

Asymmetry of the “Strongest” OHO Hydrogen Bond, in the Monoanion of (\pm)- α,α' -Di-*tert*-butylsuccinate
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We regret to announce a serious error in our recently published article. The material assigned there as the dicesium salt of the di-*tert*-butylsuccinate dianion is in fact the cesium salt of the hydrogen di-*tert*-butylsuccinate monoanion. Therefore, the short O–O distance of 2.41 Å applies only to the monoanion and not the dianion. So short a distance is not a general feature of α,α' -di-*tert*-butylsuccinate, as had been claimed, but is unique to the monoanion and common across all the monoanions. It is associated with the presence of an intramolecular hydrogen bond in the monoanion.

We now report the preparation and crystal structure of an authentic sample of the dipotassium salt of (\pm)- α,α' -di-*tert*-butylsuccinate dianion (**6**), prepared from the diacid + excess KH and crystallized slowly from dimethylformamide. Table 1

Table 1. Selected Bond Lengths (*d*, Å), Bond Angles (ϕ , deg), and Torsional Angles (τ , deg) in Dipotassium (\pm)- α,α' -Di-*tert*-butylsuccinate, Averaged over Inequivalent Sites, along with Earlier Data on Tetrapropylammonium Hydrogen (\pm)- α,α' -Di-*tert*-butylsuccinate

	K ⁺ ₂ A ²⁻	Pr ₄ N ⁺ HA ⁻
<i>d</i> _{O–O}	2.98	2.416
<i>d</i> _{C=O_{exo}}	1.258	1.228
<i>d</i> _{C–O_{endo}}	1.262	1.281
<i>d</i> _{Me₃CC–CCMe₃}	1.550	1.524
<i>d</i> _{Me₃C–C}	1.573	1.589
<i>d</i> _{C–CO^a}	1.533	1.529
ϕ _{O–H–O}	66 ^a	166
ϕ _{Me₃C–C–CCMe₃}	114.1	114.1
ϕ _{O₂C–C–CCO₂}	113.3	116.2
ϕ _{Me₃C–C–CO₂}	110.4	111.5
τ _{Me₃C–C–C–CMe₃}	127.6	166.7
τ _{O₂C–C–C–CO₂}	22.6	70.5
τ _{Me₃C–C–C–CO₂}	105	61.4
τ _{O_{exo}–C–C–CCO₂}	107	133
τ _{O_{endo}–C–C–CCO₂}	74	49

^a O_{endo}–K–O_{endo}.

lists selected bond lengths and angles, along with earlier data on tetrapropylammonium hydrogen di-*tert*-butylsuccinate monoanion (**5**) for comparison. The O–O distance in the dianion is 2.98 Å, considerably longer than the 2.41 Å in the monoanion. It would then appear that the unusually short distance in the latter is a sign of a very strong H-bond.

However, that H-bond in the monoanion is not symmetric, according to both NMR isotopic perturbation and X-ray crystal data. Therefore, it is still necessary to account for the exceptionally large ΔpK_a of di-*tert*-butylsuccinic acid, which has been taken as evidence for a strong H-bond in its monoanion.

Other features of the X-ray structure of the dianion clarify that large ΔpK_a . Whereas the monoanion is nearly staggered, the dianion has twisted about the central C–C bond toward an

eclipsed conformation, with 128° and 23° dihedral angles, as listed in Table 1. In part, this is to allow the O_{endo}—K—O_{endo} angle to close down to 66° and allow the K⁺ to bridge the two oxygens. More revealing is the twisting of the carboxylates, whereby the two O—C—C—C dihedral angles (of O_{exo} and O_{endo}) have become more similar, corresponding to carboxylates nearly perpendicular to the central C—C bond. One of the most striking differences between the monoanion and dianion is the COOC torsional angle (not shown in Table 1), which is <10° in the former but close to 90° in the latter. This is not a torsional angle about any bond but reflects the twisting of the carboxylates toward perpendicularity in the dianion from the coplanarity of the CCOHOCC fragment in the monoanion. These distortions all reflect the severe electrostatic repulsion between the carboxylates in the dianion.

The electrostatic repulsion of the dianion is relieved in the monoanion by inserting a proton between the carboxylates. However, the resulting H-bond is found to be asymmetric not only in the crystals but also in solution. We therefore reaffirm the conclusions that there is no H-bond that is stabilized by symmetry *per se*, nor any special stabilization associated with symmetric H-bonds. Moreover, the large difference between the first and second p*K*_a in (±)-α,α'-di-*tert*-butylsuccinic acid is due to relief of electrostatic repulsion in the dianion and not to any exceptional strength of the H-bond in the monoanion.

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Supporting Information Available: X-ray crystallographic file in CIF format and a table summarizing crystallographic data for the dipotassium salt of (±)-α,α'-di-*tert*-butylsuccinate dianion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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