2.893595	1.696661	1.921065	
H	4.798837	2.776609	2.100608	
H	6.767613	1.602285	4.050886	
H	6.826083	4.109546	2.333791	
H	9.229401	5.149160	2.720155	
H	10.836730	3.171345	0.976517	
H	4.989457	1.610180	5.627274	
H	3.369513	2.238495	5.812194	
H	3.612369	0.541643	5.416732	
H	10.197106	1.535227	2.217332	
H	8.652049	0.960171	2.837726	
H	8.795010	1.433300	1.172511	
O	10.644234	1.770291	4.836964	-.83400
O	10.092079	8.483254	1.912007	-.83400
H	9.611930	8.392394	2.758063	.41700
H	10.985973	8.183144	2.186975	.41700
H	10.101545	1.820676	4.034866	.41700
H	10.441720	2.652640	5.208705	.41700
HLA	12.190502	5.125350	-0.725477	

4.3 Excited state structure of the Rhodopsin conical intersection featuring a C_{11}-C_{12} dihedral angle of -120 degrees

In this section we present a freshly computed structure of the Rhodopsin model. It was obtained accordingly to the procedure of the reported relaxed scan along the reactive C_{11}=C_{12} bond,[14] performing a further step and fixing the value of the C_{11}=C_{12} dihedral to -120 degrees.

Cartesian coordinates (in Å) of optimized CASSCF/6-31G*/AMBER S_1 structure, together with AMBER charges of the MM atoms. Atoms in bold font have been kept frozen during the geometry optimization. Atom HLA denotes the hydrogen link atom.

M (S_1-120°-Rh) – Excited-state (S_1) structure of Rh obtained by constraining the C_{10}-C_{11}-C_{12}-C_{13} dihedral to -120°. CASSCF two-root state-average calculations with equal weights (0.5) for S_0 and S_1.

Atom	x	y	z	charge

N	1.115000	6.263000	-5.371000	-.51630
C	0.802000	5.176000	-4.440000	.03970
C	1.939000	4.161000	-4.361000	.53660
O	2.403000	3.834000	-3.272000	-.58190
H	0.490880	6.403990	-6.155220	.29360
H	0.662240	5.589200	-3.441300	.11050
C	-0.489000	4.470000	-4.871000	.05600
C	-1.315000	3.910000	-3.725000	.01360
C	-0.537000	2.945000	-2.849000	.80540
O	0.016000	1.956000	-3.391000	-.81880
O	-0.487000	3.178000	-1.614000	-.81880
H	-0.314450	3.720260	-5.641100	-.01730
H	-1.159730	5.222770	-5.250980	-.01730
H	-2.210400	3.426000	-4.109320	-.04250
H	-1.646270	4.758730	-3.123840	-.04250
N	1.945000	-1.516000	4.990000	-.39800
C	1.831000	-0.073000	5.101000	-.24000
C	1.950000	0.463000	6.511000	.68390
O	1.822000	1.662000	6.713000	-.63950
H	1.151438	-2.054694	4.672565	.22455
H	2.687121	0.361449	4.584792	.14260
C	0.577926	0.472742	4.384844	-.00940
C	0.652707	0.209505	2.878913	.01870
C	-0.694030	0.398986	2.169895	.00000
C	-0.746363	-0.512190	0.935525	
N	0.204105	-0.087320	-0.074709	
H	0.492648	1.542748	4.525293	.03620
H	-0.322493	0.058203	4.818361	.03620
H	0.986634	-0.809680	2.724037	.01030
H	1.397200	0.869186	2.430545	.01030
H	-0.831242	1.446665	1.890511	.06210
H	-1.507973	0.113512	2.838475	.06210
H	-1.743274	-0.493864	0.522660	
H	-0.491745	-1.517884	1.225511	
H	0.006576	0.766276	-0.551919	
C	1.222689	-0.822977	-0.479341	
C	2.094931	-0.497806	-1.490142	
C	3.283007	-1.286185	-1.734549	
C	4.365523	-0.748295	-2.350937	
C	5.464842	-1.580857	-2.899962	
C	6.736577	-1.448960	-2.456347	
C	7.883383	-2.187728	-2.919695	
C	8.843434	-2.479340	-1.935356	
C	10.015455	-3.184453	-2.124542	
C	10.936711	-3.578318	-1.064205	
C	3.360454	-2.670068	-1.121411	
C	8.045965	-2.576788	-4.365675	
H	1.347819	-1.724255	0.083948	
H	1.974040	0.441489	-1.997765	
H	4.255438	0.222532	-2.800717	
H	5.257255	-2.095019	-3.831948	
H	6.864811	-0.886266	-1.543373	
H	8.585332	-2.183107	-0.937268	
H	10.243296	-3.547050	-3.115606	
H	3.483647	-2.593523	-0.046111	
H	2.454594	-3.232981	-1.319677	
H	4.187947	-3.249876	-1.499830	
H	8.741438	-1.883125	-4.832501	
H	8.424182	-3.583837	-4.497461	
H	7.115327	-2.489954	-4.910761	
C	11.194521	-2.787277	0.024043	

```
C      12.109544          -3.238804           1.144792
C      10.641134          -1.393554           0.252092
C      13.001642          -4.421435           0.786479
H      12.721520          -2.398068           1.459575
H      11.473625          -3.482117           1.998183
C      12.189136          -5.474939           0.051515
H      13.843555          -4.090851           0.186841
H      13.412400          -4.844067           1.700327
C      11.604322          -4.958138          -1.274263
C      11.604322          -4.958138          -1.274263
H      12.795483          -6.351082          -0.157561
H      11.374242          -5.806666           0.694332
C      12.713611          -4.838919          -2.335822
C      10.560083          -5.990924          -1.745264
H      12.331762          -4.420031          -3.264578
H      13.545224          -4.230655          -1.997361
H      13.107489          -5.823358          -2.570852
H      10.188334          -5.793377          -2.745958
H      11.011636          -6.977677          -1.766922
H       9.709660          -6.031440          -1.068716
H      11.412071          -0.780218           0.708426
H      10.313762          -0.883602          -0.643144
H       9.807037          -1.421092           0.951415
O       0.998594          -2.111082          -3.657963       -.83400
H       1.228878          -1.813796          -2.750381        .41700
H       1.386380          -1.332804          -4.107987        .41700
O      -2.093878           1.331812          -0.773794       -.83400
H      -1.468274           2.062471          -1.031398        .41700
H      -2.820829           1.498053          -1.387415        .41700
HLA    -0.712290           0.081360           1.739601
```

5. Energetics and electronic properties

5.1 Energetics and electronic properties for isoRh (derived from 1HZX model) relaxed scan.

Table 2S. Isorhodopsin CASPT2//CASSCF(12,12)/6-31g*/Amber, three-root (weights 0.333, 0.333, 0.333) state-average calculation.

Structure	***State***	***CASPT2***		***CASSCF***			
		E(a.u.)	***E(kcal/mol)***	f_{CASSCF}	μ ***(D)***	***E(a.u.)***	***E(kcal/mol)***
S_0-isoRh	S_0	-871.280045	0.00		15.75	-868.587517	0.00
	S_1	-871.180118	62.71	0.911	24.83	-868.436637	94.68
	S_2	-871.141589	86.88	0.563	18.06	-868.416254	107.47
S_1-22°-isoRh	S_0	-871.262222	11.18		17.70	-868.550717	23.09
	S_1	-871.199707	50.41	0.784	24.46	-868.470719	73.29
	S_2	-871.178039	64.01	0.609	21.12	-868.440183	92.45
S_1-30°-isoRh	S_0	-871.261107	11.88		18.54	-868.545673	26.06
	S_1	-871.209188	44.46	0.852	28.23	-868.476956	69.38
	S_2	-871.177356	64.44	0.402	20.01	-868.440097	92.51

S_1-40°-isoRh	S_0	-871.258153	13.74		18.26	-868.542895	28.00
	S_1	-871.209184	44.47	0.799	29.03	-868.476273	69.81
	S_2	-871.175069	65.87	0.340	19.73	-868.437942	93.86
S_1-50°-isoRh	S_0	-871.255148	15.62		18.99	-868.537780	31.21
	S_1	-871.217435	39.29	0.735	33.44	-868.482418	65.95
	S_2	-871.171742	67.96	0.139	18.67	-868.436762	94.60
S_1-60°-isoRh	S_0	-871.243230	23.10		16.97	-868.528146	37.26
	S_1	-871.208108	45.14	0.593	32.35	-868.472206	72.36
	S_2	-871.161910	74.13	0.801	17.70	-868.427343	100.51
S_1-70°-isoRh	S_0	-871.236578	27.28		16.84	-868.522443	40.83
	S_1	-871.213138	41.98	0.419	36.22	-868.474891	70.67
	S_2	-871.155875	77.92	< 0.005	16.39	-868.427243	100.57
S_1-80°-isoRh	S_0	-871.226052	33.88		15.84	-868.514316	45.93
	S_1	-871.212165	42.60	0.176	39.99	-868.473481	71.56
	S_2	-871.150403	81.35	0.033	15.71	-868.425172	101.87
S_1-90°-isoRh (isoRh-CI)	S_0	-871.217265	39.40		15.21	-868.506548	50.81
	S_1	-871.214229	41.30	0.262	42.18	-868.474624	70.84
	S_2	-871.145132	84.66	0.826	15.51	-868.419865	105.20
S_0-I (BathoRh)	S_0	-871.246016	21.35		14.78	-868.549247	24.01
	S_1	-871.155078	78.42	0.691	25.45	-868.403905	115.22
	S_2	-871.113776	104.33	0.584	18.56	-868.378796	130.97

Table 3S. Charge-transfer (Δq) computed at the three-roots (weights 0.333, 0.333, 0.333) state average CASSCF/6-31G*/Amber level.

Structure	Δq[a]	
	S_0->S_1	S_0->S_2
S_0-isoRh	-0.2471	-0.0822
S_1-22°-isoRh	-0.2365	-0.1084
S_1-30°-isoRh	-0.3265	-0.0449
S_1-40°-isoRh	-0.3671	-0.0485
S_1-50°-isoRh	-0.4794	0.0149
S_1-60°-isoRh	-0.5372	-0.0265
S_1-70°-isoRh	-0.6854	0.0299
S_1-80°-isoRh	-0.8566	0.0201
S_1-90°-isoRh (isoRh-CI)	-0.9517	0.0061
S_0-I (BathoRh)	-0.2755	-0.1273

[(a)] The magnitude of charge transfer induced by the vertical transition is evaluated as the change in the positive charge of the –NH=C_{15}- fragment. We use Mulliken charges as we only need to characterize the electronic transition and not to accurately fit point charges. Mulliken charges are calculated by using the CASSCF functions.

5.2 Energetics and electronic properties of isoRh-1U19

Table 4S. Isorhodopsin CASPT2//CASSCF(12,12)/6-31g*/Amber, three-roots (weights 0.333, 0.333, 0.333) state-average calculation.

Structure	***State***	***CASPT2***		***CASSCF***			
		E(a.u.)	***E(kcal/mol)***	f_{CASSCF}	μ ***(D)***	***E(a.u.)***	***E(kcal/mol)***
S_0-isoRh-1U19	S_0	-871.303103	0.00		13.41	-868.609020	0.00
	S_1	-871.208837	59.15	0.943	25.13	-868.465503	90.06
	S_2	-871.167050	85.37	0.511	16.70	-868.440833	105.54
S_0-I-1U19	S_0	-871.279473	14.83			-868.580094	18.15
	S_1	-871.193553	68.74	0.778		-868.442118	104.73
	S_2	-871.140219	102.21	0.363		-868.405284	127.85

Table 5S. Charge-transfer (Δq) computed at the three-roots (weights 0.333, 0.333, 0.333) state average CASSCF/6-31G*/Amber level.

Structure	Δq[a]	
	S_0->S_1	S_0->S_2
S_0-isoRh-1U19	-0.2588	-0.0873
S_0-I-1U19	-0.3353	-0.0635

[(a)] The magnitude of charge transfer induced by the vertical transition is evaluated as the change in the positive charge of the –NH=C_{15}- fragment. We use Mulliken charges as we only need to characterize the electronic transition and not to accurately fit point charges. Mulliken charges are calculated by using the CASSCF functions.

5.3 Energetics and electronic properties of the conical intersection structure M (S_1-120°-Rh)

Table 6S. Rhodopsin CASPT2//CASSCF(12,12)/6-31g*/Amber, three-roots (weights 0.333, 0.333, 0.333) state-average calculation.

Structure	***State***	***CASPT2***		***CASSCF***			
		E(a.u.)	***E(kcal/mol)***[(b)]	f_{CASSCF}	μ ***(D)***	***E(a.u.)***	***E(kcal/mol)***[(c)]
M or S_1-120°Rh[(a)]	S_0	-871.212772	46.96		13.66	-868.504319	55.65
	S_1	-871.208820	49.44	0.131	36.76	-868.467598	78.70
	S_2	-871.167050	75.65	0.0418	13.30	-868.407688	116.29

[(a)] see section **4.3.**
[(b)] Energies are given relative to the ground state of **S_0-Rh** (-871.287600 a.u.) from ref**.** 14**.**
[(c)] Energies are given relative to the ground state of **S_0-Rh** (-868.593007 a.u.) from ref**.** 14**.**

Table 7S. Charge-transfer (Δq) computed at the three-roots (weights 0.333, 0.333, 0.333)state average CASSCF/6-31G*/Amber level.

Structure	Δq[a]	
	S_0->S_1	S_0->S_2
M (S_1-120°Rh)	-0.8808	0.0287

[(a)] The magnitude of charge transfer induced by the vertical transition is evaluated as the change in the positive charge of the –NH=C_{15}- fragment. We use Mulliken charges as we only need to characterize the electronic transition and not to accurately fit point charges. Mulliken charges are calculated by using the CASSCF functions.

6. Comparison with available experimental data

6.1 Spectroscopic data

Table8S. Absorption maxima for the listed structures (the energy gap in kcal·mol^{-1} is given in parenthesis).

Structure	Absorption		Observed	
	S_0->S_1	S_0->S_2	S_0->S_1	S_0->S_2
S_0-Rh	(59.8) 478 nm	(87.3) 328 nm	498 nm	340 nm
S_0-Rh-1U19	(55.7) 513 nm	(84.1) 340 nm		
S_0-isoRh	(62.7) 456 nm	(86.9) 329 nm	483 nm	≅340 nm[a]
S_0-isoRh-1U19	(59.2) 484 nm	(85.4) 335 nm		
S_0-I	(57.2) 500 nm	(82.6) 346 nm	543 nm	n.a.
S_0-I-1U19	(53.9) 531 nm	(87.4) 327 nm		

[a] see Absorption Spectra published in Spalink *et al*[15].
n.a. Experimental data not available.

6.2 Structural data

Table9S. Geometric parameters (Angstroms and degrees) for both of our computed models of 9-*cis* retinal in the protein matrix (**S_0-isoRh** and **S_0-isoRh-1U19**) and the experimental ones become recently available[16,17].

BOND LENGTH	**6-7**	**7-8**	**8-9**	**9-10**	**10-11**	**11-12**	**12-13**	**13-14**	**14-15**	**15-N**
1st set unit A[a]	1.49	1.36	1.47	1.37	1.44	1.37	1.46	1.36	1.44	1.32
1st set unit B[b]	1.49	1.35	1.46	1.37	1.46	1.37	1.46	1.37	1.45	1.32
2st set unit A	1.47	1.37	1.45	1.39	1.40	1.39	1.42	1.41	1.42	1.32
2st set unit B	1.47	1.36	1.45	1.39	1.43	1.40	1.41	1.42	1.43	1.33
S_0-isoRh	1.49	1.35	1.47	1.36	1.45	1.36	1.46	1.37	1.43	1.29
S_0-isoRh-1U19	1.50	1.36	1.48	1.37	1.45	1.36	1.47	1.37	1.44	1.29
BOND ANGLE	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
1st set unit A	121.7	134.5	127.0	119.4	127.0	118.4	123.5	116.0	125.0	120.5
1st set unit B	121.2	132.9	128.7	118.4	126.4	117.7	125.0	115.7	124.5	122.1
2st set unit A	123.1	126.4	124.0	123.4	127.3	122.2	124.2	117.9	123.2	119.6
2st set unit B	122.7	124.7	125.7	122.3	127.1	121.2	125.4	117.7	122.7	121.2
S_0-isoRh	122	125	124	124	127	123	124	118	121	126
S_0-isoRh-1U19	123	128	123	126	131	121	126	119	121	127
DIHEDRAL ANGLE	**6-7**	**7-8**	**8-9**	**9-10**	**10-11**	**11-12**	**12-13**	**13-14**	**14-15**	**15-N**
1st set unit A	-34.3	178.9	172.2	-12.3	-171.4	166.9	165.8	171.5	153.0	-171.6
1st set unit B	-34.8	180.0	168.4	-18.7	-172.8	166.4	158.1	174.9	164.7	-173.8
2st set unit A	-48.4	-177.2	-179.1	-12.0	-171.1	169.7	164.5	171.3	156.3	-174.7
2st set unit B	-48.9	-178.3	177.8	-16.3	-172.3	169.9	155.5	174.3	167.6	-176.7
S_0-isoRh	-60	175	178	-8	175	172	176	174	174	176
S_0-isoRh-1U19	-54	177	-176	-6	-174	175	174	177	160	175

[a] Experimental data are reported for monomer A and [b] monomer B in the asymmetric unit. 1st and 2nd indicate that data are obtained using different initial parameters in the crystallographic refinement as described in ref. 16, 17.

6.3 Comparison with a recent published computed model for 9-*cis* retinal

Table10S. Geometrical parameters (Angstroms and degrees) of 9-*cis* retinal model computed in the protein environment reported by Sekharan *et al*.[17]

BOND LENGTH	**6-7**	**7-8**	**8-9**	**9-10**	**10-11**	**11-12**	**12-13**	**13-14**	**14-15**	**15-N**
9-cis pe[a]	1.45	1.37	1.44	1.39	1.42	1.38	1.43	1.40	1.41	1.31
BOND ANGLE	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
9-cis pe[a]	122	126	123	123	125	123	123	119	123	124
DIHEDRAL ANGLE	**6-7**	**7-8**	**8-9**	**9-10**	**10-11**	**11-12**	**12-13**	**13-14**	**14-15**	**15-N**

9-cis pe[a]	-40	176	173	-9	178	174	172	173	173	176

[a] According to the definition in Sekharan paper: protein-embedded 9-*cis* retinal.

Table11S. CASPT2 energy gaps of the computed model of 9-*cis* retinal reported by Sekharan *et al*.[17] To compare see Table 2S (top rows) and Table 3S of this Supporting Material.

Structure	Absorption		Observed	
	S_0->S_1	S_0->S_2	S_0->S_1	S_0->S_2
9-cis pe[a]	(58.3) 490 nm	(69.2) 413 nm	483 nm	≅340 nm[b]
Oscillator strength (f)	0.80	0.00		

[a] According with the definition in Sekaharan paper: protein-embedded 9-*cis* retinal.
[b] See Absorption Spectra published in Spalink *et al*.[15]

7. CASSCF/AMBER energy profiles isoRh and Rh.

We report the CASSCF (three root, weights 0.333, 0.333, 0.333, state average)/AMBER energy profile for isoRh. Here we show also previous results obtained with the same approach for Rhodopsin in order to compare them (see ref. 21 of the manuscript for further details). All energies (ΔE, in kcal mol^{-1}) are given relative the ground-state energy of the equilibrium Rh (**S_0-Rh**).

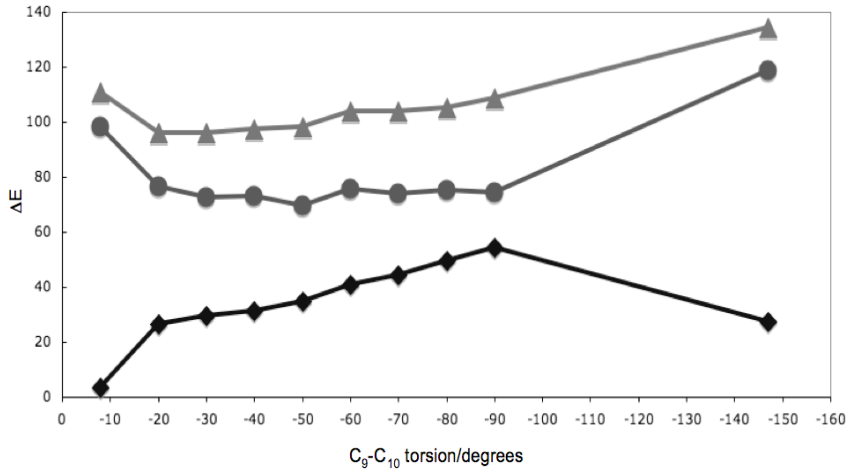

Figure 1S. Isorhodopsin CASSCF(12,12)/6-31G*/AMBER three-root (weights 0.333, 0.333, 0.333) state average. Squares indicate S_0, circles indicate S_1, and triangles indicate S_2.

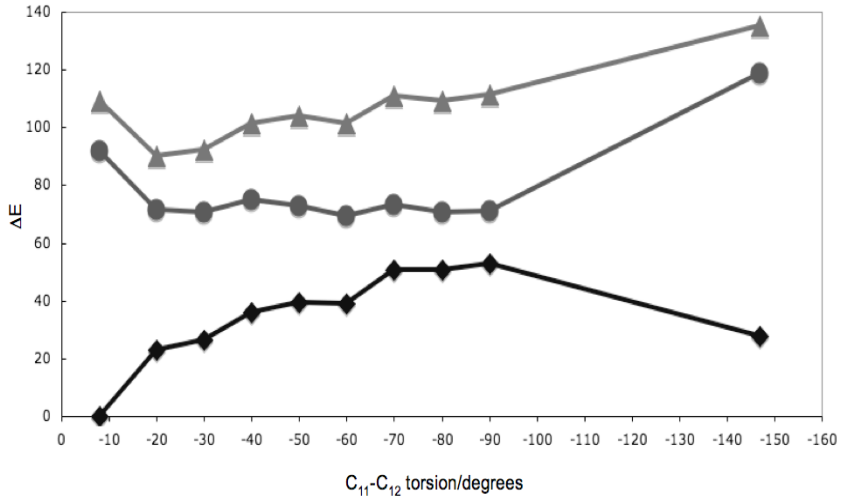

Figure 2S. Rhodopsin CASSCF(12,12)/6-31G*/AMBER three-root (weights 0.333, 0.333, 0.333) state average. Squares indicate S_0, circles indicate S_1, and triangles indicate S_2.

8. Bare chromophore energy profile (geometry optimized in the full protein)

In order to estimate the magnitude of the protein effect on the computed energy profile (and on the appearance of the energy minimum observed at -50°), we performed single point calculations of the **PSB9** *in vacuo* at the CASPT2//CASSCF/6-31G* level. This has been done for each structure obtained along the S_1 scan and keeping the chromophore with the geometry optimized in the protein matrix. As shown in the Figure 3S, the two profiles are quite similar, the minimum at -50° is still detectable but with a lower energy barrier (ca. 1.5 kcal/mol). With this approach it is possible to separate the whole contribution of the protein from the one of the geometrical distortion of the chromophore itself. A further decomposition of the protein effect has been done excluding the electrostatic effect. This is possible adding to the bare **PSB9** energies the **MM term** which in our protocol includes the pure MM energy, the van der Waals energy between the QM system and the protein matrix and the additional bonded energy relative to the frontier region (see section 2 pag S1 for the expression og the hybrid Hamiltonian). The comparison between the bare **PSB9** profile and the bare **PSB9+MM term** is shown in Figure 4S. It has to be stressed that the MM term represents a sum of effects itself and its further decomposition would require a systematic investigation to distinguish residues which give the bigger contribution and it has not been done in the present work. Our analysis anyway shows that the energy barrier of the very shallow minimum at -50° in the bare **PSB9** profile becomes roughly the double when the **MM term** is added, the remaining part being attributable to the electrostatic interaction between the chromophore and the protein matrix.

Table12S. CASPT2//CASSCF/6-31G* energies (real level shift 0.3 and casscf wavefunction computed at three-root (weights 0.333, 0.333, 0.333) state average level). [a] Energy differences are given relative to the first root of **S_0-PSB9**.

Structure	State	E(a.u.)	ΔE (kcal/mol)[a]
S_0-PSB9	S_0	-870.863021	0.00
	S_1	-870.775354	55.01
	S_2	-870.726900	85.42
S_1-22°-PSB9	S_0	-870.849174	8.69
	S_1	-870.789626	46.06
	S_2	-870.755859	67.24
S_1-30°-PSB9	S_0	-870.845606	10.93
	S_1	-870.794355	43.09
	S_2	-870.753882	68.49
S_1-40°-PSB9	S_0	-870.843058	12.53
	S_1	-870.794948	42.72
	S_2	-870.751709	69.85
S_1-50°-PSB9	S_0	-870,836629	16.56
	S_1	-870.798457	40.51
	S_2	-870.745206	73.93
S_1-60°-PSB9	S_0	-870.830011	20.71
	S_1	-870.796085	42.00
	S_2	-870.740161	77.10
S_1-70°-PSB9	S_0	-870.823003	25.11
	S_1	-870.800555	39.20
	S_2	-870.734812	80.45
S_1-80°-PSB9	S_0	-870.813893	30.83
	S_1	-870.804816	36.52
	S_2	-870.732769	81.73
S_1-90°-PSB9	S_0	-870.800915	38.97
	S_1	-870.805922	35.83
	S_2	-870.727800	84.85

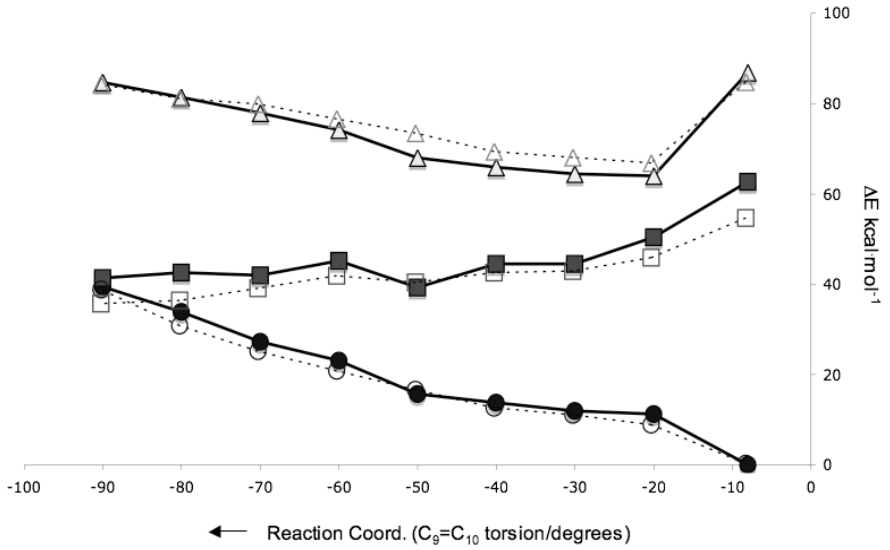

Figure 3S. Superimposition of the CASPT2//CASSCF/AMBER energy profile of **isoRh** and the CASPT2//CASSCF energy profile of **PSB9**. Circles, squares, and triangles indicate respectively S_0, S_1 and S_2 of **isoRh**. Open circles, open squares, and open triangles indicate respectively S_0, S_1 and S_2 of **PSB9.** All energies for **isoRh** are given relative the ground-state energy of the **S_0-isoRh**; all energies for bare **PSB9** are given relative the ground-state energy of the **S_0-PSB9**.

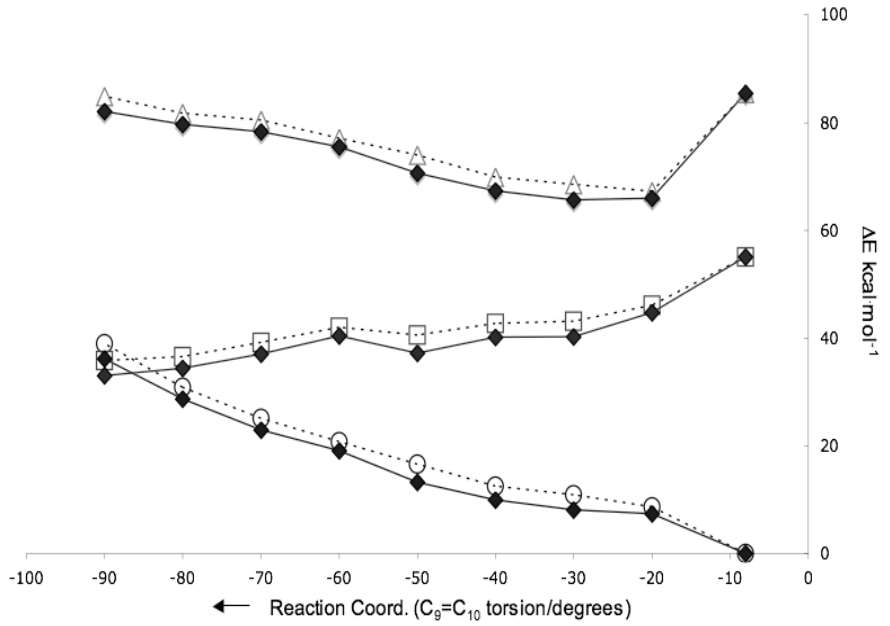

Figure 4S. Superimposition of the CASPT2//CASSCF energy profile of bare **PSB9** and the profile of bare **PSB9+MM Term** containing non-bonded interactions. Open circles, open squares, open triangles indicate respectively S_0, S_1 and S_2 of **PSB9** while diamonds indicate respectively S_0, S_1 and S_2 of the summation. All energies for bare **PSB9** are given relative the ground-state energy of the **S_0-PSB9**; all energies for summation are given relative to the ground state **S_0-PSB9+MM Term** energy.

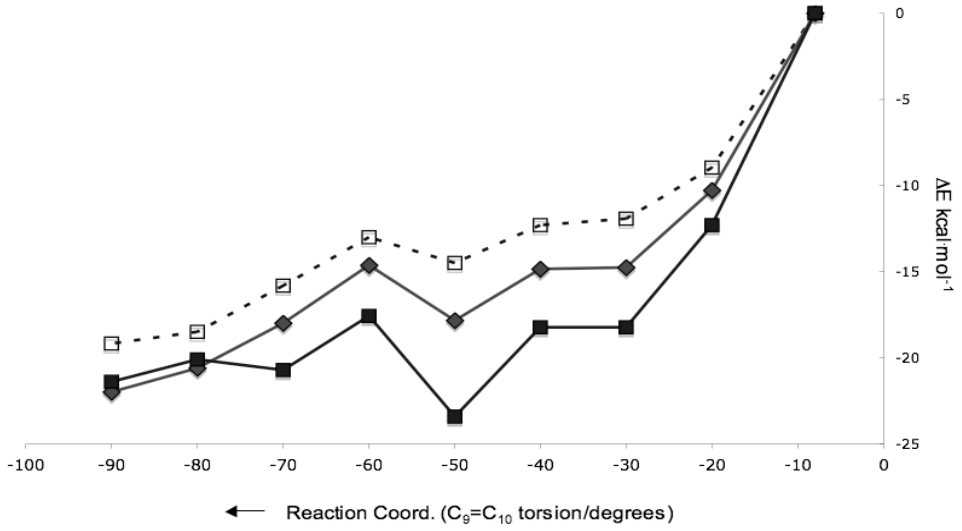

Figure 5S. Superimposition of (i) the CASPT2//CASSCF excited state (S_1) energy profile of bare **PSB9** (open squares), (ii) the excited state (S_1) profile of bare **PSB9+MM Term** containing non-bonded interactions (diamonds) and (iii) the CASPT2//CASSCF/AMBER excited state (S_1) of **isoRh** (squares). For each set, energies are given relative to the corresponding Franck-Condon structure.

9. Twisting motion along isoRh → isoRh-CI reaction coordinate

Table 13S List of the dihedral angles (in degrees) which undergo the bigger change; a part of this table is reported in the main text. (" subs* " indicates the dihedral of the "subsequent" bond with respect to the reactive bond. " prev* " indicates the dihedral of the "previous" bond with respect to the reactive bond. Data for **Rh** from ref. 21 of the manuscript.

isoRh	**Rh**
C_9-C_{10} ≅ - 82°	C_{11}-C_{12} ≅ - 72°
C_{11}-C_{12} ≅ + 32°	C_9-C_{10} ≅ + 30°
C_{13}-C_{14} ≅ + 19°	C_{13}-C_{14} ≅ + 16°
C_7-C_8 ≅ -17°	C_{12}-C_{13}(subs*) ≅ + 30°
C_6-C_7 ≅ +17°	C_6-C_7 ≅ + 16°
C_{10}-C_{11}(subs*) ≅ +12°	C_8-C_9 ≅ - 9°
C_8-C_9(prev*) ≅ -10°	

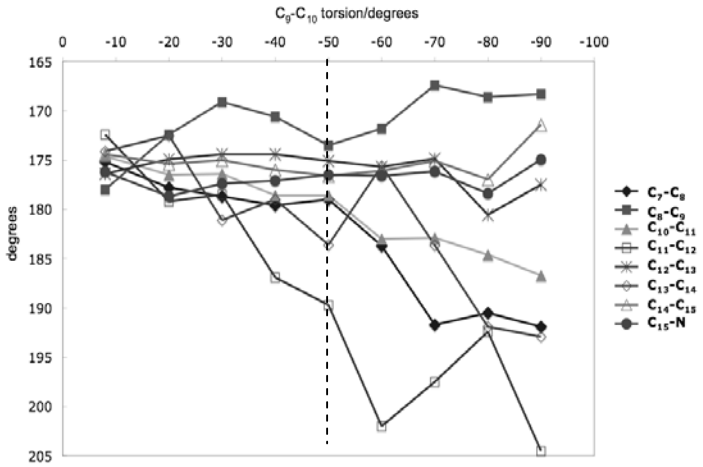

Figure 6S. isoRh: dihedral angles (in degrees) changes in the scan along the torsional coordinate C_9-C_{10} (see below Figure 9S for the C_6-C_7 not included in this diagram). The dashed line indicates a change in the reaction coordinate charaterized by a fast variation in the C_{11}-C_{12} and C_{13}-C_{14}.

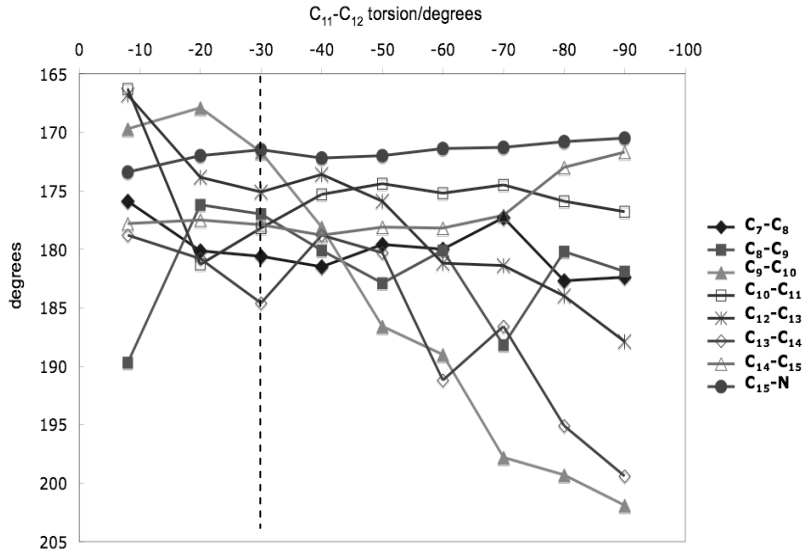

Figure 7S. **Rh**: dihedral angles (in degrees) changes in the scan along the torsional coordinate C_{11}-C_{12} (see below Figure 9S for the C_6-C_7 not included in this diagram). The dashed line indicates a change in the reaction coordinate charaterized by a fast variation in the C_9-C_{10} and C_{13}-C_{14}. Data from ref. 21 of the manuscript.

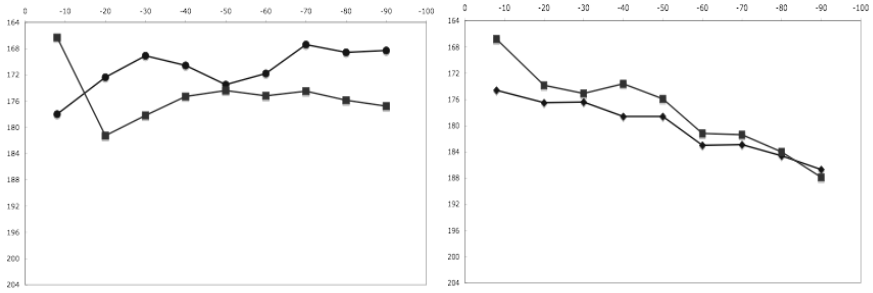

Figure 8S. Left: previous dihedral angle (degrees) with respect to the reactive one (C_8-C_9 in isoRh, C_{10}-C_{11} in Rh); Right: subsequent dihedral angle (degrees) with respect to the reactive one **(**C_{10}-C_{11} in isoRh, C_{12}-C_{13} in Rh). Circles: **isoRh**, Squares: **Rh**. Reaction coordinate (X axis) is C_9=C_{10} and C_{11}=C_{12} torsion in degrees for isoRh and Rh respectively. Data for **Rh** from ref. 21 of the manuscript.

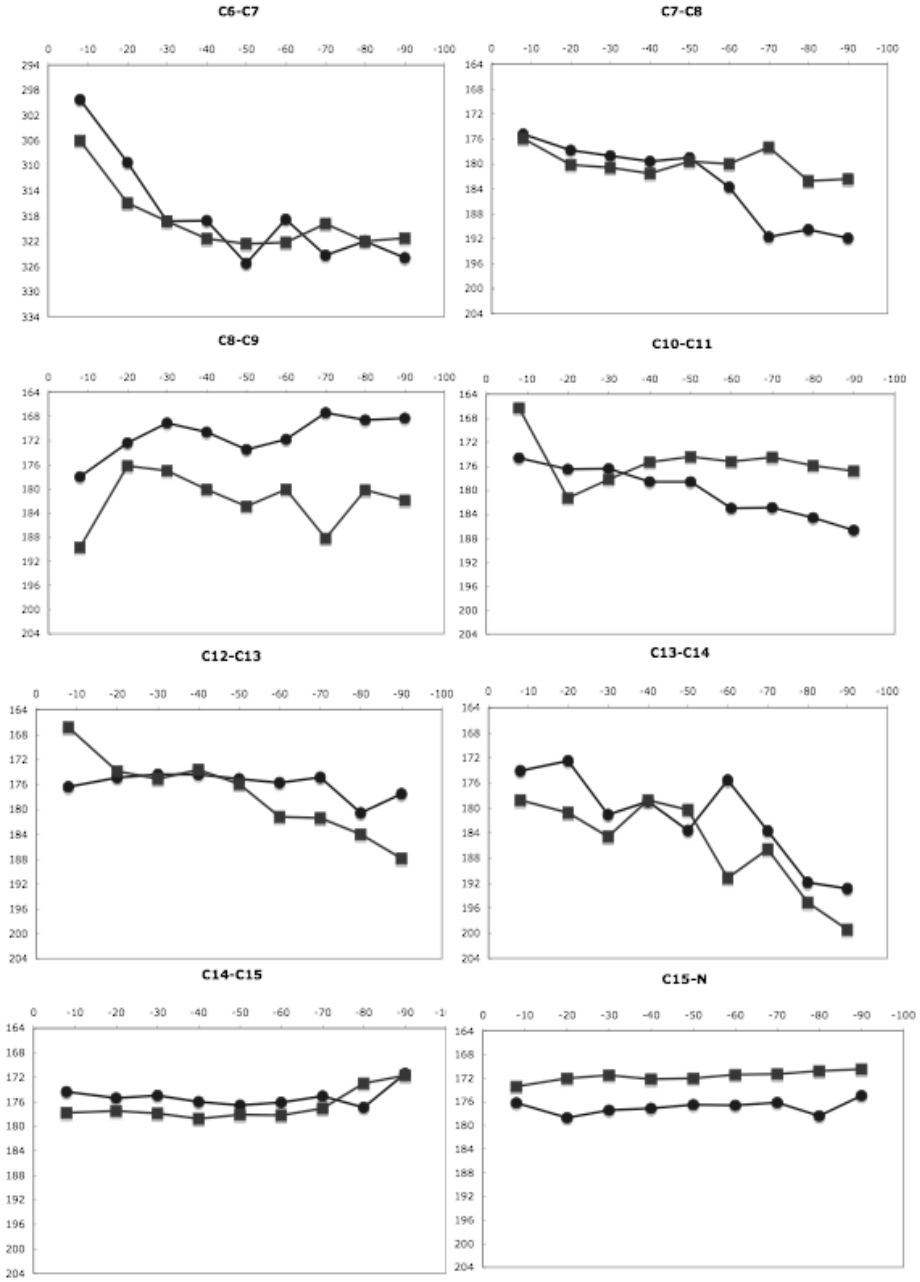

Figure 9S. Comparison of each dihedral angle (degrees) along the scans (as previously defined). Circles: **isoRh**, Squares: **Rh**. Reaction coordinate (X axis) is C_9=C_{10} and C_{11}=C_{12} torsion in degrees for **isoRh** and **Rh** respectively. Data for **Rh** from ref. 21 of the manuscript.

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