On the Aromaticity and Acidity of 1-Hydroxy-4,5-benzotropylium Derivatives

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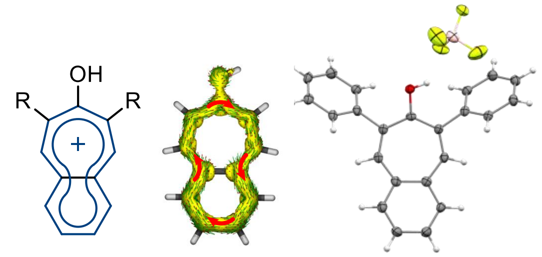
Abstract

The aromaticity of 1-hydroxy-4,5-benzotropylium was assessed based on experimental and theoretical investigations. An X-ray crystallographic analysis revealed a decrease of bond alternation in the seven-membered ring of 1-hydroxy-4,5-benzotropylium derivatives compared with that of the parent 4,5-benzotropones, which is indicative of an increase in aromaticity upon protonation. NICS and AICD calculation also supported the increased aromaticity of 1-hydroxy-4,5-benzotropylium. The pK_a values for a series of 1-hydroxy-4,5-benzotropylium derivatives were also determined.

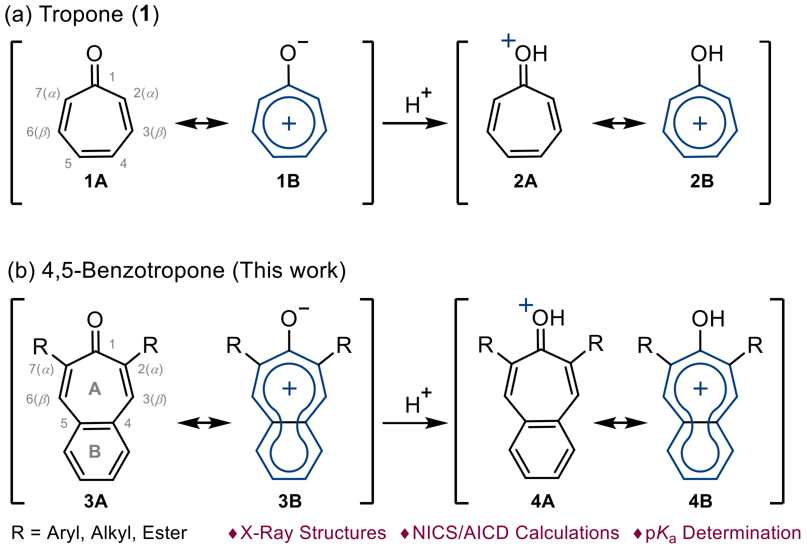


♦X-Ray Structures ♦NICS/AICD Calculations ♦pK_a Determination

Since the first synthesis of cyclohexa-2,4,6-trienone, or tropone (**1**) in the early 1950s,[1,2] , it has been considered to be a representative scaffold of non-benzenoid aromatic compounds[3,4] because the 6π aromaticity is expected when the contribution of the polar canonical structure **1B** is significant (Chart 1). Although computational studies suggested that **1** possesses some degree of aromatic character derived from **1B**,[5] the physical properties of **1**, including the dipole moment,[6a,6c] the ^{1}H NMR chemical shifts of the compound,[6b] the C=O stretching frequency in IR spectra,[6d] and the fact that it reacts[4a–4e, 4g,4h,4j] as a polyenoic compound rather than an aromatic compound all indicate that the contribution of **1B** to the characteristics of the compound is insignificant. Nucleus-independent chemical shift (NICS)[7] calculations also indicate that the degree aromaticity of **1** is not quite strong (NICS(0) : -1.3).[8] In contrast, the corresponding conjugate acid of **1**, hydroxytropylium **2**,[1a,2,9] which is generated by the protonation of **1**, shows increased aromatic properties, which is supported by NMR data[10a] and NICS calculations (NICS(0) : -5.3).[10b] The crystal structure of **2** (X = Cl) was recently reported by the Pöthig group[11] which displayed a planer geometry with C–C bonds alternation of the seven-membered ring. These results indicate that the protonated form of tropone **2A** and hydroxytropylium **2B** both contribute to the characteristics of the molecule.

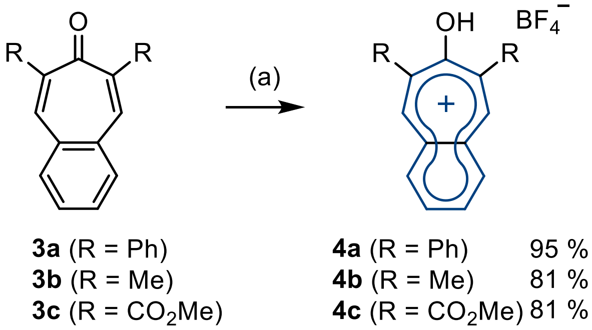
The structure, electronic properties, reactivities, and metal coordination mode of troponoid compounds, as represented by tropone and tropolone, markedly vary by the annulation of extra fused aromatic rings.[4g,4j,12–14] In addition to the effect of annulation, the introduction of substituents at the 2,7-positions of 4,5-benzotropone also affects the dipole moment[12d,12i] or C1–C2 and C1–C7 single bond lengths of the molecule.[13g,13i] Although numerous fused tropone derivatives have been synthesized over the past 100 years,[4f,4j] the effect of annulation on the aromaticity of the corresponding conjugate acid[12b,12f,12k,13d,13h,13j] (*i.e.*, **4**) has not been investigated thus far, to the best of our knowledge. Here, we report on the protonation of some 4,5-benzotropone derivatives **3** and the characterization 1-hydroxy-4,5-benzotropylium derivatives **4** by NMR measurements, X-ray crystallographic analysis and computational methods.

Chart 1. Schematic Representation of Protonation of Tropone



To investigate the effect of substituents on 4,5-benzotropyrium derivatives, we focused on the synthesis of a series of 2,7-disubstituted-4,5-benzotropones, including those bearing aryl (**3a**, **3d**) alkyl (**3b**, **3e**) and ester (**3c**, **3f**) groups. The 4,5-benzotropones **3a**–**3f** were synthesized by the Knoevenagel condensation of *o*-phthalaldehyde and the corresponding ketones in the presence of a suitable base (NaOH for **3a**, **3d**; piperidine for **3b**, **3e**; NaOEt for **3c**, **3f**) (Scheme S1).[15] Treatment of **3** with two equivalents of $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 at room temperature successfully afforded good yields of the corresponding 1-hydroxy-4,5-benzohydroxytropylium derivatives **4a**, **4b** and **4c** as BF_4 salts (Scheme 1).

Scheme 1. Synthesis of 1-Hydroxy-4,5-benzotropyriums **4**.[a]



[a] **3** (1.0 mmol), $HBF_4{\cdot}Et_2O$ (2.0 mmol) in CH_2Cl_2 at rt for 15 min.

1-Hydroxy-4,5-benzohydroxytropylium **4a**, **4b** and **4c** could be crystalized from CH_2Cl_2 to form pale yellow crystals that were suitable for X-ray crystallographic analysis. The ORTEP drawings of **4a**, **4b** and **4c** are shown in Figure 1 and the structural parameters are summarized in Table 1. The molecular structures of **4a** and **4c** were slightly distorted, and the C2 and C7 carbons of **4a**/**4c** deviated from the mean plane of the 4,5-benzotropylium ring by

0.016/0.163 and 0.088/0.147 Å, respectively, which is in sharp contrast to the higher planarity displayed by **4b**. This difference can be attributed to the bulkiness of the C2 and C7 substituents (*i.e.*, Ph and CO_2Me). The C1–O bond lengths of **4a** (1.33 Å), **4b** (1.32 Å) and **4c** (1.31 Å) were elongated compared with those of the parent tropones **3a** (1.22 Å),[13g,13i] **3b** (1.24 Å), and **3c**[14] (1.22 Å) (Table 1, Figure S5 and S6). The distance for the C2–C3/C6–C7 bonds in **4** were also elongated while the C1–C2/C7–C1 and C3–C4/C5–C6 bond lengths were shorter compared with those of **3a**,[13g,13i] **3b**, and **3c**.[14] The bond alternations for the seven-membered ring (ring A) of the 1-hydroxy-4,5-benzotropylium derivatives became smaller compared to those of the parent 4,5-benzotropone derivatives, while the bond alternations for the fused benzene ring (ring B) became slightly larger upon protonation. To further evaluate the aromaticity of **3** and **4** in more detail, harmonic oscillator model for aromaticity (HOMA)[16] values were calculated for both the seven-membered ring (ring A) and the fused benzene ring (ring B) of **3a**–**3c**, **4a**–**4c**. The HOMA values for ring A of **4a**(0.809), **4b** (0.681), and **4c** (0.678) were larger compared to those of **3a**[13g,13i] (-0.019), **3b** (0.071), and **3c**[14] (-0.015), which are close to zero. Concerning ring B, the HOMA values of **4a**–**4c** were decreased slightly compared to those of **3a**–**3c** but still remained high. These results indicate that the polar resonance form **4B** (Chart 1) is the dominant contributor to the structures of 1-hydroxy-4,5-benzotropylium derivatives whereas **3A** is more dominant contribution for the 4,5-benzotrones derivatives. The aromaticity of **4** was also assessed by DFT calculations. NICS(1) values of 1-hydroxy-4,5-benzotropylium with no substituents [*i.e.*, **4** (R = H)] calculated at the GIAO-B3LYP/6-31+G(d,p)//ωB97XD/6-31G(d,p) level were -6.55 and -12.11 for rings **A** and **B**, respectively. The diatropicity of heptagonal ring A was significantly increased compared to the parent 4,5-benzotropone (-1.06), as was reported for the corresponding tropone/hydroxytropylium system.[8,10] The contribution of **4B** was also supported by anisotropy of induced current density (AICD)[17] calculations, in which a diatropic ring current originating from a 10π macrocyclic system was observed (Figure 2b). In contrast, the AICD plot for **3** (R = H) revealed that a strong diatropic ring current was observed only in the fused benzene ring (ring B), while the seven-membered ring possesses a more polyenic character (Figure 2a).

To evaluate the acidity of 1-hydroxy-4,5-benzotropylium derivatives, NMR titration measurements were carried out using more soluble 4,5-benzotropone derivatives **3d**–**3f**. Upon the addition of 0–10 equivalents of $HBF_4 \cdot Et_2O$ to the 4,5-benzotropone derivatives **3d**–**3f**, the resonance of the β-protons of **3d**–**3f** displayed a down shield–shift. The pK_a values for the conjugate acids **4d**, **4e**, and **4f** were determined by non-linear least squares of a plot of the changes in ^{1}H-NMR chemical shifts of β-protons $\Delta\delta$ as a function of the initial HBF_4 concentration to be 1.54, 1.70, and 1.49, respectively (Table 2, Figure S7, and Table S1). The 1-hydroxy-4,5-benzotropylium derivative bearing electron-withdrawing groups at the 2,7-positions were slightly more acidic than the derivative that contained electron-donating groups, which can be attributed to the stability of the generated 1-hydroxy-4,5-benzotropylium.

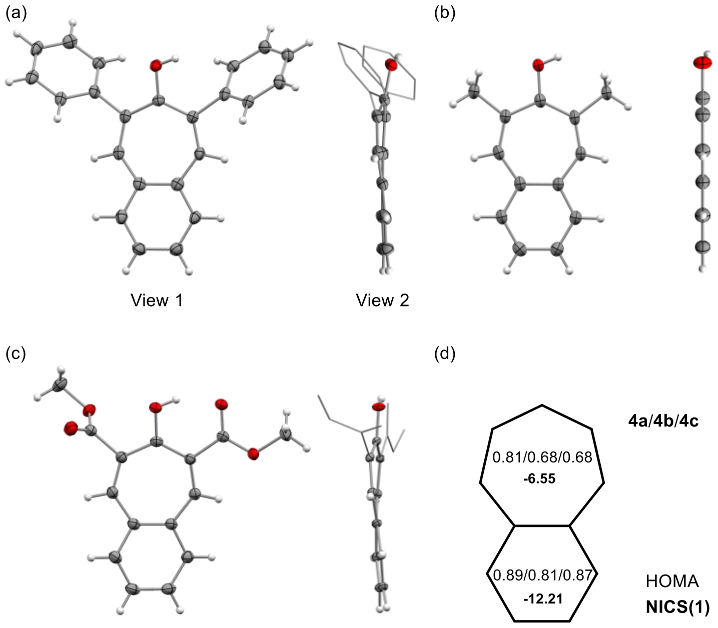


Figure 1. ORTEP drawing of (a) **4a** at the 30% probability level and (b) **4b** and (c) **4b** at 50% probability level. BF_4^- anions were omitted for clarity. Hydrogen atoms of the substituents on the 2,7-positions in View 2 were omitted for the sake of clarity. (d) HOMA values for **4a**–**4c** and NICS(1) values of ring A and B for non-substituted analog of **4**.

Table 1. Selected C–C and C–O bond length/Å of 4,5-benzotropone scaffold of **3a**–**3c** and **4a**–**4c** and HOMA values.[a]

	bond length / Å				distance / Å	HOMA	
	O–C1	C1–C2/C7–C1	C2–C3/C6–C7	C3–C4/C5–C6	C2–m1/C7–m2	ring **A**	ring **B**
3a	1.217	1.217/1.218	1.350/1.354	1.448/1.447		-0.019	0.943
4a	1.327(6)	1.427(8)/1.423(8)	1.381(8)/1.389(8)	1.411(8)/1.412(8)	0.016/0.088	0.809	0.888
3b	1.237(2)	1.447(2)/1.476(2)	1.355(2)/1.354(2)	1.443(2)/1.447(2)		0.071	0.896
4b	1.321(6)	1.438(5)/1.431(5)	1.368(6)/1.380(2)	1.423(6)/1.417(6)	0.000/0.000	0.681	0.812
3c	1.222(2)	1.479(2)/1.480(2)	1.353(2)/1.349(2)	1.445(2)/1.452(2)		-0.015	0.927
4c	1.307(2)	1.426(2)/1.429(2)	1.373(2)/1.362(2)	1.425(2)/1.429(2)	0.163/0.147	0.678	0.869

[a] Structural parameters for **3a** (CCDC 1145437) and **3c** (CCDC 2036613) were abstracted from the Cambridge Structural Database. m1 and m2 are projection points of C2 and C7 on the mean plane of a benzotropone scaffold, respectively.

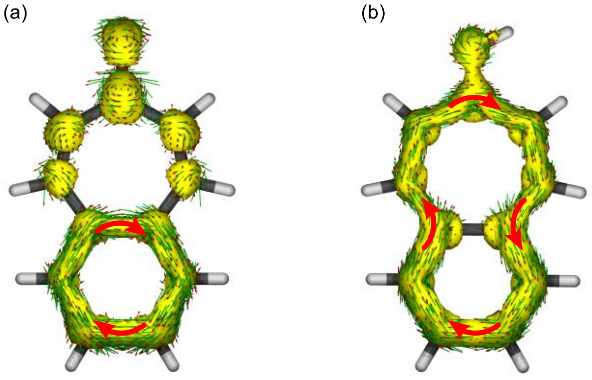


Figure 2. AICD plots of the π system of (a) 4,5-benzotropone and (b) 1-hydroxy4,5-benzotropylium. The red arrow denote the induced ring current: clockwise for diatropic (isosurface value 0.05 a. u.).

Table 2. pK_a Values of **4d**–**4f** in CH_2Cl_2.

	4d	**4e**	**4f**
pK_a	1.54	1.70	1.48

In summary, 1-hydroxy-4,5-benzotropylium derivatives were synthesized and characterized by X-ray crystallographic analysis, NMR measurements and quantum calculations. In contrast to 4,5-benztotropone, in which the fused benzene ring has an explicit local aromatic character, an increase in the HOMA values, the negative NICS(1) values for seven-membered ring, and a ring current in the 10π macrocyclic system in the AICD plot indicated that the polar canonical structure, in which the aromaticity of the seven-membered ring is enhanced, is the major contributor to its characteristics. The structure of 1-hydroxy-4,5-benzotropylium was distorted by the presence of bulky substituents at the 2,7-positions. The introduction of substituents at the 2,7-positions affected on pK_a values of 1-hydroxy-4,5-benzotropylium in which electron-donating groups cause it to be less acidic, whereas electron withdrawing groups cause it to be more acidic.

Supporting Information

Experimental procedures and supporting characterization data and spectra (PDF)
Compound **3b**, **4a**, **4b**, and **4c** crystal structure (CIF)

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Notes

The authors declare no competing financial interest.

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