

Electronic Supplementary Information (ESI)

for

Stabilization of D_{5h} and C_{2v} valence tautomers of the croconate Dianion

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Synthesis of **1**: 96 mg (0.461 mmol) of tetrahydroxy-1,4-quinone¹² was neutralized with two molar equivalents of aqueous tetra-*n*-propylammonium hydroxide (Aldrich, 1.0 M solution in water diluted to 0.35 M solution). Next, five molar equivalents of urea were added and the solution was stirred for about 5 minutes and then filtered. The yellow filtrate was subjected to slow evaporation at room temperature in a desiccator charged with anhydrous silica gel. Deposition of yellow rectangular prisms occurred in nearly quantitative yield over a period of several weeks. M.p. 88-91°C (dec.). IR(KBr): 3385, 3184, 2987, 2942, 1677, 1630, 1541, 1431, 1409, 1177, 992, 824, 782, 700, 596, 532 cm⁻¹.

Synthesis of **2**: The above procedure was repeated with 82 mg of tetrahydroxy-1,4-quinone, two molar equivalents of aqueous tetra-*n*-butylammonium hydroxide (40 wt. % solution in water diluted to 0.2175M), and four molar equivalents of 1,3-dimethylurea to give a bright orange-red filtrate. This was stored in a desiccator charged with anhydrous calcium chloride, yielding a nearly quantitative crop of large yellow block-like crystals after about one month. M.p. 150-152°C (dec.), IR(KBr): 3375, 2962, 2875, 1662, 1537, 1412, 1383, 1312, 1272, 1173, 884, 630 cm⁻¹.

Reference

13. *Org. Synth. Collect. vol. 5*, 1011-1013.

Supplementary Figures referred to in the Manuscript

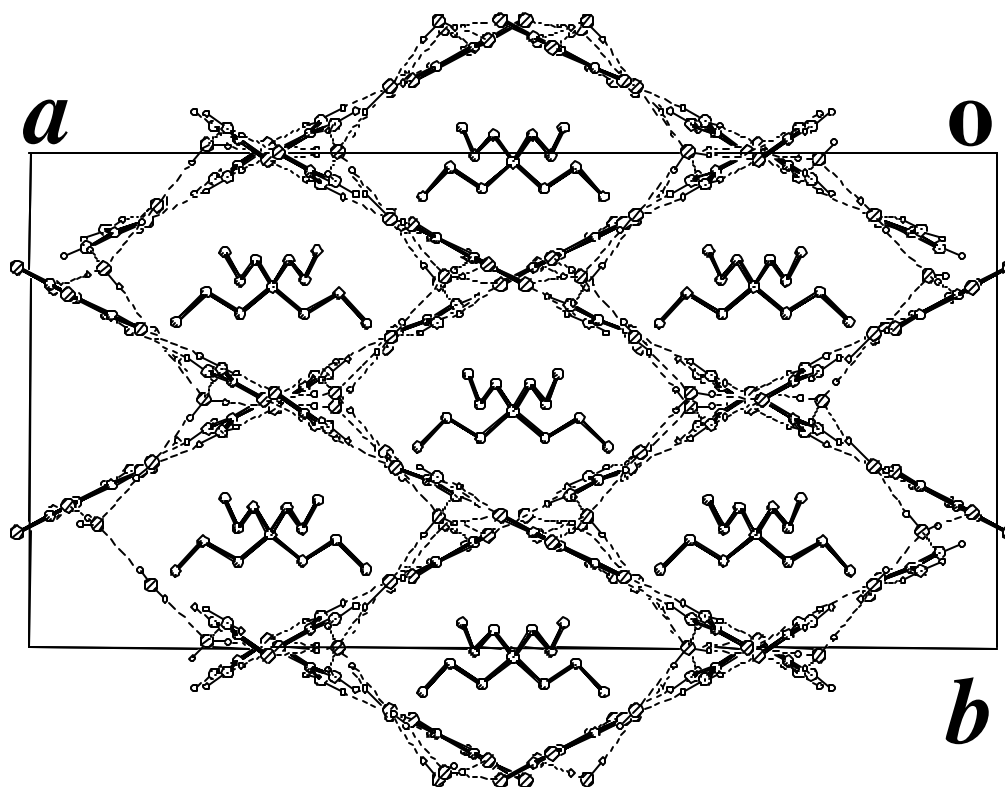


Fig. 4 Rhombic channel system with cross-section $12.8 \text{ \AA} \times 9.6 \text{ \AA}$ running parallel to the *c*-axis. Well-ordered tetra-*n*-propylammonium cations are accommodated in a single column along each channel. Broken lines represent hydrogen bonds and atom types are distinguished by different size and shading.

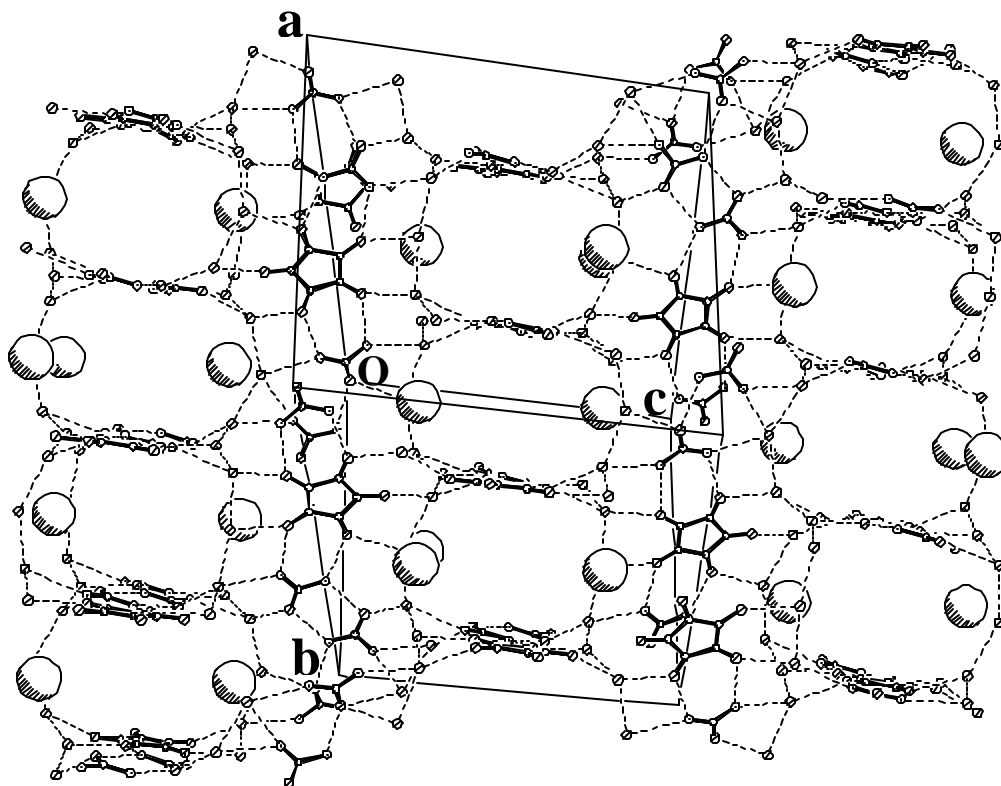


Figure 5. Perspective view of a portion of the crystal structure of $[(n\text{-C}_3\text{H}_7)_4\text{N}^+]_2\text{C}_5\text{O}_5^{2-} \cdot 3(\text{NH}_2)_2\text{CO} \cdot 8\text{H}_2\text{O}$ (**1**) showing a channel system running parallel to the $[110]$ direction. Two columns of well-ordered tetra-*n*-propylammonium cations (represented by large spheres for clarity) can be accommodated within each channel with the same dimensions as $[1\bar{1}0]$ channel system. Broken lines represent hydrogen bonds and atom types are distinguished by different sizes and shadings.

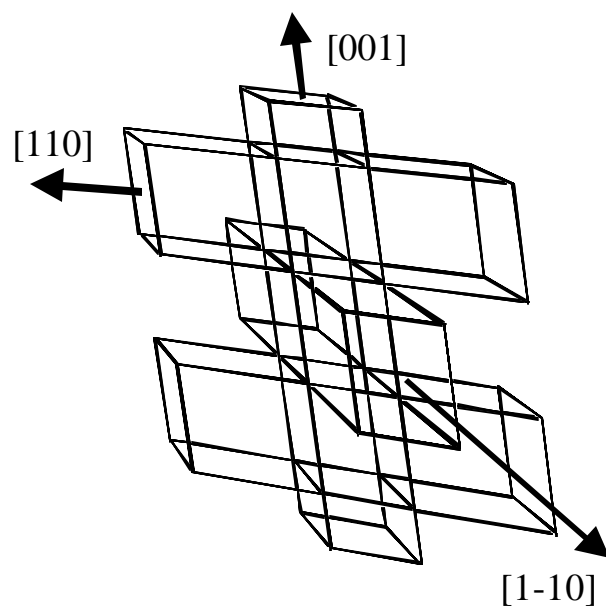


Figure 6. Schematic diagram showing the arrangement and orientation of three intersecting channel systems in $[(n\text{-C}_3\text{H}_7)_4\text{N}^+]_2\text{C}_5\text{O}_5^{2-} \cdot 3(\text{NH}_2)_2\text{CO} \cdot 8\text{H}_2\text{O}$ (**1**).

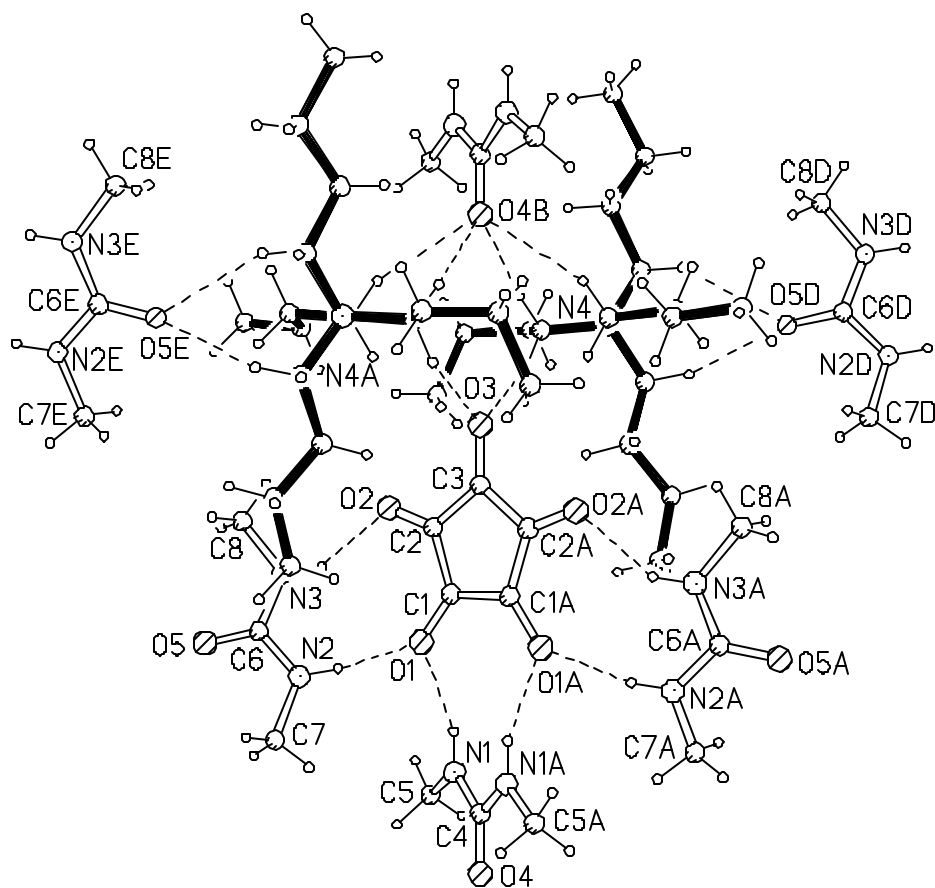


Fig. 7 A portion of the hydrogen-bonded layer showing extensive C—H···O hydrogen-bonding between the $C_5O_5^{2-} \cdot 3(CH_3NH)_2CO$ aggregate and its neighboring tetra-*n*-butylammonium ions. Symmetry transformations: A(1-*x*, *y*, 1/2 -*z*), B(*x*, *y*-1, *z*), C(1-*x*, *y*-1, 1/2 -*z*), D(*x*-1/2, *y*-1/2, *z*) and E(3/2-*x*, *y*-1/2, 1/2-*z*).

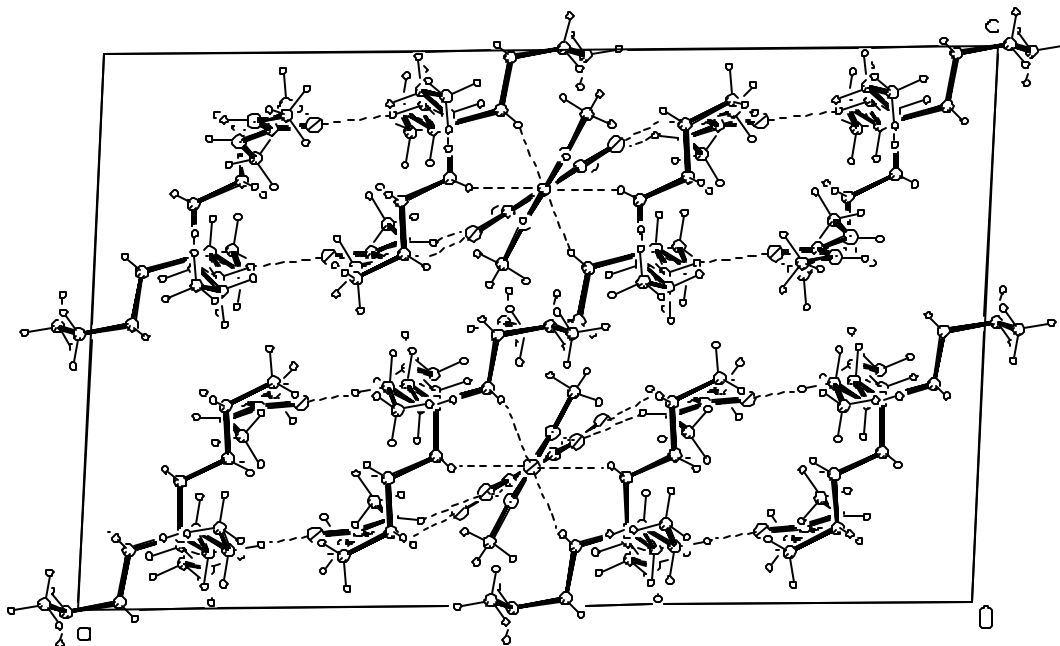


Figure 8. Crystal structure of $[(n\text{-C}_4\text{H}_9)_4\text{N}^+]_2\text{C}_5\text{O}_5^{2-} \cdot 3(\text{CH}_3\text{NH})_2\text{CO}$ (**2**) viewed along the b -axis showing the well-ordered tetra- n -butylammonium cations sandwiched between anionic host layers. The crystal packing is significantly consolidated by an extensive system of weak $\text{C}(sp^3)\text{—H}\cdots\text{O}$ donor hydrogen bonds from the organic cations to the croconate and 1,3-dimethylurea molecules.

Supplementary Tables referred to in the Manuscript

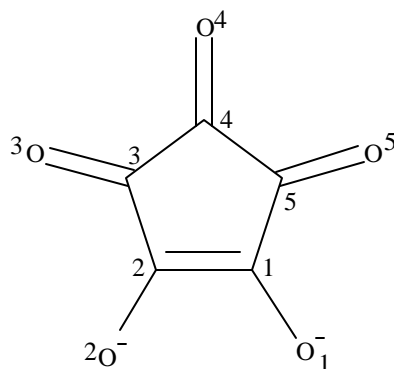


Table 1. Optimized C—C and C—O Bond Lengths* of the Charge-Localized Form of an isolated $C_5O_5^{2-}$ (C_{2v}).

Level of Theory	C3–C4 (Å)	C2–C3 (Å)	C1–C2 (Å)	C4–O4 (Å)	C3–O3 (Å)	C2–O2 (Å)	Imaginary frequency
HF/STO-3G	1.494826	1.494909	1.494800	1.264735	1.264750	1.264682	0
HF/3-21G(d)	1.462797	1.462855	1.462812	1.248500	1.248456	1.248426	0
HF/3-21+G(d)	1.466508	1.466570	1.466516	1.252758	1.252743	1.252684	0
HF/6-31G(d)	1.472719	1.472713	1.472723	1.227288	1.227294	1.227292	0
HF/6-31+G(d)	1.476345	1.476340	1.476362	1.225849	1.225848	1.225848	2
HF/6-311+G(d)	1.475215	1.475212	1.475225	1.220894	1.220894	1.220894	0
B3 LYP /3-21G(d)	1.484892	1.484843	1.484845	1.273472	1.273252	1.273390	0
B3 LYP /3-21+G(d)	1.483551	1.483441	1.483486	1.278979	1.279090	1.279084	0
B3 LYP /6-31G(d)	1.490359	1.490331	1.490227	1.253708	1.253613	1.253712	0
B3 LYP /6-31+G(d)	1.490305	1.490215	1.490157	1.253115	1.253111	1.253178	0
B3 LYP /6-311+G(d)	1.488465	1.488487	1.488403	1.246756	1.246746	1.246744	0
MP2/6-31+G(d)	1.487339	1.487238	1.487244	1.264625	1.264550	1.264653	2
MP2(FULL)/6-31G(d)	1.484741	1.484767	1.484756	1.261331	1.261287	1.261307	0
MP2(FULL)/6-311+G(d)	1.487149	1.487072	1.487055	1.253567	1.253512	1.253602	**
MP2(FULL)/ 6-31+G(2df,p)	1.478737	1.478693	1.478643	1.249415	1.249310	1.249415	**
B3PW91/6-31+G(2df,p)	1.485612	1.485565	1.485360	1.244547	1.244520	1.244606	0

* The calculated bond lengths (in Å) shown here have six significant figures, instead of the usual three, after the decimal point. This is because, if we only report three significant figures after the decimal points, the optimized C_{2v} geometry cannot be distinguished from the D_{5h} geometry.

** Vibrational frequency calculation is used to determine the nature of a stationary point found by a geometry optimization. For structures optimized by very high level calculations such as those marked by **, vibrational frequency analysis has not been conducted due to the limitation of computational power.

Table 2. Optimized* C—C and C—O Bond Lengths of the Charge-Delocalized Form of an isolated $C_5O_5^{2-}$ (D_{5h}).

Level of Theory	C—C (Å)	C—O (Å)	Imaginary frequency
HF/STO-3G	1.494	1.264	0
HF/3-21G(d)	1.462	1.248	0
HF/3-21+G(d)	1.466	1.252	0
HF/6-31G(d)	1.472	1.227	0
HF/6-31+G(d)	1.476	1.225	2
HF/6-311+G(d)	1.475	1.220	0
B3 LYP /3-21G(d)	1.484	1.273	0
B3 LYP /6-31G(d)	1.490	1.253	0
B3 LYP /6-31+G(d)	1.490	1.253	**
B3 LYP /6-311+G(d)	1.488	1.246	**
B3LYP/6-31+G(2df,p)	1.488	1.247	**
MP2(FULL)/3-21G(d)	1.496	1.291	0
MP2(FULL)/6-31G(d)	1.484	1.261	0
MP2(FULL)/6-31+G(d)	1.485	1.263	2
QCISD/6-31+G(d)	1.486	1.257	**
B3PW91/aug-cc-pvtz	1.482	1.243	**
CASSCF(2,4)/3-21G(d)	1.464	1.250	0
CASSCF(2,4)/6-31+G(d)	1.477	1.227	**
CASSCF(6,4)/ 3-21G(d)	1.460	1.252	0
CASSCF(6,6)/ 3-21G(d)	1.458	1.260	1
CASSCF(6,8)/ 3-21G(d)	1.464	1.250	0
CASSCF(10,8)/3-21G(d)	1.458	1.261	0
CASSCF(10,8)/3-21+G(d)	1.461	1.263	0
CASSCF(10,8)/6-31G(d)	1.469	1.235	0
CASSCF(10,8)/6-31+G(d)	1.473	1.233	**
CASSCF(10,8)/6-311+G(d)	1.471	1.229	**
CASSCF(10,8)/aug-cc-pvtz	1.473	1.220	**
CASSCF(12,8)/3-21G(d)	1.456	1.257	0
CASSCF(12,8)/3-21+G(d)	1.459	1.259	0
CASSCF(12,8)/6-31G(d)	1.469	1.232	0
CASSCF(12,8)/6-31+G(d)	1.471	1.231	**
CASSCF(12,8)/6-311+G(d)	1.474	1.224	**
Experiment	1.451-1.465	1.241-1.254	

* The C—C and C—O bond lengths of croconate dianion optimized at certain theoretical levels are very close to the experimental values. These levels are marked in blue. It appears that the HF/3-21G(d), CASSCF(2,4)/3-21G(d) and CASSCF(6,8)/ 3-21G(d) yields the best results for $C_5O_5^{2-}$ as a whole.

** For structures optimized by very high level calculations such as those marked by **, vibrational frequency analysis has not been conducted due to the limitation of computational power.

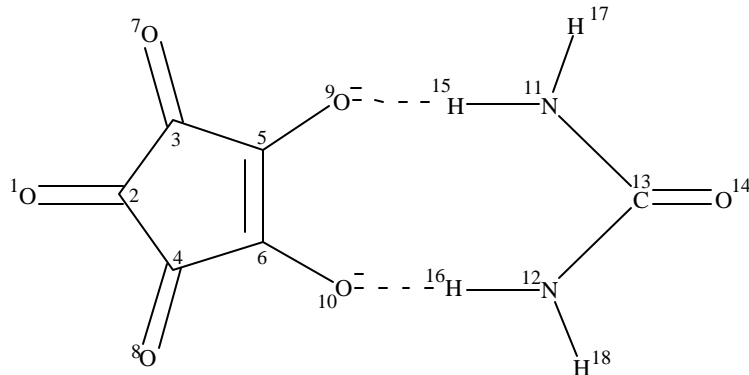


Table 3. Optimized C—C and C—O Bond Lengths of the Charge-Localized Form of a hydrogen-bonded $C_5O_5^{2-}$ (C_{2v}).

Level of Theory	C2–C3 (Å)	C3–C5 (Å)	C5–C6 (Å)	O1–C2 (Å)	C3–O7 (Å)	C5–O9 (Å)	O9–H15 (Å)	N11–H15 (Å)	N11–H17 (Å)	N11–C13 (Å)	C13–O14 (Å)	Imag Frec
HF/STO-3G	1.530	1.530	1.417	1.233	1.240	1.316	1.287	1.141	1.022	1.394	1.254	4
HF/3-21G(d)	1.477	1.457	1.433	1.232	1.238	1.267	1.721	1.026	0.994	1.351	1.246	0
HF/3-21+G(d)	1.482	1.458	1.440	1.237	1.244	1.268	1.767	1.021	0.995	1.350	1.269	0
HF/6-31G(d)	1.484	1.466	1.451	1.215	1.219	1.241	1.853	1.013	0.991	1.348	1.226	2
HF/6-31+G(d)	1.487	1.469	1.454	1.214	1.219	1.239	1.877	1.012	0.992	1.347	1.230	4
HF/6-311+G(d)	1.486	1.468	1.454	1.209	1.214	1.234	1.888	1.007	0.989	1.347	1.224	3
B3 LYP /3-21G(d)	1.492	1.478	1.459	1.262	1.264	1.286	1.671	1.053	1.012	1.372	1.265	0
B3 LYP /3-21+G(d)	1.493	1.475	1.463	1.268	1.271	1.289	1.705	1.047	1.012	1.369	1.290	0
B3 LYP /6-31G(d)	1.496	1.484	1.470	1.244	1.246	1.264	1.768	1.039	1.006	1.366	1.248	2
B3 LYP /6-31+G(d)	1.498	1.483	1.471	1.244	1.247	1.262	1.788	1.037	1.007	1.363	1.255	2
B3 LYP /6-311+G(d)	1.496	1.481	1.469	1.238	1.240	1.256	1.797	1.032	1.004	1.362	1.248	2
MP2(FULL)/3-21G(d)	1.496	1.490	1.482	1.287	1.285	1.296	1.723	1.042	1.010	1.379	1.272	1
MP2(FULL)/6-31G(d)	1.487	1.479	1.472	1.256	1.256	1.268	1.790	1.035	1.006	1.362	1.251	2
MP2(FULL)/6-311+G(d)	1.492	1.481	1.474	1.247	1.249	1.260	1.811	1.027	1.003	1.361	1.248	*

* For structures optimized by very high level calculations such as those marked by *, vibrational frequency analysis has not been conducted due to the limitation of computational power.

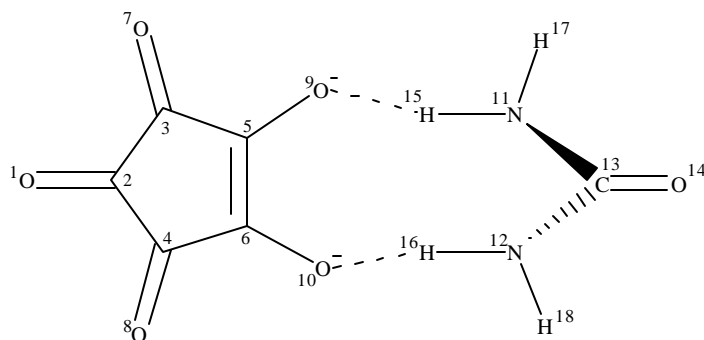


Table 4. Optimized C—C and C—O Bond lengths of the charge-localized form of $C_5O_5^{2-}$ (C_2).

Level of Theory	C2—C3 (Å)	C3—C5 (Å)	C5—C6 (Å)	O1—C2 (Å)	C3—O7 (Å)	C5—O9 (Å)	O9—H15 (Å)	N11—H15 (Å)	N11—H17 (Å)	N11—C13 (Å)	C13—O14 (Å)	Ir F
HF/STO-3G	1.532	1.495	1.417	1.233	1.241	1.317	1.293	1.149	1.031	1.418	1.246	
HF/3-21G(d)	1.477	1.457	1.433	1.232	1.238	1.267	1.720	1.026	0.994	1.351	1.246	
HF/6-31G(d)	1.484	1.466	1.450	1.215	1.219	1.241	1.859	1.014	0.993	1.353	1.223	
B3 LYP /3-21G(d)	1.492	1.478	1.459	1.262	1.264	1.286	1.670	1.053	1.012	1.372	1.265	
B3 LYP /6-31G(d)	1.497	1.484	1.470	1.244	1.246	1.264	1.774	1.041	1.010	1.373	1.245	
B3 LYP /6-311+G(d)	1.496	1.481	1.469	1.238	1.240	1.257	1.800	1.033	1.005	1.365	1.247	
MP2(FULL)/3-21G(d)	1.496	1.490	1.482	1.287	1.286	1.295	1.722	1.042	1.010	1.379	1.272	
MP2(FULL)/6-311+G(d)	1.492	1.480	1.473	1.247	1.249	1.260	1.811	1.030	1.006	1.368	1.245	

* For structures optimized by very high level calculations such as those marked by *, vibrational frequency analysis has not been conducted due to the limitation of computational power.

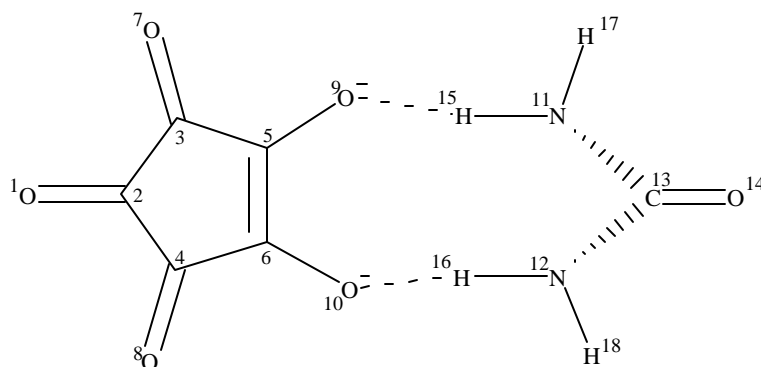


Table 5. Optimized C—C and C—O Bond lengths of the charge-localized form of $C_5O_5^{2-}$ (C_s).

Level of Theory	C2—C3 (Å)	C3—C5 (Å)	C5—C6 (Å)	O1—C2 (Å)	C3—O7 (Å)	C5—O9 (Å)	O9—H15 (Å)	N11—H15 (Å)	N11—H17 (Å)	N11—C13 (Å)	C13—O14 (Å)	Ir F
HF/STO-3G	1.535	1.496	1.412	1.232	1.240	1.320	1.297	1.152	1.034	1.424	1.246	
HF/3-21G(d)	1.477	1.457	1.433	1.232	1.238	1.267	1.720	1.026	0.994	1.351	1.246	
HF/6-31G(d)	1.484	1.466	1.450	1.215	1.219	1.241	1.862	1.014	0.994	1.356	1.222	
B3 LYP /3-21G(d)	1.492	1.478	1.459	1.262	1.264	1.286	1.669	1.053	1.011	1.372	1.265	
B3 LYP /6-31G(d)	1.497	1.484	1.470	1.244	1.246	1.264	1.776	1.042	1.011	1.376	1.245	
B3 LYP /6-311+G(d)	1.496	1.481	1.469	1.237	1.240	1.257	1.803	1.033	1.007	1.369	1.245	
MP2(FULL)/3-21G(d)	1.496	1.490	1.482	1.287	1.286	1.295	1.722	1.042	1.010	1.379	1.272	
MP2(FULL)/6-311+G(d)	1.492	1.480	1.473	1.247	1.248	1.260	1.815	1.030	1.007	1.371	1.244	

* For structures optimized by very high level calculations such as those marked by *, vibrational frequency analysis has not been conducted due to the limitation of computational power.