

Structure and Hydrogen Bonding in the Enol Form of 5,6-Diacetyl-2,9-dimethyl-4,7-decanedione in the Solid State

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Low temperature (-165°C) diffractometer data for 5,6-diacetyl-2,9-dimethyl-4,7-decanedione, $\text{C}_{18}\text{H}_{36}\text{O}_4$, were collected to $2\theta = 70^{\circ}$ using graphite-monochromated $\text{MoK}\alpha$ radiation. There are 2 molecules in a $P\bar{1}$ cell with dimensions $a = 8.938(1)$, $b = 9.406(1)$, $c = 11.030(2)$ Å, $\alpha = 67.09(1)$, $\beta = 70.26(1)$, $\lambda = 74.57(1)^{\circ}$. Full matrix least-squares refinements have yielded a conventional R value of 0.040. The compound crystallizes in the dienol form with two short, asymmetric, intramolecular hydrogen bonds of lengths 2.457(1) and 2.438(1) Å. A slight double- and single-bond localization exists in the enol rings.

Interest in the structural chemistry of enolized β -diketones stems from the fact that these compounds possess a short intramolecular hydrogen bond. Structure determinations of these compounds differ on the issue of the symmetry of the hydrogen bond. From gas phase electron diffraction studies it has been deduced that the enol ring of acetylacetone,^{1,2} and its trifluoro¹ and hexafluoro derivatives³ possess C_{2v} symmetry, implying symmetrical hydrogen bonds. X-Ray and neutron diffraction investigations seem to indicate that this is the exception rather than the rule in the solid state. Evidence of C_{2v} symmetry has hereto only been obtained in the crystal structure of bis(*m*-bromobenzoyl)methane⁴ whereas small, though significant, departures from such symmetry have been found in the crystal structures of dibenzoylmethane,^{5,6} benzoylacetone,⁷ and tetraacetylene.⁸ In all enolized β -diketones so far studied in the solid state, there are intramolecular non-bonded repulsions

which may account for the relative broad range in hydrogen bond lengths observed (2.45–2.50 Å). A crystal structure determination of 5,6-diacetyl-2,9-dimethyl-4,7-decanedione was carried out to study the influence from such interactions on the enol ring geometry. A low temperature study was chosen in order to increase the amount of data and to minimize the thermal motions.

EXPERIMENTAL

Synthesis. The synthesis of the title compound was carried out by a procedure slightly modified from that used for tetraacetylene.⁹ Commercially obtained 6-methyl-2,4-heptanedione (*1*) was first converted into its sodium salt by addition of a stoichiometric amount of sodium hydride in ether. To the resulting suspension a slight excess of finely granulated *I*, was slowly added. When the reaction had ceased, ether was added to dissolve the crude reaction product, and sodium iodide was filtered off. By slow evaporation large transparent colourless crystals of 5,6-diacetyl-2,9-dimethyl-4,7-decanedione (*2*) were formed, m.p. 96°C . The yield was 60–70%. (Synthesis of several other β -diketone dimers have also successfully been carried out by this procedure. The yield of tetraacetylene was found to be higher by this modified procedure than by that previously reported.⁹) IR and NMR spectroscopy on *2* as well as *1* confirmed the reaction product to be 5,6-diacetyl-2,9-dimethyl-4,7-decanedione. The NMR spectra of *1* and *2* were virtually identical, except for the CH_2 (keto form) and vinyl-CH resonances in the spectrum of *1*, which were absent in the spectrum of *2*, and that the broad enol-OH signal at δ 15.4 in the spectrum of *1* reappeared as a sharp signal at δ 17.0 in the spectrum of *2*.

X-Ray crystallography. The compound was recrystallized from ether and well developed

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crystals were obtained. Preliminary film investigations revealed triclinic symmetry. A nearly spherical crystal with approximate diameter 0.35 mm was arbitrarily mounted on the SYNTEX PI diffractometer equipped with an Enraf-Nonius gas-flow cooling device, modified by H. Hope. The temperature in the stationary N_2 stream was $-165^\circ C$ at the crystal site. Cell dimensions at $-165^\circ C$ were determined by a least-squares adjustment of the setting angles of 30 high-angle reflections. Intensity data were collected with graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) and the $\omega-2\theta$ scanning mode. The scan speed varied from 2 to $4^\circ/\text{min}$ (in 2θ), dependent on intensity calculated from a fast prescan. A symmetrical scan range of 2° corrected for spectral dispersion was applied and the ratio of the total background time to the time of integration was 0.7. Data were collected in one hemisphere of the reciprocal lattice in two steps. In the second step ($40^\circ \leq 2\theta \leq 70^\circ$) a rejection level was applied so as to avoid measurements of reflections with intensities less than $\sim 5\sigma(I)$. The intensities of three standard reflections were measured at regular intervals showing no significant decline in intensity. A total of 4840 reflections were measured of which 4663 had intensities greater than $2\sigma(I)$, estimated from counting statistics, and were considered to be observed. The remaining 177 were rejected from the structure refinement. Corrections for Lorentz and polarization effects were applied to the intensities and their

e.s.d. and a 2% uncertainty due to instrument instability was included in the latter.

Structure solution and refinements. Statistical tests strongly indicated the space group $P\bar{1}$. The structure was solved by direct methods^{10*} and refined by full-matrix least-squares techniques. The function minimized was $M = \sum w(F_o - F_c)^2$, $w = \sigma(F_o)^{-2}$. The coordinates of the hydrogen atoms were calculated and included in the refinement with isotropic thermal parameters. Refinements terminated with $R_w = 0.051$, $R = 0.041$, and $S = 2.55$.** A refinement involving only the heavy atom parameters and the 2700 structure factors for which $\sin \theta/\lambda > 0.55 \text{ \AA}^{-1}$, was finally carried out. The values arrived at were $R_w = 0.039$, $R = 0.038$, and $S = 1.38$. However, only small parameter shifts ($< 2.0\sigma$) were obtained by exclusion of low angle data. The following calculations, as well as the discussion, are based upon parameters from the latter refinement except for results involving hydrogen atoms. These are derived from the refinement of the full data set. Atomic scattering factors were those of Doyle and Turner¹² for carbon and oxygen atoms; for the hydrogen atoms those of Stewart, Davidson, and Simpson.¹³ Positional and thermal parameters are given in Table 1, and atom numbering

* Unless otherwise stated programs used are described in Ref. 11.

** Standard deviations of unit weight $S = [\sum W(F_o^2 - F_c^2)^2 / (m - n)]^{1/2}$

Table 1. Fractional coordinates and thermal parameters with estimated standard deviations. Expression for anisotropic vibration is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$. Hlmn is bonded to Clm.

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
O1A	1.06776(10)	.67196(11)	-.03827(8)	.0147(2)	.0235(3)	.0169(2)	-.0042(2)	.0016(2)	-.0007(2)
O2A	1.18392(9)	.66725(13)	.17453(9)	.0185(2)	.0346(4)	.0212(3)	-.0052(2)	-.0005(2)	-.0140(3)
O1B	.44269(11)	.09567(11)	.28476(11)	.0163(3)	.0190(3)	.0268(3)	-.0023(2)	-.0005(2)	-.0075(2)
O2B	.41818(9)	.08439(10)	.32672(9)	.0180(2)	.0210(3)	.0222(3)	-.0028(2)	-.0015(2)	-.0064(2)
C1A	.01143(13)	.71141(13)	-.07677(10)	.0219(3)	.0208(3)	.0139(3)	-.0024(3)	-.0056(2)	-.0055(2)
C2A	.01489(11)	.70161(10)	.00928(9)	.0185(3)	.0143(3)	.0121(3)	-.0016(2)	-.0038(2)	-.0055(2)
C3A	.04546(10)	.72237(10)	.13892(8)	.0122(2)	.0149(3)	.0117(2)	-.0036(2)	-.0014(2)	-.0042(2)
C4A	.04939(10)	.70112(11)	.21835(9)	.0113(3)	.0199(3)	.0141(3)	-.0048(2)	-.0018(2)	-.0065(2)
C5A	.08591(12)	.71015(15)	.36088(10)	.0138(3)	.0321(4)	.0154(3)	-.0008(3)	-.0009(2)	-.0105(3)
C6A	.108422(11)	.74959(13)	.41134(10)	.0146(3)	.0225(3)	.0159(3)	-.0049(2)	-.0043(2)	-.0071(2)
C7A	.03533(10)	.73802(10)	.06313(12)	.0253(4)	.0352(5)	.0161(3)	-.0068(3)	-.0053(3)	-.0102(3)
C8A	.104083(17)	.91514(16)	.33009(14)	.0267(4)	.0246(4)	.0259(4)	-.0110(3)	-.0002(3)	-.0095(3)
C1B	.08808(10)	.105237(12)	.08674(12)	.0256(4)	.0142(3)	.0225(3)	-.0050(3)	-.0036(3)	-.0039(3)
C2B	.09426(12)	.02156(11)	.19785(10)	.0174(3)	.0147(3)	.0161(3)	-.0013(2)	-.0046(2)	-.0052(2)
C3B	.06995(10)	.76282(10)	.19068(9)	.0115(2)	.0134(2)	.0131(2)	-.0019(2)	-.0026(2)	-.0040(2)
C4B	.07139(10)	.64728(11)	.27696(9)	.0112(2)	.0156(3)	.0143(3)	-.0029(2)	-.0027(2)	-.0044(2)
C5B	.03598(11)	.47598(11)	.31777(10)	.0145(3)	.0145(3)	.0177(3)	-.0043(2)	-.0049(2)	-.0024(2)
C6B	.02033(12)	.37378(12)	.32892(11)	.0176(3)	.0191(3)	.0168(3)	-.0004(2)	-.0012(2)	-.0059(2)
C7B	.09164(12)	.02199(15)	.38084(15)	.0421(6)	.0166(3)	.0200(4)	-.0106(4)	-.0109(4)	-.0023(3)
C8B	.46558(16)	.41458(16)	.19164(14)	.0244(4)	.0277(4)	.0265(4)	-.0040(3)	-.0104(3)	-.0121(3)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H1A1	.0764(19)	.0794(18)	-.1523(17)	4.4(2)	H1A2	.7556(19)	.0145(19)	-.1003(16)	4.4(4)
H1A3	.7293(19)	.6460(18)	-.0241(16)	4.4(4)	H5A1	.0562(17)	.0643(17)	.4210(14)	3.3(2)
H5A2	.7855(18)	.7805(16)	.3667(14)	3.3(4)	H6A	1.1013(19)	.6777(14)	.4017(12)	2.5(2)
H7A1	1.0115(19)	.7599(18)	.0976(16)	3.3(2)	H7A2	.9118(19)	.6247(20)	.6172(17)	3.5(4)
H7A3	.8378(20)	.0079(19)	.0782(16)	3.3(4)	H8A1	1.1171(20)	.9398(18)	.3539(16)	3.3(2)
H8A2	.9441(20)	.9928(19)	.3408(17)	3.3(4)	H8A3	1.0633(19)	.9205(18)	.2318(17)	3.3(4)
H1B1	.6208(20)	1.1465(19)	.0499(16)	6.3(2)	H1B2	.7356(19)	1.0418(19)	-.0187(17)	6.3(4)
H1B3	.762(20)	1.0567(18)	.0992(17)	6.3(4)	H5B1	.0548(17)	.4451(16)	-.4135(15)	2.9(2)
H5B2	.7421(17)	.4586(16)	.2522(14)	2.9(4)	H6B	.4181(15)	.3940(14)	.3955(13)	2.3(2)
H7B1	.5251(19)	.1332(19)	.3879(16)	4.2(2)	H7B2	.6125(19)	.1773(18)	.4676(17)	4.2(4)
H7B3	.0972(21)	.1863(18)	.3142(17)	4.2(4)	H8B1	.4160(20)	.3427(19)	.1998(16)	3.3(2)
H8B2	.5898(20)	.0993(18)	.1191(17)	3.3(4)	H8B3	.4307(19)	.5263(19)	.1595(16)	3.3(4)
H9A	1.1138(22)	.6610(21)	.0659(19)	6.4(4)	H9B	.3976(22)	.0073(23)	.2070(18)	6.5(4)

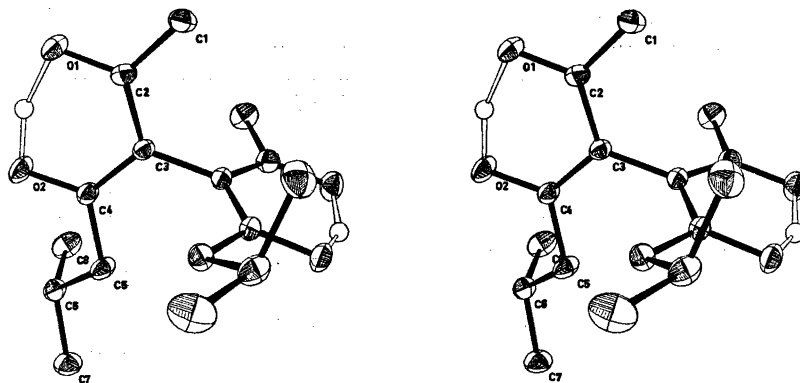


Fig. 1. Stereoscopic illustration of the molecule, showing atom numbering scheme. Thermal ellipsoids are scaled to include 50 % probability [Johnson, C. K. *ORTEP* ORNL-3794, Oak Ridge National Laboratory, Oak Ridge 1965].

is shown in Fig. 1. Bond lengths and angles are given in Table 2. Estimated standard deviations were derived from the final correlation matrix of least-squares refinements.

CRYSTAL DATA

5,6-Diacetyl-2,9-dimethyl-4,7-decanedione
 $C_{16}H_{26}O_4$, triclinic; $P\bar{1}$, $a = 8.937(1)$, $b = 9.406(1)$,
 $c = 11.030(2)$ Å, $\alpha = 67.09(1)$, $\beta = 70.26(1)$, $\gamma =$
 $74.57(1)$, $V = 794.2$ Å³. (Dirichlets reduced cell),
 $D_{obs} = 1.14$ g cm⁻³, $D_{calc} = 1.18$ g cm⁻³, $Z = 2$,
 $M = 282.4$ g mol⁻¹, $F(000) = 308$.

RESULTS AND DISCUSSION

The molecule crystallizes in the *cis*-dienolic form and the structure therefore comprises two independent determinations of the enol system (A and B). The π -electrons in the enol rings appear to be almost entirely delocalized, although a slight, but significant, single and double bond fixation is apparent. Except for the C1–O1 bonds, equivalent bonds between heavy atoms in the enol rings agree to within twice their combined estimated standard deviations. These bond lengths correspond closely to those given in a recent neutron diffraction study of tetraacetylene.⁸ The somewhat shorter C–O bonds of the neutron study may be explained by the higher thermal motions of the oxygen atoms at room temperature. The short intramolecular hydrogen bonds of the enol rings [O1A–O2A; 2.457(1) Å, O1B–O2B; 2.438(1) Å], agree reasonably well with that of

tetraacetylene [2.450(3) Å]. In agreement with the findings in the neutron study of tetraacetylene, the protons HA and HB appear to be located asymmetrically in these bonds. The observed deviations from C_{2v} symmetry in the heavy atom positions are consistent with the asymmetries in the proton positions. The hydrogen atoms in both enol rings thus seem to be more closely attached to the oxygen atoms tied to the carbon atom carrying the more branched substituent. This is to be expected since a hydrogen atom at this position would tend to be somewhat less acidic. The difference in the asymmetry of the proton positions in the two enol rings is not significant.

As may be seen from Table 2, the sp^3-sp^3 and sp^2-sp^2 carbon-carbon bond lengths are normal, with mean values of 1.528 and 1.499 Å, respectively. The average angle at sp^3 -carbon atoms is 111.4°. C–H bond lengths range from 0.90 to 1.04 Å with estimated standard deviations of 0.03 Å. C–C–H and H–C–H angles are found between 104 and 119° (e.s.d. $\sim 2^\circ$).

Least-squares planes through the enol rings and surrounding atoms are given in Table 3. Deviations from planarity probably arise from non-bonded repulsions (see below). The angle between the normals to the enol ring planes was calculated to be 85.7°. A rigid-body motion analysis¹⁴ for each of the enol rings was carried out including the atoms in plane 2A and B. The good agreement between observed and calculated vibration tensor elements (A; $\Delta U_{ij} = 0.0008$ Å², B; $\Delta U_{ij} = 0.0007$ Å²) suggests that

Table 2. Bond distances and bond angles. Upper values from the refinement with an inner cut off at $\sin \theta/\lambda = 0.55$, lower values from the refinement of all data.

Bond distances (Å)	Bond angles (°)				
	A	B			
C1–C2	1.492(1) 1.490(2)	1.498(1) 1.495(2)	C1–C2–C3	121.5(1) 121.7(1)	121.8(1) 121.9(1)
C2–C3	1.422(1) 1.420(1)	1.422(1) 1.417(1)	C2–C3–C4	118.2(1) 118.5(1)	118.0(1) 118.3(1)
C3–C4	1.409(1) 1.406(1)	1.407(1) 1.405(1)	C2–C3–C3'	121.0(1) 121.0(1)	120.2(1) 120.2(1)
C4–C5	1.508(1) 1.508(2)	1.499(1) 1.499(2)	C3–C4–C5	121.7(1) 121.9(1)	122.9(1) 123.6(1)
C5–C6	1.528(1) 1.527(2)	1.535(1) 1.534(2)	C4–C5–C6	115.0(1) 115.3(1)	113.6(1) 113.8(1)
C6–C7	1.530(2) 1.525(2)	1.523(2) 1.524(2)	C4–C3–C3'	120.7(1) 120.5(1)	121.8(1) 121.5(1)
C6–C8	1.523(2) 1.522(2)	1.529(2) 1.525(2)	C5–C6–C7	109.6(1) 109.8(1)	109.6(1) 109.6(1)
C3A–C3B	1.482(1) 1.487(1)		C5–C6–C8	111.3(1) 111.3(1)	111.0(1) 111.0(1)
O1–C2	1.288(1) 1.289(1)	1.282(1) 1.281(1)	C7–C6–C8	110.2(1) 110.3(1)	110.6(1) 110.5(1)
O2–C4	1.295(1) 1.295(1)	1.298(1) 1.299(1)	O1–C2–C3	121.4(1) 121.1(1)	121.4(1) 121.4(1)
O1...O2	2.457(1) 2.454(1)	2.439(1) 2.439(1)	O2–C4–C3	121.6(1) 121.5(1)	121.3(1) 121.0(1)
O2–H	1.20 1.20(2)	1.08 1.08(2)	O1–C2–C1	117.2(1) 117.2(1)	116.7(1) 116.7(1)
O1...H	1.30 1.30(2)	1.42 1.42(2)	O2–C4–C5	116.7(1) 116.5(1)	115.8(1) 115.7(1)
			C2–O1...H	99.4	100.1
			C4–O2–H	99.9	103.3
			O1...H–O2	160. 160.(1)	156. 156.(1)

the enol rings may be regarded oscillating rigid bodies. Corrections in bond lengths range from 0.002 to 0.003 Å and have not been applied. These do not, however, alter the observed asymmetries in the enol ring bond lengths. The principal axes of the thermal vibration ellipsoids for the individual carbon and oxygen atoms were also calculated. Maximum root

mean squares amplitudes range from 0.139 to 0.229 Å for carbon atoms and 0.174 to 0.208 Å for oxygen atoms.

The shortness of the intramolecular hydrogen bond in bis-3-(6-methyl-2,4-heptanedione) is essentially due to various short non-bonded repulsive contacts between the bulky substituents at the α position and the alkyl substituents

Table 3. Deviations (\AA) from least-squares planes. For atom numbering see Fig. 1. Deviations of atoms not defining the planes in parentheses.

	1 A	2 A	1 B	2 B
O1	0.011	0.028	-0.004	0.000
O2	-0.006	0.000	0.005	0.021
C1	(-0.103)	-0.073	(0.013)	-0.011
C2	-0.020	0.001	0.004	-0.006
C3	0.012	0.029	0.003	-0.010
C4	0.002	0.011	-0.009	-0.007
C5	(-0.065)	-0.060	(-0.022)	-0.023
C3**	(0.033)	0.054	(0.061)	0.030

* The C3 atom of the adjacent enol ring.

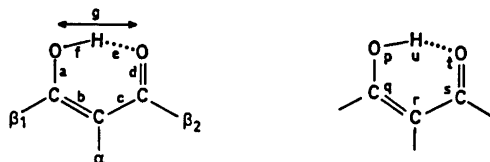
at the β positions. In particular the contacts from C3A to C2B (2.51 \AA), to C4B (2.52 \AA), and to H5B2 (2.56 \AA)*, and contacts from C3B to C2A (2.53 \AA), to C4A (2.51 \AA), and to H5A2 (2.59 \AA) lead to decrease in the internal angles at C3A and C3B from the expected value of 120 to 118.2 and 118.0 $^\circ$, respectively. On the other hand, the internal angles at C2 A,B and

* H5B2 is attached to C5B.

C4 A,B are opened as a result of non-bonded repulsions between the oxygen atoms, and repulsions between the enolic proton and C2 and C4. The enol ring geometry represents a compromise between these forces and as a result the hydrogen bond is shorter than the equilibrium distance for this type of hydrogen bond, and there is an increase of conjugation in the alternating bond system. The enolic proton is "pinched" between the two oxygen atoms — its presence reduces the oxygen-oxygen repulsive forces.

The effect of non-bonded repulsions on the enol ring geometry becomes evident when systems carrying large substituents in the α - and β -positions are compared. Table 4 gives a summary of bond distances and angles from some of the more accurate studies so far reported. In benzoylacetone⁹ and dibenzoylmethane^{5,6} the phenyl substituents are almost coplanar with the enol ring, the steric repulsions from these substituents resist the opening of the enol ring angle adjacent to this group (q and s). Repulsions are therefore relieved by opening the central angle (r). In benzoylacetone there is only one phenyl substituent and the

Table 4. Bond distances and angles in some *cis*-enolized β -diketones.



Compound	a	b	c	d	e	f	g	Ref.
Tetraacetylene	1.289(3)	1.402(3)	1.423(3)	1.277(3)	1.319(9)	1.194(9)	2.450(4)	8
5,6-Diacetyl-2,9-dimethyl-4,7-decane-dione	1.294(1)	1.409(1)	1.422(1)	1.289(1)	1.30	1.20	2.457(1)	—
	1.299(1)	1.407(1)	1.422(1)	1.282(1)	1.42	1.08	2.439(1)	—
Dibenzoylmethane	1.304(2)	1.382(3)	1.408(3)	1.287(3)	1.28	1.22	2.468(2)	6
Benzoylacetone	1.294(2)	1.376(3)	1.401(3)	1.276(2)	1.40	1.18	2.498(2)	7

Compound	p	q	r	s	t	u	Ref.
Tetraacetylene	102.8	121.7	117.9	121.6	101.6	154.3	8
5,6-Diacetyl-2,9-dimethyl-4,7-decane-dione	99	121.6	118.2	121.4	100	160.	—
	100	121.3	118.0	121.4	103	156.	—
Dibenzoylmethane	100.0	120.3	121.1	119.8	100.	159.	6
Benzoylacetone	104.	120.4	121.9	120.6	102.	151.	7

hydrogen bond in this compound [2.498(2) Å] is therefore longer than that in dibenzoylmethane [2.460(2) Å], although not as long as that of the *trans*-enol arrangement of dimedone [2.593(2) Å],¹⁵ where non-bonded intermolecular repulsions preferentially would give an elongation of the O—O distance.

Some other consistencies and trends may also be pointed out. Although only moderate agreement between corresponding bonds is found, all these systems possess a high degree of conjugation in the essentially planar enol rings. The compounds of Table 4 have all asymmetric hydrogen bonds, with deviations from C_{2v} symmetry in the heavy atom skeleton consistent with the asymmetry in the proton positions. As already mentioned in the crystal structure of bis(*m*-bromobenzoyl)methane a crystallographic symmetrical hydrogen bond has been found ($R(O\cdots O) = 2.47$ Å).⁴ In fact, several of the above compounds (Table 4) have hydrogen bonds shorter than that of bis(*m*-bromobenzoyl)methane. Probably small differences in the crystallographic or chemical environment are responsible for the asymmetries found in these compounds. The hydrogen bond geometry in the enol rings of β -diketones is very similar to that found in the neutron diffraction determination of $\{Ni(C_6H_{11}N_2O_2)H\}^+ \cdot Cl^- \cdot H_2O$,¹⁶ where it was concluded that the proton potential has one broad, flat minimum which is slightly shifted towards one of the oxygen atoms.

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