

PROTONATION OF INDANE-1,2,3-TRIONE: FORMATION OF 1,2,3-TRIHYDROXYINDANE
TRICATION - A NEW AROMATIC SYSTEM

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Formation of doubly charged conjugate-acids by protonation of the respective dicarbonyl compounds has been investigated in a few systems². Until now, no 1,2,3-tricarbonyl derivatives have been known to undergo triple protonation. In the aromatic series, doubly charged molecules have previously been reported; their formation and properties demonstrate the applicability of Huckel's rule to such cations³. In principle, triply charged Huckeloid systems i.e. 9C-6 π or 5C-2 π systems, should exhibit aromatic properties, but such systems have as yet not been prepared. Aromatic stabilization is expected to facilitate triprotonation of triketones whenever such stabilization can be achieved. We report the protonation of indane-1,2,3-trione (ninhydrin) (1) which is the first 1,2,3-tricarbonyl system known to undergo triple protonation. Moreover, this triprotonated species represents the 1,2,3-trihydroxyindane trication (2), which can be considered either a 5C-2 π or a 9C-6 π bridged Huckeloid system.

The ¹HNMR spectrum of 1 (hydrate)⁴ consists of two bands (singlets 2:1) at 8.30 and 7.75 ppm assigned to the aromatic and hydroxyl protons, respectively. Protonation of 1 produces 2, which exhibits only one singlet at 9.40 ppm. Even at -70⁰ no OH⁺ band was observed. The ¹³CNMR of 1 shows the following bands⁵: δ_{ppm} 197.3 (carbonyls at positions 1 and 3), 138.8 (ipso carbon atoms), 137.6 (aromatic carbons 5 and 6), 124.2 (aromatic carbons 4 and 7), and 88.0 (hydrated carbonyl at the 2 position). The protonated species 2 showed the following ¹³CNMR spectrum⁵: δ_{ppm} 191.3 (carbon atoms 1 and 3), 172.0 (carbon atom 2), 153.5 (aromatic carbons 5 and 6), 138.7 (ipso carbons), 136.4 (aromatic carbon atoms 4 and 7). The above spectra were compared with those of indane-1,3-dione (3) and its diprotonated species, a "normal" diprotonated dicarbonyl compound. The ¹HNMR spectrum⁴ of 3 displays two singlets: one at 8.2

and the other at 3.6 ppm (2:1), assigned to the aromatic and methylene protons, respectively. In SO_2 -magic acid, compound 4 bands appear at 15.7, 8.94, and 5.2 ppm (1:2:1; OH^+ , aromatic and methylene protons, respectively). In the carbon spectrum⁵, compound 3 bands appear at 198.3 ppm (carbonyl), 143.3, 135.8 and 122.9 ppm (aromatic), 45.4 ppm (methylene). Compound 4 shows carbon bands⁵ which appear at 213.2 ppm (assigned to protonated carbonyl groups), 147.8 and 134.5 ppm (aromatic ring carbons 4,7,5, and 6). The ipso carbon atoms appear at 138.0 ppm, and the methylene carbon atom appears at 43.9 ppm.

A significant downfield shift is observed in the ^1H NMR spectrum of 2 compared to that of 4, (Table I). In benzene rings bearing two protonated carbonyls, e.g. diprotonated dimethylphthalate and dimethylterephthalate, the aromatic protons appear at 8.50 and 8.70 ppm, respectively⁶. In protonated ortho-diacetylbenzene, the aromatic protons are revealed at 8.52-8.72 ppm⁷. These shifts are in agreement with those observed for 4. The aromatic protons of 2, which appear at 9.40 ppm, are extremely low. Though the OH^+ band of 4 is readily discerned, its absorption being that expected for a protonated ketone, the OH^+ band of 2 is not detectable due to rapid exchange. This behavior is similar to that of the hydroxytropylium ion⁸, the latter attributable to reduction of the $\text{C}=\text{OH}^+$ double bond character. The difference in the shielding of the protonated carbonyl carbon absorptions between 2 and 4 (and other protonated ketones) relative to those of the parent carbonyl carbons should be noted: the carbonyl carbon absorptions of 2 are shielded, those of 4 are deshielded. This "anomaly" may be explained by the reduction of the double bond character of the carbonyl groups as a consequence of charge delocalization in 2.

The significant downfield shift of the benzo protons points to a high degree of charge delocalization, greater than in any oxygen-containing dication (Table I). It manifests delocalization over the whole framework. However, it may be that there is rapid exchange between an equilibrating set of the diprotonated and triprotonated system. Evidence for a higher degree of protonation than diprotonation occurring in 2 is the downfield shift of the benzene ring carbons which are deshielded relative to those of 4. Moreover, if a fast exchange would occur between the three possible diprotonates, then the carbons and hydrogens would be less

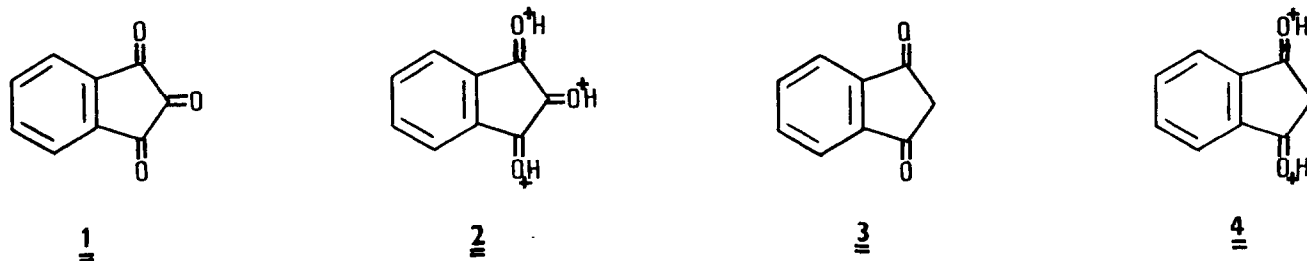
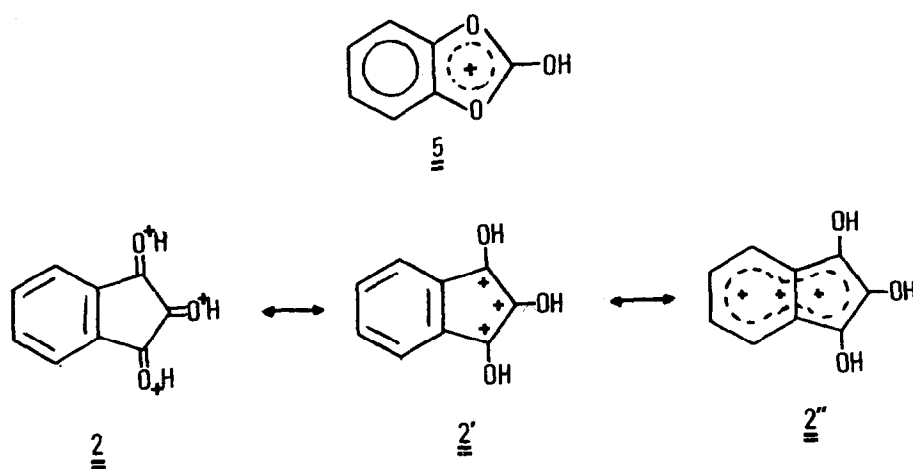


Table I: Chemical Shift Data

Compound	Shift of Aromatic Protons (ppm) ^a			Shifts of Benz ^o Carbons (ppm) ^b		
	Parent Compound	Protonated Compound	$\Delta\delta$ ^c	Parent Compound Total ^d	Protonated Compound Total	$\Delta\delta$ ^c
Indane-1,2,3-trione (<u>1</u>)	8.30	9.40		801.4	857.2	55.8
Indane-1,3-dione (<u>3</u>)	8.20	8.94	0.74	804.0	840.6	36.6
Catechol Carbonate (<u>5</u>) ¹⁰	7.20-7.25	8.00	0.75-0.80	764.2	775.2	11.0
Terephthalic Acid ⁶	8.25	8.68	0.43	789.0	781.8	-7.2
Benzocyclobutane-1,2-dione ^{2c}	7.86-8.08	8.82	0.76-0.74	867.6	886.6	19.0

(a) See reference 4; (b) See reference 5; (c) Chemical shift difference between parent and protonated compound; (d) Sum of shifts of the benzo carbon atoms.

affected than in 4 due to "lack of conjugation" between position 2 and the aromatic ring. If carbon atoms 1, 2, and 3 are excluded and the total deshielding of the benzene carbon atoms is calculated, it may be seen (Table I) that due to protonation, 1 undergoes a downfield shift of 55.8 ppm, 3 of 36.6 ppm, and a new, singly-charged molecule: protonated catechol carbonate (5) of 11.0 ppm (Table I)⁹. In view of the fact that biacetyl does not readily undergo diprotonation⁷ it should be concluded that additional stability is involved in the triprotonated system. From the conclusion that the three carbonyl groups of 1 are protonated, the fact that conjugation of the β -carbonyl with the aromatic ring ($\delta = 172$ ppm) and the low field shift of the benzene ring and carbon protons do occur, it appears that 2 is a triprotonated species and its stability is most likely due to the formation of a new type of triply-charged Huckeloid system, a $5C-2\pi$ or $9C-6\pi$ system, viz. 2' or 2'' respectively.



References and Notes

1. Taken in part from Ph.D. Thesis of D. Bruck.
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4. Proton nmr measurements were carried out with a Varian HA-100D spectrometer operating at 100 MHz. Me₄Si served as reference. Chemical Shifts are reported downfield to the reference band. The ketones were measured in DMSO-d₆, 0.2M, and the protonates were measured in SO₂-magic acid 1:1 v/v, 0.2M solutions.
5. Carbon nmr spectra were taken in DMSO containing 30% of DMSO-d₆ (DMSO band appears at 40.78 ppm relative to Me₄Si) or in SO₂-magic acid⁴ on a Varian CFT-20 spectrometer operating at 20 MHz for carbon. In SO₂-magic acid system the reference (acetone-d₆ δ carbonyl=204.3 ppm relative to Me₄Si) was placed in a sealed capillary. The assignments were assisted by off-resonance experiments.
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