

Supplementary info

Automated generation of radical species in crystalline carbohydrate using *ab initio* MD simulations

Siv G. Aalbergsjø^{1*}, Ewald Pauwels², Andy Van Yperen-De Deyne³,
Veronique Van Speybroeck³ and Einar Sagstuen¹

¹Department of Physics, University of Oslo, P. O. Box 1048 Blindern, N-0316, Oslo, Norway.

²UGent HPC, Ghent University, Krijgslaan 281 S9, B-9000 Gent, Belgium

³Center for Molecular Modeling, Ghent University, Technologiepark 903, B-9052 Zwijnaarde, Belgium

*E-mail: s.g.aalbergsjo@fys.uio.no

A. Radical product formation

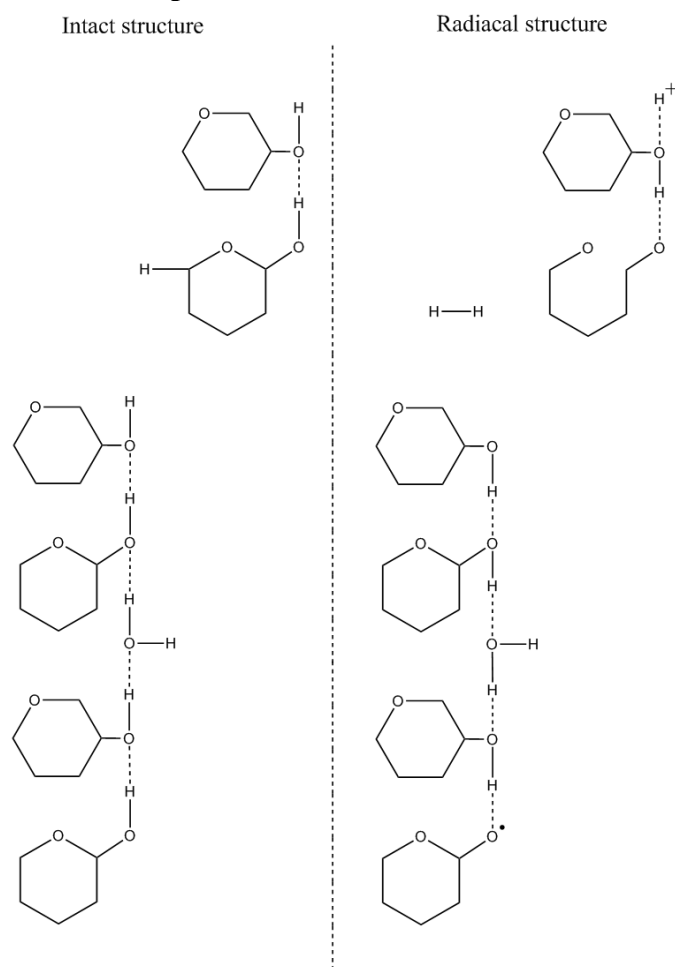


Figure 1: Oxidative alkoxy deprotonation product formation including hydrogen molecule formation. An alkoxy radical is stabilized on O1 by deprotonation along O1-O2-Ow-... hydrogen bond chain. Proton from deprotonation reaction chain has attracted a hydrogen anion from the C5 position of another rhamnose which has maintained neutrality by deprotonation from O1.

B. Hyperfine couplings of radical structures produced by MD simulations

Table 1: Calculated hfcs for the dehydroxylation products. Isotropic (A_{iso}) and anisotropic (A_{ani}) hyperfine couplings are in MHz. Principal directions are given with respect to the orthogonal crystallographic axes a^*bc .

Structure	Atom	A_{iso}	A_{ani}	Direction cosines		
				a^*	b	c
(a)	H1	-52.3	-33.5	0.657	-0.353	-0.667
			-3.2	0.592	0.789	0.167
			36.7	-0.467	0.504	-0.727
	H2	6.6	-6.6	0.587	-0.578	0.567
			-3.4	0.638	0.761	0.115
			10.0	-0.499	0.294	0.816
	H5	10.0	-3.9	-0.324	-0.391	0.862
			-2.8	0.026	0.907	0.421
			6.7	0.946	-0.158	0.284
	HO2	15.8	-5.2	-0.786	0.417	-0.456
			-2.3	0.322	0.907	0.273
			7.5	-0.528	-0.068	0.847
(b)	H1	24.0	-5.8	-0.735	0.613	0.291
			-3.6	-0.655	-0.752	-0.071
			9.4	-0.176	0.242	-0.954
	H2	-49.0	-34.2	0.208	-0.375	0.903
			-3.7	-0.654	-0.740	-0.156
			37.9	0.727	-0.559	-0.400
	H3	122.8	-5.3	-0.401	0.555	0.730
			-2.4	0.475	0.806	-0.353
			7.7	-0.784	0.205	-0.590
	HO1	7.5	-5.0	0.164	-0.802	-0.574
			-1.9	0.981	0.193	0.011
			6.9	0.102	-0.565	0.819
(c)	H1	12.7	-1.9	0.690	0.706	0.156
			-1.0	-0.463	0.266	0.846
			2.9	-0.556	0.656	-0.510
	H2	10.8	-3.6	0.740	0.590	-0.323
			-1.5	0.417	-0.026	0.908
			5.0	-0.527	0.807	0.265
	H3	43.4	-5.1	0.749	0.305	-0.589
			-4.0	0.662	-0.300	0.687
			9.1	-0.033	0.904	0.426
	H4	-40.2	-32.9	-0.541	0.275	0.795
			-3.3	0.705	-0.367	0.607
			36.2	-0.458	-0.889	-0.004
	H5	21.3	-6.2	-0.226	0.775	0.589
			-3.1	-0.767	0.231	-0.599
			9.3	-0.600	-0.588	0.543
	HO4	-3.0	-8.6	-0.888	-0.093	0.451
			0.5	-0.422	-0.227	-0.878
			8.2	-0.184	0.969	-0.162
	Hw	-3.0	-9.1	0.164	-0.836	-0.523
			1.0	-0.208	-0.548	0.810
			8.1	-0.964	-0.024	-0.264

Table 2: Calculated hfcs for the ring-opened reduction products. Isotropic (A_{iso}) and anisotropic (A_{ani}) hyperfine couplings are in MHz. Principal directions are given with respect to the orthogonal crystallographic axes a^*bc .

Structure	Atom	A_{iso}	A_{ani}	Direction cosines		
				a^*	b	c
(d)	H4	8.4	-5.8	-0.233	-0.901	0.365
			-3.0	0.590	0.168	0.790
			8.9	-0.773	0.400	0.492
	H5	-48.2	-34.3	-0.439	-0.405	0.802
			-3.3	0.713	0.387	0.585
			37.6	-0.547	0.829	0.119
	H6	103.7	-4.8	0.981	-0.188	-0.041
			-3.2	0.190	0.906	0.379
			8.1	0.034	0.379	-0.925
	H6	91.8	-4.9	-0.028	0.668	0.744
			-3.6	0.831	-0.398	0.388
			8.4	0.555	0.629	-0.544
	H6	2.0	-4.3	0.796	-0.073	-0.600
			-3.6	0.571	0.419	0.706
			7.8	-0.200	0.905	-0.376
HO4	-5.3	-9.1	-0.995	-0.042	-0.089	
		-1.5	-0.067	-0.365	0.929	
		10.6	-0.071	0.930	0.360	
HOring	9.4	-3.5	-0.730	0.574	0.372	
		-1.5	-0.427	-0.807	0.408	
		5.0	-0.534	-0.139	-0.834	
(e)	H1	-19.9	-33.1	-0.506	-0.719	0.477
			-4.1	-0.850	0.511	-0.132
			37.2	0.149	0.472	0.869
	H2	72.7	-5.7	-0.583	-0.801	-0.137
			-4.7	0.788	-0.598	0.147
			10.4	-0.199	-0.022	0.980
	HO1	-5.7	-10.6	-0.260	-0.704	0.661
			-6.8	-0.867	0.472	0.162
			17.5	-0.426	-0.531	-0.733
	H6	-0.7	-7.0	0.0293	0.420	0.907
			-6.03	-0.217	-0.883	0.416
			13.0	0.976	-0.209	0.065

Table 3: Calculated hfcs for the dehydrogenated reduction products. Isotropic (A_{iso}) and anisotropic (A_{ani}) hyperfine couplings are in MHz. Principal directions are given with respect to the orthogonal crystallographic axes a^*bc .

Structure	Atom	A_{iso}	A_{ani}	Direction cosines		
				a^*	b	c
(f)-I	H2	12.3	-5.8	-0.332	0.014	0.943
			-3.3	0.642	0.736	0.215
			9.0	-0.691	0.677	-0.253
	H4	100.2	-5.2	-0.003	-0.374	0.927
			-1.4	-0.981	-0.179	-0.076
			6.7	0.195	-0.910	-0.366
	HO2	-4.2	-7.4	-0.126	0.992	0.018
			0.2	0.428	0.037	0.903
			7.1	0.895	0.122	-0.429
	HO3	13.9	-11.0	-0.522	0.608	0.598
			-8.2	0.700	0.706	-0.107
			19.2	-0.487	0.362	-0.794
	H (H ₂)	13.5	-3.5	0.308	-0.951	0.011
			-2.9	0.591	0.182	-0.786
			6.4	0.746	0.248	0.619
(f)-II	H2	7.2	-5.7	-0.378	0.019	0.926
			-3.3	0.662	0.705	0.256
			9.0	-0.647	0.709	-0.278
	H4	101.5	-4.8	-0.213	-0.426	0.880
			-2.0	0.960	0.076	0.269
			6.8	-0.181	0.902	0.393
	HO2	-4.7	-8.0	-0.139	0.985	0.106
			0.4	0.427	-0.037	0.904
			7.6	0.894	0.171	-0.415
	HO3	3.4	-11.2	-0.444	0.617	0.650
			-8.2	0.762	0.642	-0.088
			19.4	-0.471	0.456	-0.755
	H (H ₂)	3.3	-3.7	-0.279	-0.807	0.522
			-3.0	-0.455	0.589	0.668
			6.7	-0.846	-0.052	-0.531
H (H ₂)	5.3	-3.7	-0.504	0.831	0.236	
		-3.4	-0.414	-0.472	0.778	
		7.1	-0.758	-0.295	-0.582	
(g)	H4	99.0	-5.5	0.629	0.778	0.022
			-1.3	0.563	-0.474	0.677
			6.8	-0.537	0.413	0.735
	H6	31.9	-4.7	-0.004	0.892	0.451
			-4.1	0.862	-0.225	0.453
			8.8	0.506	0.391	-0.769
	H6	14.8	-4.9	0.069	0.028	0.998
			-4.0	0.780	-0.624	-0.036
			8.9	0.622	0.781	-0.065
	H6	108.3	-4.1	0.140	0.480	0.866
			-2.6	0.987	-0.137	-0.083
			6.7	0.079	0.866	-0.493
	H (H ₂)	84.0	-3.1	0.134	0.392	0.910

		-2.7	-0.324	-0.851	0.414
		5.8	0.937	-0.350	0.013
H (H ₂)	-11.2	-13.6	0.163	0.408	0.899
		-11.2	-0.308	-0.844	0.439
		24.8	0.937	-0.348	-0.012

Table 4: Calculated hfcs for the dehydrogenated reduction products with H₂ molecules removed from the crystal structure. Isotropic (A_{iso}) and anisotropic (A_{ani}) hyperfine couplings are in MHz. Principal directions are given with respect to the orthogonal crystallographic axes a^*bc .

Structure	Atom	A_{iso}	A_{ani}	Direction cosines		
				a^*	b	c
(f-I)	H2	9.9	-5.7	-0.311	0.024	0.950
			-3.3	0.642	0.742	0.192
			9.0	-0.700	0.670	-0.246
	H4	97.8	-5.1	-0.036	-0.375	0.926
			-1.6	-0.980	-0.169	-0.107
			6.7	0.196	-0.912	-0.361
	HO2	-4.1	-7.4	-0.134	0.991	0.009
			0.2	0.431	0.050	0.901
			7.1	0.892	0.125	-0.434
	HO3	3.7	-12.1	-0.482	0.591	0.646
			-8.9	0.713	0.694	-0.103
			21.0	-0.509	0.411	-0.756
(f-II)	H2	6.1	-5.7	-0.359	0.036	0.933
			-3.3	0.666	0.710	0.229
			9.0	-0.654	0.703	-0.279
	H4	97.4	-4.8	-0.235	-0.419	0.877
			-2.0	0.959	0.048	0.280
			6.7	-0.159	0.907	0.391
	HO2	-4.6	-7.9	-0.151	0.984	0.092
			0.4	0.416	-0.021	0.909
			7.5	0.897	0.175	-0.406
	HO3	-0.8	-11.9	-0.379	0.624	0.683
			-8.8	0.796	0.596	-0.103
			20.7	-0.472	0.505	-0.723
(g)	H4	95.4	-5.4	0.644	0.764	0.031
			-1.4	0.516	-0.464	0.720
			6.8	-0.564	0.448	0.693
	H6	37.0	-4.7	-0.706	0.686	-0.174
			-4.5	0.467	0.637	0.613
			9.2	-0.532	-0.352	0.770
	H6	14.6	-4.8	-0.130	0.153	0.980
			-4.4	0.752	-0.629	0.198
			9.2	0.646	0.762	-0.033
	H6	122.9	-4.0	0.076	0.485	0.871
			-2.6	0.991	-0.135	-0.011
			6.6	0.113	0.864	-0.490

Table 5: Calculated hfcs for alkoxy radicals not observed in experiments. Isotropic (A_{iso}) and anisotropic (A_{ani}) hyperfine couplings are in MHz. Principal directions are given with respect to the orthogonal crystallographic axes a^*bc .

Structure	Atom	A_{iso}	A_{ani}	Direction cosines		
				a^*	b	c
(h)	H1	128.9	-5.3	0.371	0.724	-0.581
			-3.8	-0.289	0.685	0.669
			9.2	-0.882	0.080	-0.464
	H2	-7.6	-9.3	-0.844	0.161	-0.511
			-2.0	-0.275	0.689	0.671
			11.3	-0.460	-0.707	0.537
	HO2	20.4	-5.7	0.595	0.122	0.794
			-4.5	-0.111	0.991	-0.069
			10.2	0.796	0.047	-0.603
	HO3	11.8	-2.8	0.776	0.534	-0.336
			-1.5	-0.406	0.830	0.381
			4.3	-0.483	0.159	-0.861
(i)	H3 neighbor	10.3	-1.2	-0.602	0.683	0.414
			-0.5	0.472	-0.114	0.874
			1.7	-0.644	-0.721	0.254
	HO3 neighbor	-4.7	-7.4	0.843	-0.035	-0.537
			-0.9	0.140	-0.949	0.282
			8.3	0.520	0.313	0.795
	H2	264.6	-10.5	-0.797	-0.233	-0.557
			-8.7	-0.592	0.483	0.645
			19.1	-0.119	-0.844	0.523
	H3	-5.8	-6.3	-0.400	0.059	0.914
			-1.7	0.470	0.870	0.149
			8.1	-0.786	0.490	-0.376
	H4	6.7	-4.6	-0.092	0.204	0.975
			1.3	0.113	-0.970	0.214
			3.3	0.989	0.130	0.066
	HO2 deprot	-1.2	-6.3	0.388	-0.731	0.561
			-5.6	0.736	0.612	0.289
			11.9	-0.555	0.301	0.776
	HO3	-3.0	-5.6	-0.739	0.532	0.413
			-2.5	-0.529	-0.838	0.133
			8.1	-0.417	0.120	-0.901
	H H-bonded to O2	-1.8	-6.9	-0.639	0.574	0.512
			-5.9	0.714	0.691	0.115
			12.8	-0.288	0.439	-0.851
(j)	H2	41.1	-4.4	-0.888	0.417	0.193
			0.6	0.163	-0.106	0.981
			3.8	0.430	0.903	0.026
	H3	36.9	-4.8	-0.122	-0.241	0.963
			-3.7	-0.575	-0.773	-0.267
			8.5	0.809	-0.586	-0.044
	H4	4.1	-8.6	0.375	0.671	0.640
			-0.2	0.678	0.273	-0.683
			8.8	-0.633	0.690	-0.352
	H6	8.9	-1.3	-0.794	0.455	-0.403

		-0.5	0.492	0.871	0.013
		1.8	-0.357	0.188	0.915
HO3	-0.8	-7.8	-0.785	0.530	0.320
deprot		-5.7	-0.485	-0.848	0.214
		13.6	-0.385	-0.012	-0.923
H2	12.7	-7.3	0.780	0.084	0.621
neighbor		-6.3	-0.528	-0.444	0.724
		13.6	-0.336	0.892	0.301

Table 6: Calculated hfcs for alkoxy radical matching experimentally observed data. Isotropic (A_{iso}) and anisotropic (A_{ani}) hyperfine couplings are in MHz. Principal directions are given with respect to the orthogonal crystallographic axes a^*bc .

Structure	Atom	A_{iso}	A_{ani}	Direction cosines		
				a^*	b	c
(k) I	H2	81.4	-4.2	0.816	0.441	-0.374
			-1.8	0.512	-0.251	0.821
			6.1	-0.268	0.862	0.431
	H3	5.4	-8.9	-0.150	-0.230	0.962
			-1.0	-0.827	0.562	0.005
			9.9	-0.542	-0.794	-0.275
	H4	37.6	-6.0	0.252	-0.707	0.660
			-3.2	0.429	-0.530	-0.731
			9.2	0.867	0.468	0.170
	HO3	-6.0	-8.7	0.586	0.744	-0.322
			-1.4	0.690	-0.666	-0.283
			10.1	-0.425	-0.057	-0.904
	HO4	-1.8	-7.0	0.518	-0.004	0.856
			-6.3	0.836	-0.211	-0.507
			13.3	0.182	0.978	-0.106
Hw	-0.7	-6.1	0.242	-0.598	0.764	
		-4.9	0.321	-0.694	-0.645	
		11.0	0.916	0.401	0.024	
(k) II	H2	81.0	-4.2	-0.852	0.381	0.358
			-1.7	0.468	0.250	0.848
			5.9	-0.234	-0.890	0.391
	H3	7.1	-8.3	-0.157	0.178	0.972
			-1.1	0.788	0.615	0.015
			9.4	-0.595	0.768	-0.236
	H4	22.3	-6.2	0.269	0.666	0.696
			-2.9	-0.434	-0.561	0.705
			9.1	0.860	-0.491	0.138
	HO3	-6.7	-9.4	-0.631	0.684	0.367
			-1.9	-0.638	-0.726	0.257
			11.2	-0.442	0.071	-0.894
	HO4	-2.3	-7.5	0.638	0.006	0.770
			-6.9	0.765	0.115	-0.634
			14.4	-0.093	0.993	0.069
(k) III	H2	82.2	-4.3	0.822	0.404	-0.402
			-1.7	0.523	-0.255	0.813
			5.9	-0.226	0.878	0.421
	H3	4.5	-9.0	-0.161	-0.182	0.970
			-0.9	-0.813	0.581	-0.026
			10.0	-0.559	-0.793	-0.241
	H4	38.4	-6.0	0.232	-0.681	0.694
			-3.3	0.409	-0.579	-0.705
			9.3	0.882	0.448	0.145
	HO3	-6.1	-8.6	0.603	0.718	-0.348
			-1.3	0.677	-0.691	-0.253
			9.9	-0.422	-0.083	-0.903
	HO4 deprot	-2.9	-7.5	0.293	-0.037	0.955
			-7.1	0.949	-0.108	-0.295

			14.6	0.114	0.993	0.003
(k)	H2	83.0	-4.2	-0.818	0.423	0.389
			-1.5	0.516	0.242	0.822
IV	H3	5.0	5.7	-0.253	-0.873	0.416
			-9.1	-0.154	0.177	0.972
			-0.9	0.815	0.579	0.023
H4	36.8	10.0	-0.558	0.796	-0.234	
		-6.1	0.249	0.656	0.713	
		-3.1	-0.421	-0.590	0.690	
HO3	-6.4	9.2	0.872	-0.472	0.129	
		-9.0	0.608	-0.712	-0.351	
		-1.5	-0.671	-0.698	0.251	
HO4	-2.5	10.5	-0.424	0.083	-0.902	
		-7.4	0.506	-0.026	0.862	
		-6.7	-0.844	-0.218	0.490	
deprot	-0.7	14.0	0.175	-0.976	-0.132	
		-6.2	0.215	0.538	0.815	
		-4.9	-0.324	-0.748	0.579	
Hw	-0.7	11.1	0.921	-0.389	0.013	

Table 7: Calculated hfcs for ring-opened oxidation product. Isotropic (A_{iso}) and anisotropic (A_{ani}) hyperfine couplings are in MHz. Principal directions are given with respect to the orthogonal crystallographic axes a^*bc .

Structure	Atom	A_{iso}	A_{ani}	Direction cosines		
				a^*	b	c
(l)	H4	-4.7	-8.5	-0.653	-0.754	0.074
			-2.0	0.174	-0.054	0.983
			10.5	0.737	-0.655	-0.166
H5	94.7	-5.3	0.703	0.706	-0.084	
		-4.4	-0.278	0.381	0.882	
		9.7	-0.654	0.597	-0.464	
H6	10.2	-3.3	-0.655	0.727	-0.209	
		-0.8	0.258	0.474	0.842	
		4.1	-0.711	-0.497	0.498	
H6	8.1	-3.1	0.940	-0.276	-0.200	
		-2.0	0.266	0.225	0.938	
		5.2	0.214	0.935	-0.284	
HO4	-4.3	-8.6	0.534	0.839	-0.105	
		-3.7	-0.235	0.266	0.935	
		12.2	-0.812	0.474	-0.339	
HO3 neighbor H-bonded to ring oxygen	-4.0	-9.1	-0.739	0.617	0.270	
		-7.8	-0.543	-0.783	0.304	
		16.9	-0.399	-0.078	-0.914	

C. On the Schonland ambiguity for the C3-centered radical

The hfc of radical (f) show a good match with the radical described as Radical 3 and 4 in the experimental work of Sagstuen *et al.*¹ except for the sign of the *c*-components of the principal directions of the hfc tensor. A change in sign of the *c*-component is not an allowed site transformation in this crystal as there are only two asymmetric units per unit cell and the *b*-axis is the only twofold symmetry axis (space group P2₁). It is well known that the experimental analysis of hyperfine coupling- and g-tensors result in two possible solutions, the physical solution and an unphysical solution. This is called the Schonland ambiguity^{2, 3}. Specific experiments must be performed in order to resolve this ambiguity. This was not done in the experimental work by Sagstuen *et al.*¹, one of the two solutions was chosen almost arbitrarily, as they were very similar.

The calculation of the second solution (the Schonland conjugate) variant has been made using the procedures of Vrielinck *et al.* under the assumption that it was the high-frequency ENDOR line which was used to determine the tensor by the experimentalists and using B-field values from two extreme points of the EPR spectrum from the radical (339-343 mT). In addition the Schonland conjugate was calculated by only changing signs in the off-diagonal elements of the squared hfc matrix. These two different versions of the Schonland conjugate were nearly indistinguishable, as expected for a β -coupling³.

The two versions of the experimental tensor are given in Table 8 and it can be seen that distinguishing between these tensors is difficult considering only the overall shape of the coupling. Table 9 displays the C3 \cdots H4 directions in the intact crystal structure as determined by neutron diffraction⁴ as well as the corresponding directions in the two versions of this radical seen in the DFT analyses. It is clear that the originally published experimental tensor has as its largest principal value direction along the line connecting the two atoms in the crystal structure. It is therefore natural to assume that this was the main reason for choosing between the two Schonland conjugates in the experimental work. The present analysis on the other hand, shows that the direction between the same atoms in the optimized radical structure is similar to the original except for that the sign of the *c*-component is changed. The direction of interaction between these two atoms in the radical therefore actually fits better with the other Schonland conjugate. Comparing the DFT calculated hfc tensors with the Schonland conjugate of the experimentally published tensor demonstrates an excellent agreement. This is the reason for why the Schonland conjugate of the published experimental tensor is assumed to be the correct physical solution and consequently used for comparison with the DFT data obtained in the present study.

Table 8: Experimental hfc (MHz) tensor¹ for C3-centered net hydrogen abstracted radical before and after Schonland conjugation.

	A_{iso}	A_{ani}	Direction cosines		
			a^*	b	c
Original	96.07	6.63	-0.177	0.923	-0.342
		-1.4	0.945	0.062	-0.322
		-5.24	0.276	0.380	0.883
Schonland conjugate	96.10	6.73	0.207	-0.913	-0.351
		-1.77	0.976	0.166	0.144
		-4.96	-0.073	-0.373	0.925

Table 9: C3 ... H4 direction in intact crystal structure vs. radical structure (f).

Structure	Direction cosines		
	<i>a</i> *	<i>b</i>	<i>c</i>
Intact crystal structure	-0.010	0.928	-0.372
Radical f-I	-0.114	0.928	0.355
Radical f-II	-0.063	0.917	0.394

D. References

1. E. Sagstuen, M. Lindgren and A. Lund, *Radiat. Res.*, 1991, **128**, 235-242.
2. D. S. Schonland, *Proceedings of the Physical Society*, 1959, **73**, 788-792.
3. H. Vrielinck, H. De Cooman, M. A. Tarpan, E. Sagstuen, M. Waroquier and F. Callens, *Journal Of Magnetic Resonance*, 2008, **195**, 196-205.
4. S. Takagi and G. A. Jeffrey, *Acta Crystallogr. Sect. B-Struct. Commun.*, 1978, **34**, 2551-2555.