

The Adverse Effect of Benzannelation on the Aromaticity of Oxocinyl Anion: A Combined Experimental and Theoretical Study

by Hamid S. Kasmai^{a)}, Xiaodong Wang^{a)}, Hanh-Nhon Doan^{a)}, Josef F. Femia^{b)}, Thad M. Yablonsky^{b)}, Mary E. Read^{b)}, and David T. Dutton^{b)}

^{a)} Department of Chemistry, East Tennessee State University, Johnson City, TN 37614, USA
(phone: +1-423-4394367; fax: +1-423-4395835; e-mail: kasmai@etsu.edu)

^{b)} Department of Chemistry, Hamilton College, Clinton, NY 13323, USA

A synthesis of 2*H*-1-benzoxocin from readily available compounds was accomplished. The potentially 'aromatic' π -excessive systems 2*H*-1-benzoxocinyl and 6*H*-dibenz[*b,f*]oxocinyl anions were generated from their corresponding conjugate acid precursors **7c** and **8**, respectively. It was found that 2*H*-1-benzoxocinide **3d** lacks the type of π -frame stability associated with the parent 2*H*-oxocinide **1d** and that the dibenzo analog **5b** is more unstable than **3d**. Both **3d** and **5b** undergo rapid structural reorganization to form their corresponding stable isomeric anions. We were able to characterize the proton-quenched products of these anions as the ring-opened structures **15** and **18**, respectively. ¹H-NMR and an *ab initio* calculation at the 6-31g* level indicated that, unlike the 'aromatic' parent 2*H*-oxocinide **1d** and the aza analog **3c**, **3d** incorporates a non-planar oxocinyl ring in which the negative charge is primarily localized on the pentadienyl moiety of the ring, but also partial delocalization of π -electron density onto the benzene ring occurs.

Introduction. – The synthesis and study of aromatic and heteroaromatic compounds constitute a fundamentally significant part of basic research in the field of organic chemistry. In addition to the importance of these studies in the development of basic theoretical and experimental concepts [1], the applied areas such as material sciences [2] and biomedical chemistry [3] have found practical applications of this field of research.

Our work on the study of heteroaromatic compounds has focused on the generation and characterization of benzo-fused analogs of bis- π -excessive heterocinyl anions **1b** – **1d**, which are iso- π -electronic with the aromatic 10 π -electron cyclooctatetraene dianion **1a** [4] (Fig. 1).

In 1987, *Prinzbach* and co-workers [5] reported that the 4-cyano-substituted analogs **2a** – **2c** are also planar aromatic 10 π anions. Theoretically, the development of 'aromatic character' [6] in the $(4n + 2)\pi$ ribbons of **1a** – **1d** and **2a** – **2c** may be discussed in terms of structural demand imposed by π -electron mobility on the corresponding eight-membered rings, *i.e.*, in terms of factors that primarily influence the transformation of the flexible molecular frame from buckled to flat, energetics of which are governed by the well-known free-energy relationship (Eqn. 1).

$$\Delta G_0 (\text{B} \rightarrow \text{P}) = \Delta H_0^\pi + \Delta H_0^\sigma - T \Delta S_0. \quad (1)$$

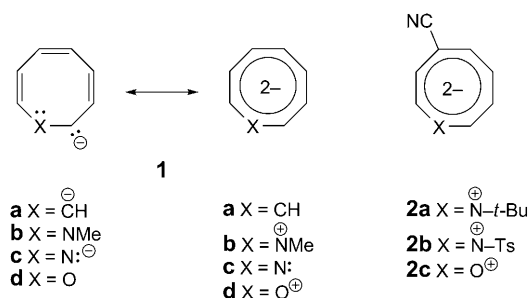
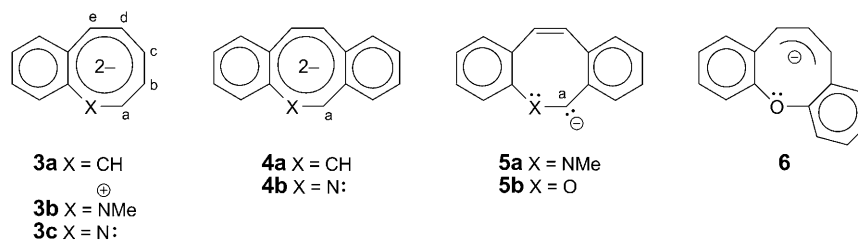


Fig. 1. Heterocynyl anions

Within a specified direction of change, *i.e.*, buckled (B) to planar (P), ΔH_0^π (a negative quantity for $(4n+2)\pi$ systems) denotes the stabilizing influence of electron delocalization, ΔH_0^σ (a positive quantity) represents the destabilizing effect of sigma strain, and ΔS_0 (a negative quantity) describes the loss of molecular flexibility attending the change from buckled to planar. In the case of the five-membered-ring heterocycles pyrrole and furan which are skeletally less flexible and strain-free, the ΔH_0^π term is the controlling factor in the development of the aromatic character. For the eight-membered rings in **1a–1d** and **2a–2c**, the effects of the ΔH_0^π and $\Delta H_0^\sigma - T \Delta S_0$ terms oppose each other, and the former has to exert a controlling influence for the system to develop a planar delocalized frame.

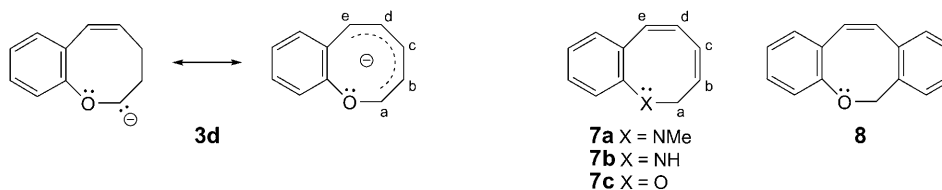
In a closer examination, one observes that, while the extent of the development of ‘aromatic character’ in the five-membered-ring heterocycles follows the decreasing order of pyrrole > furan due to the electronegativity effect of the heteroatom [7], the extent of heteroatomic lone-pair participation in cyclic delocalization in heterocynyl anions **2a–2c** does not appear to play a significant role in the development of aromaticity. Thus **2c**, carrying the electronegative heteroatom O sustains a diatropic character as does **2a**, which contains the electron-rich-alkyl substituted heteroatom N. This phenomenon may be explained in terms of *Eqn. 1*, where the stabilizing influence of $(4n+2)\pi$ -electron delocalization (ΔH_0^π) in **2a–2c** more than compensates for the combined destabilization introduced by the electron-repulsion component, skeletal strain, and reduced molecular flexibility ($\Delta H_0^\sigma - T \Delta S_0$).

We have been interested in studying the effect of further perturbation caused by benzo-fusion on the development of aromaticity in eight-membered-ring heterocynyl anions. In the case of the cyclooctatetraene dianion **1a**, it has been documented that the π -electron delocalization persists under the adverse effect of benzo-fusion, and in fact benzocyclooctene dianion **3a** [8] and the dibenzo analog **4a** [9] (*Fig. 2*) were found to be 14π - and 18π -electron diatropic systems, respectively. On the other hand, in the case of anions **1b–1d**, the persistence of the aromatic character under the benzo-fusion is expected to modulate with the electronegativity of the heteroatomic center. In fact, our earlier studies indicate that while the monobenzo members **3b** and **3c** are planar diatropic anions [10], in the dibenzo series [10], only **4b** containing an N-atom with a higher lone-pair mobility is found to have a flattened central ring with a diatropic character, whereas the *N*-methyldibenzoazocynyl anion **5a** [11] distinctly lacks the type of π -frame stability normally associated with ‘aromatic’ systems.

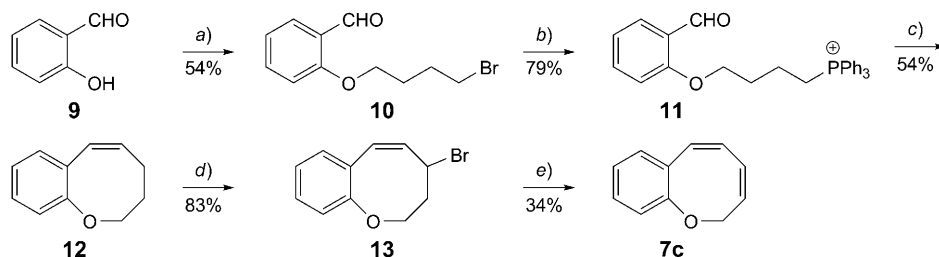
Fig. 2. Benzo- and Dibenzoheterocynyl Anions **3–6**

The central question of how does the 10π -electron oxocynyl anion **1d** compare with benzene in terms of π -electron delocalization, and what effect will the perturbation of benzo-fusion have on its π -delocalization largely remains unanswered to date. We have shown that a nonlinear dibenzo-fused derivative **6** does not contain a diatropic central 8-membered ring [12]. The lack of aromaticity in **6** is presumably due to a periphery-induced ('peri' H-H) [13] skeletal inability of the central ring to adopt a planar geometry.

In this work, we describe the synthesis of a conjugate-acid precursor of the anion *2H*-1-benzoxocinide (**3d**), namely *2H*-1-benzoxocin (**7c**) and the generation and NMR characterization of **3d**. The generation of a linearly dibenzo-fused oxocynyl anion, namely *6H*-dibenz[*b,f*]oxocinide (**5b**), from its precursor **8** [14] (Fig. 3), will also be included, and the chemical reactivities of anions **3d** and **5b** will be discussed. Finally, the results of an *ab initio* calculation at the 6-31g* level on the anions **1c** and **1d**, and on the benzo-fused analogs **3c** and **3d** along with the corresponding conjugate-acid precursors shown in the Table (*cf.* below) will be presented and discussed.

Fig. 3. *2H*-1-Benzoxocin-2-ide (**3d**), *2H*-1-benzheterocins **7a–7c**, and *6H*-dibenz[*b,f*]oxocin (**8**)

Results and Discussion. – *Syntheses.* The synthesis of *2H*-1-benzoxocin (**7c**) is shown in Scheme 1. The preparation of the key intermediate **12** is based on the procedures prescribed by Schweizer and co-workers [15] with some modifications to improve the yields. In the reported procedures, the phosphonium salt **11** (obtained from **9** via **10**) was treated with EtONa in DMF to yield **12** along with an isomeric compound (95:5 ratio) in 19% yield. In our procedure, **12** was obtained in 54% yield by slow addition of the slurry of excess *t*-BuOK in DMF to a refluxing dilute solution of **11**. It is noteworthy to point out that a dihydro derivative of **12**, namely, (+)-helianane [16a], a marine natural product (synthesis reported in 1974 [16b]), as well as the sunflower-derived close relative heliannuol A [17] have been investigated for their bioactivity.

Scheme 1. Synthesis of 2H-1-Benzoxocin (**7c**)

a) $\text{Br}(\text{CH}_2)_4\text{Br}$, OH^- . b) Ph_3P , AcOEt . c) $t\text{-BuOK}$, DMF , reflux. d) NBS , CCl_4 , $h\nu$. e) DBU , NaI , MeCN , 0° .

Allylic bromination of **12** with *N*-bromosuccinimide (NBS) under light catalysis yielded **13** in a quantitative yield, and chromatography at -20° afforded pure **13** in 83% yield. The elimination of HBr from **13** was best achieved by treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of NaI in MeCN at 0° . The crude product was chromatographed at -20° to afford pure **7c** in 34% yield. This compound is thermally unstable at room temperature and had to be stored in a freezer.

The synthesis of 6*H*-dibenz[*b,f*]oxocin (**8**), the precursor for anion **5b**, was accomplished according to the published method [14].

Generation and Characterization of Anions. 2*H*-1-Benzoxocin-2-ide (**3d**). Exposure of the conjugate-acid precursor **7c** to KNH_2/NH_3 (liq.) at -78° followed by warming to 0° , which was necessary to obtain a homogeneous solution for the NMR measurement, resulted in the formation of an intensely colored solution. The recorded ^1H -NMR spectrum (Fig. 4) was consistent with the structure of anion **3d**.

To assess the diatropicity of **3d**, we compared the key features of the ^1H -NMR spectrum of **3d** with those of **2c** and **3c** and with those of their corresponding conjugate acids **7c**, **14**, and **7b**, respectively (Fig. 4). Notable in these comparisons are:

1) On passing from the conjugate-acid progenitors to the corresponding anions, the observed NMR-chemical-shift changes (in ppm) *i*) for the H-atoms of the former sp^3 C-atoms (**2c** ($\text{H}-\text{C}_c$): $\Delta\delta = +2.31$; **3c** ($\text{H}-\text{C}_a$): $\Delta\delta = +3.4$; **3d** ($\text{H}-\text{C}_a$): $\Delta\delta = -0.31$) and *ii*) for the key $\text{H}-\text{C}_a$ of **2c** ($\Delta\delta = +0.62$) and $\text{H}-\text{C}_c$ of **3c** ($\Delta\delta = -0.02$) and **3d** ($\Delta\delta = -2.9$) are indicative of substantial localization of the negative charge on the C_a-C_c allylic section of the pentadienyl moiety of the eight-membered ring in **3d**, in contrast to **2c** [6] and **3c** [10], which were recognized as delocalized 10π - and 14π -electron systems, respectively.

2) While the average chemical shift of the ring H-atoms in the parent anion **2c** (δ 6.1) is 0.15 ppm higher than the corresponding H-atoms of the conjugate-acid precursor (δ 5.96), in the case of **3d**, the average chemical shift of the eight-membered-ring H-atoms (δ 5.11) is 0.80 ppm lower than that of **7c** (δ 5.91 for 4 olefinic H-atoms). The comparison of the average chemical shift of the eight-membered-ring H-atoms indicate that, while in **2c** the expected high-field shift of the H-signals as a result of higher electron density in the anion, compared to its conjugate acid, is offset by a diamagnetic-ring-current effect, such an effect does not appear to be present in **3d**.

3) In contrast to the N-analog **3c**, where there is a downfield shift of NMR signals for some of the benzo H-atoms [10] on the transformation of **7b** to **3c**, we observed an

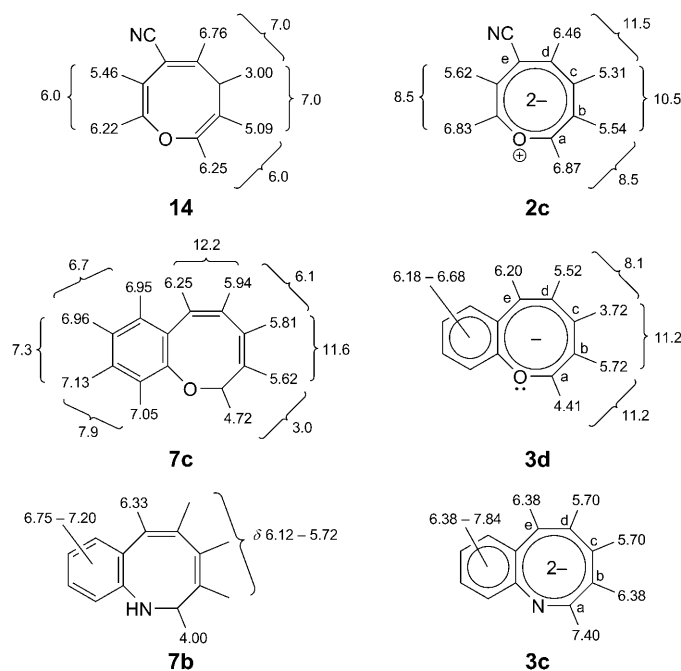


Fig. 4. ^1H -NMR Data (δ in ppm, J in Hz) for Anions **2c**, **3c**, **3d**, and the corresponding conjugate-acid precursors **14**, **7b**, and **7c**. For convenience, the H-atoms at the cyclic structures are represented by their bonds (without attached H).

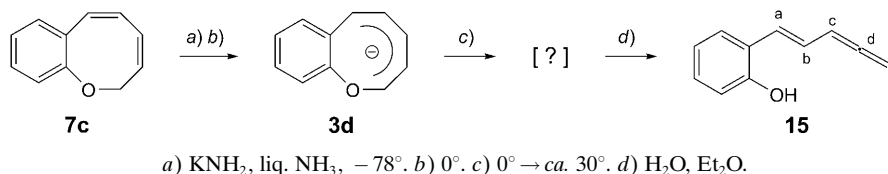
upfield shift of these signals in going from **7c** (δ 6.96–7.13) to **3d** (δ 6.18–6.68). This upfield shift of aromatic H-atoms is typical of systems such as diphenylmethanide [18] and the atropic dibenzo member of the oxocinide family, namely anion **6** [12]. Thus, the NMR data presented above are not consistent with a diamagnetic 10π - or 14π -system, and **3d** must largely be regarded as a conventional system, *i.e.*, one in which the negative charge is primarily localized in the pentadienyl moiety of the eight-membered ring, but also partial delocalization of π -electron density onto the benzo moiety has occurred.

From a chemical view point, it is noteworthy that anion **3d** is thermally less stable than the cyano-substituted parent anion **2c** (stable at room temperature for several hours [6]). This instability did not allow us to obtain a clean ^{13}C -NMR spectrum of **3d** nor was it possible to obtain clean identifiable product(s) from the H_2O quench experiments at 0° .

Specifically, when the NMR solution of **3d** was gradually warmed from 0° to *ca.* 30° (NMR-probe temp.), a gradual change in the observed NMR spectrum occurred right after a few scans. Continued recording of the spectrum led to one which did not exhibit any quantitative or qualitative change at probe temperature. This transformation of anion **3d** to another stable species occurred with an estimated half-life of 20 min. Although from the recorded ^1H - and ^{13}C -NMR spectra we were not able to assign a

structure for the rearranged anion, we could identify the product isolated after quenching with H₂O as compound **15** (38% yield), a pale yellow solid (Scheme 2).

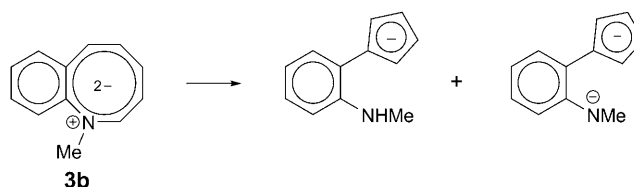
Scheme 2. Generation, Rearrangement, and H₂O-Quench Product of **3d**



The characterization of **15** was achieved by careful analysis of its mass spectrum as well as ¹H- and ¹³C-NMR and IR spectra. The key features of the NMR and IR spectra included: 1) In the ¹H-NMR, the high-field *d* at δ 4.8 (*J*(H_e,H_c) = 6.6 Hz) is assigned to 2 H–C_e. H–C_c appears as a *m* at δ 5.85–6.25, and signals due to H_a and H_b appear as *ms* along with aromatic H-atoms at δ 6.49–7.56. The OH H-atom resonance coincides with that of the 2 H–C_e at δ 4.8. Addition of the shift reagent [Eu^{III}(fod)₃] causes a downfield shift of the OH signal as expected. The chemical shifts of H_a to H_e, however, remain unchanged, presumably due to the large steric effect [19] present in the resulting complex with the shift reagent. 2) In the ¹³C-NMR spectrum, the resonances at δ 77.36 (*t*, *J*(C,H) = 168.3 Hz) and 95.15 (*d*, *J*(C,H) = 166.0 Hz) are assigned to C_e and C_c, respectively. The C_a and C_b resonances are observed at δ 116.5 (*d*, *J*(C,H) = 155.8 Hz) and/or 121.83 (*d*, *J*(C,H) = 156.3 Hz), and the allenic C_d gives rise to a typical downfield-shifted signal at δ 214.8 [20]. 3) In the IR spectrum, frequencies at 1928 (C=C=C stretching) and 858 cm^{–1} (=CH₂ bending) are clear indications of the presence of an allene functionality [21] in **15**. The proposed (*E*) configuration of the olefinic bond in **15** also follows from the IR absorption at 969 cm^{–1} due to the out-of-plane deformation of the *trans*-positioned C–H bonds [21].

It is noteworthy that the thermal reorganization of **3d**, as described above, took a different pathway compared to that of the more stable diatropic N-atom counterpart **3b**, which occurred under the same condition according to Scheme 3 [10].

Scheme 3. Rearrangement of 1-Methyl-1-benzazocin-2(1H)-ide Anion (**3b**)



Finally, to complement our experimental results on the nature of anion **3d**, we carried out an *ab initio* MO calculation at the restricted *Hartree–Fock* SCF level by using a 6-31 G* basis set [22] on the conjugate-acid precursors **1d**·H⁺, **7b**, and **7c** and the corresponding anions **1d**, **3c**, and **3d**, respectively. We might add that *i*) this level of quantum-mechanical calculation has been assessed as good for obtaining the equilibrium geometries of medium-sized organic molecules containing heteroatoms [23], and *ii*) in the discussion of the calculated bond-length alternation as a structural

criterion of aromaticity [24a] (see below), we note that according to *Kertesz* and co-workers [24b], in general, the *Hartree–Fock* calculations tend to overestimate the degree of bond-length alternation in both conjugated molecules and extended systems.

Our calculated structural parameters for the above-mentioned molecules are provided in the *Table*. The numbering of atoms and angles referred to therein as well as the calculated *Mulliken* atomic charges [25] are shown in *Fig. 5*.

Focusing on the crucial structural requirements of aromaticity in cyclic systems, namely, *i*) achieving a planar geometry which allows maximum delocalization of π -electrons, and *ii*) achieving bond equalization in the ring, our calculated results clearly indicate that 1) the *2H*-oxocin \rightarrow *2H*-oxocinide transition is accompanied by a geometry transformation from a half-chair-like geometry to a planar one (*Fig. 6*),

Table. Calculated Structural Parameters^{a)} for **14**, **1d**, **7b**, **3c**, **7c**, and **3d**^{b)}

	X = O		X = NH		X = O	
	1d ·H ⁺	1d	7b	3c	7c	3d
X–C(1)	1.336	1.347	1.394	1.347	1.351	1.366
C(1)–C(2)	1.330	1.348	1.404	1.467	1.399	1.412
C(2)–C(3)	1.476	1.424	1.496	1.426	1.493	1.438
C(3)–C(4)	1.329	1.383	1.326	1.401	1.327	1.394
C(4)–C(5)	1.470	1.383	1.474	1.380	1.470	1.380
C(5)–C(6)	1.323	1.424	1.322	1.418	1.322	1.438
C(6)–C(7)	1.504	1.348	1.511	1.382	1.503	1.329
C(7)–X	1.414	1.347	1.450	1.332	1.408	1.373
C(2)–C(8)	–	–	1.401	1.436	1.406	1.416
C(8)–C(9)	–	–	1.375	1.365	1.373	1.379
C(9)–C(10)	–	–	1.388	1.411	1.390	1.387
C(10)–C(11)	–	–	1.373	1.367	1.372	1.388
C(11)–C(1)	–	–	1.405	1.434	1.399	1.380
C(1)–X–C(7)	119.6	133.6	125.1	135.4	123.8	123.7
X–C(7)–C(6)	113.1	135.2	115.4	140.0	113.0	123.7
C(7)–C(6)–C(5)	124.2	138.9	123.8	134.5	123.0	130.1
C(6)–C(5)–C(4)	125.1	131.9	122.9	131.5	123.3	129.0
C(5)–C(4)–C(3)	126.6	134.6	126.0	136.0	126.4	138.5
C(4)–C(3)–C(2)	130.9	131.9	130.1	137.4	131.3	134.0
C(3)–C(2)–C(1)	134.5	138.9	128.9	131.4	130.2	127.2
C(2)–C(1)–X	133.0	135.2	126.8	133.9	128.9	120.9
C(11)–C(1)–X–C(7)	–	–	162.7	180.0	–175.9	–103.3
C(1)–X–C(7)–C(6)	73.6	0.13	–54.2	–0.21	68.7	–90.0
X–C(7)–C(6)–C(5)	–92.6	–0.07	89.3	0.21	–93.0	8.3
C(7)–C(6)–C(5)–C(4)	2.8	0.08	–1.3	0.11	1.5	23.6
C(6)–C(5)–C(5)–C(3)	43.7	–0.03	–51.1	–0.11	46.9	3.8
C(5)–C(4)–C(3)–C(2)	4.9	–0.08	–9.9	–0.2	9.4	–6.2
C(4)–C(3)–C(2)–C(1)	–39.9	–0.03	54.4	0.2	–48.0	–22.0
C(3)–C(2)–C(1)–X	–1.74	–0.08	4.53	0.0	–2.9	–3.8
C(2)–C(1)–X–C(7)	–1.68	0.00	–21.1	0.0	6.5	82.2
C(8)–C(2)–C(3)–C(4)	–	–	–126.5	–179.8	132.9	161.6

^{a)} Bond length [Å], angles [°], and dihedral angle [°], calculated by *ab initio Hartree–Fock* SCF with the 6-31 G* basis set. ^{b)} See *Fig. 5* for structures, atom numbering, and definitions of angles.

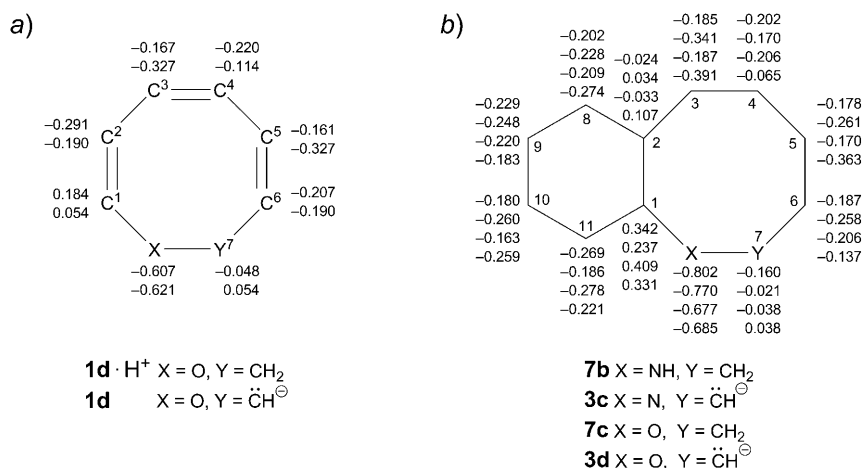


Fig. 5. Mulliken *atomic-charge distribution* a) of $1d \cdot H^+$ and $1d$, and b) of $7b$, $3c$, $7c$, and $3d$. Arbitrary atom numbering.

that 2) in the benzo-fused series, while $3c$ is nearly planar, the oxygen analog $3d$ contains a fairly buckled eight-membered-ring moiety with the O-atom lying out-of-plane of the molecule (Fig. 6), and that 3) benzo-fusion of $2H$ -oxocin does not affect the bond lengths of the oxocin ring significantly (the average bond-length alternation among eight bonds of the ring changes by 0.002 Å on going from $1d \cdot H^+$ to $7c$), while the conversion of $1d$ to $3d$ is accompanied by a significant bond alternation in the oxocinide moiety (the average bond-length alternation of the eight-membered ring changes by 0.010 Å).

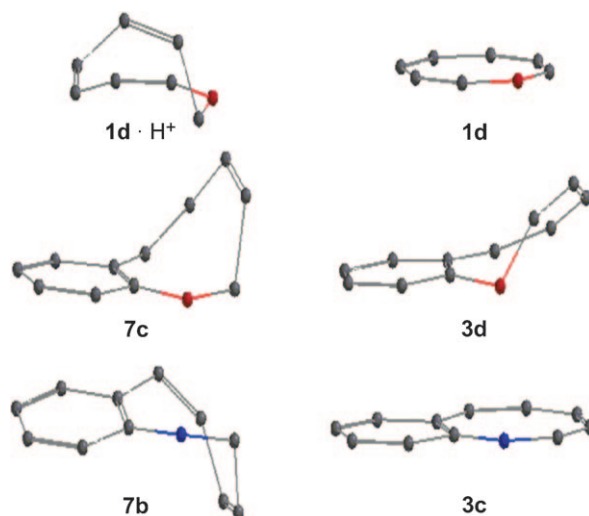


Fig. 6. Calculated equilibrium geometries of anions $1d$, $3c$, and $3d$, and their respective conjugate acids $1d \cdot H^+$, $7b$, and $7c$

We have also determined the charge distribution in **3c** and **3d** in the form of electrostatic-potential (ESP) surfaces (Fig. 7). While the calculated electronic structure indicates a substantially uniform charge distribution over the azocinyl moiety in **3c**, with some of the extra negative charge remaining on the anionic N-atom, there is significant electron density remaining on the sp^2 -hybridized O-atom in **3d**, and partial charge distributions on the pentadienyl moiety as well as on the benzo moiety are indicated, which are all consistent with our NMR studies discussed above.

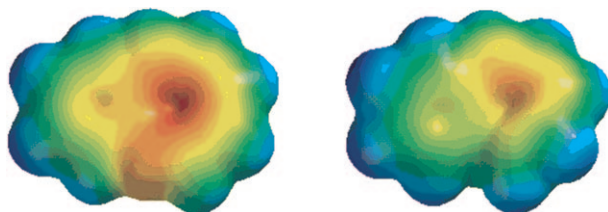


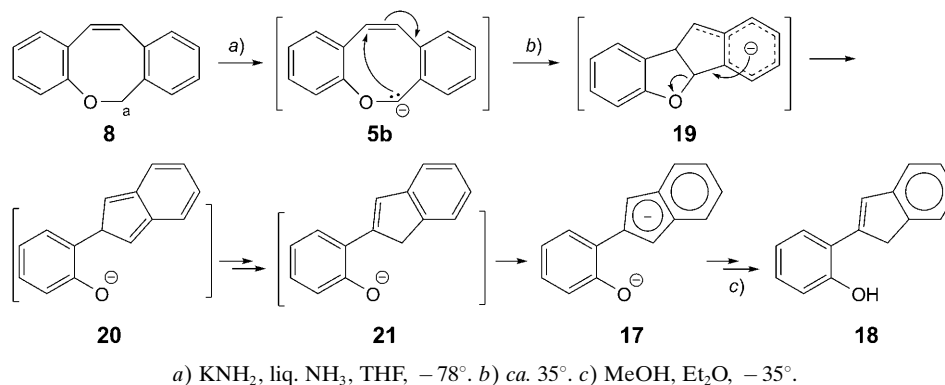
Fig. 7. Electrostatic-potential surfaces of **3c** (left) and **3d** (right) at the 0.002 electron a.u.⁻³ density iso-contour levels of -966.9 to -511.6 kJ mol⁻¹ and -596.3 to -210.8 kJ mol⁻¹, respectively

In conclusion, based on the magnetic criteria [26] (¹H-NMR chemical-shift studies) as well as the calculated structure (geometry and bond-alternation criteria [26]) discussed above, we conclude that the anion 2*H*-benzoxocinide (**3d**) lacks complete π -electron delocalization over the periphery of the eight-membered-ring moiety, and therefore, it may be classified as containing a nonaromatic (atropic) oxocinide ring. We attribute this loss of aromaticity in the oxocin moiety to the benzo-fusion, which perturbs the system to an extent that the heteroatom (O) electronegativity becomes a deciding factor in development of a completely delocalized oxocinide anion.

6H-Dibenz[b,f]oxocin-6-ide (5b). Exposure of the conjugate-acid precursor **8** dissolved in (D₈)THF to KNH₂/NH₃ (liq.) at -78° followed by warming to 0° resulted in an intensely colored solution. An immediate ¹H-NMR scan revealed the presence of an anion other than the expected anion **5b**. The observed spectrum did not change qualitatively or quantitatively with time indicating the presence of a stable species, which was characterized as the rearranged dianion **17** on the basis of ¹H-NMR absorptions (a series of *ms* at δ 6.0–7.5) and its proton-quenched product **18**. In an attempt to confirm the formation of **5b** prior to its rearrangement, **8** was treated with KNH₂/NH₃ (liq.) at -78° in THF, and the resulting mixture was warmed to -35° , stirred at this temperature for 1 h, and then quenched by dropwise addition of MeOH/Et₂O at -35° . The isolated product was characterized to be exclusively compound **18** (Scheme 4).

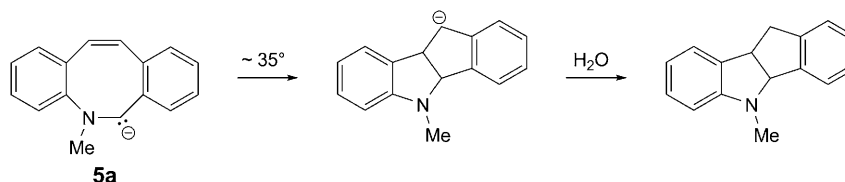
Characterization of **18**, a yellow solid, was established by its mass spectrum (m/z 208 (100%, M^+)), ¹H-NMR (signals due to aromatic H-atoms, a *s* at δ 3.86 assigned to CH₂ H-atoms, and a broad absorption at δ 5.1–5.6 due to the OH group, which disappeared in the presence of added D₂O), ¹³C-NMR (absorptions due to a benzene ring plus a *t* at δ 40.93 with $J(\text{C,H}) = 125.3$ Hz due to the CH₂ group), and IR spectrum (3519 cm^{-1} (O–H stretching) and 2922 cm^{-1} (CH₂ stretching)).

Mechanistically, the reorganization of **5b** to **17** is quite likely intermediated by formation of compounds **19**, **20**, and **21** as shown in Scheme 4 and is expected to be

Scheme 4. Generation and Thermal Reorganization of Anion **5b** to **17** and Formation of **18**

driven by the formation of the aromatically stabilized indenyl anion moiety present in **17**. This proposed mechanism carries credence from the observed rearrangement of the benzazocinyl anion **3b** shown in *Scheme 3* above.

It is worth noting that in the case of the more stable dibenzazocinyl analog **5a** [11], the rearrangement took a distinctly different pathway as shown in *Scheme 5*.

Scheme 5. Rearrangement of **5a** [11]

In conclusion, whereas the failure to directly observe the desired anion **5b** precludes the determination of the presence or absence of ring diatropicity, the observed rapid rearrangement into **17** indicates that: *i*) The linearly dibenzo-fused oxocinyl anion **5b** clearly is less stable than the monobenzo-fused anion **3d**; *ii*) **5b** also lacks the type of π -frame stability normally associated with ‘aromatic’ systems, and *iii*) the linearly dibenzo-fused oxocinyl anion is less stable than the nonlinear analog **6** [12].

Experimental Part

General. All chemicals were purchased from *Aldrich* or *Fischer Scientific* and used without purification unless stated otherwise. DMF and MeCN were refluxed over CaH_2 and distilled prior to their use. THF was refluxed over Na and benzophenone until a blue-violet color persisted and distilled before use. Compounds **11** [15] and **12** [15] were prepared according to the previously published procedures: Column chromatography = CC. IR Spectra: *Matteson-Polaris* FT-IR spectrometer; $\tilde{\nu}$ in cm^{-1} . ^1H - (90 and 500 MHz) and ^{13}C -NMR (22.5 and 125 MHz) Spectra: *JOEL-FX-90Q* and *Bruker-DRX-500* spectrometers, resp.; CDCl_3 solns.; δ in ppm rel. to Me_4Si as internal standard, J in Hz; spectra of anions were recorded in liq. NH_3 containing $(\text{D}_8)\text{THF}$ as an internal standard, and the $\delta(\text{H})$ and $\delta(\text{C})$ were measured from the central signal of the lowfield m of $(\text{D}_8)\text{THF}$ ($\delta(\text{H})$ 3.70 and $\delta(\text{C})$ 67.9 with respect to SiMe_4) and

reported rel. to Me₄Si. MS: JOEL sector-type spectrometer; in *m/z* (with the lowest isotope mass) (rel. %). The theoretical calculations were carried out with the program Spartan '06 [27].

3,4-Dihydro-2H-1-benzoxocin (12) [15]. *Modified Procedure*: To a refluxing soln. of phosphonium bromide **11** (2.0 g, 3.85 mmol) in dry DMF (20 ml) under N₂ was added a slurry of *t*-BuOK (0.60 g, 5 mmol) in DMF (13 ml) within 3.0 h. After reflux for an additional hour, the mixture was cooled to r.t. and poured into dist. H₂O (15 ml). The org. layer was extracted with Et₂O (3 × 50 ml) and the combined Et₂O layer washed with H₂O (50 ml), dried (anh. MgSO₄), and concentrated. The obtained sticky white solid (1.48 g) was triturated with AcOEt/petroleum ether (PE) 10:90 which dissolved 0.427 g of the crude mixture. The decanted soln. was subjected to CC (25 × 2 cm column, SiO₂ (230–400 mesh), packed and eluted with Et₂O/PE 10:90): **12** (309 mg, 50%). Pale oil. ¹H-NMR: identical with the published one [15].

4-Bromo-2,3-dihydro-2H-1-benzoxocin (13). To a soln. of **12** (0.50 g, 3.12 mmol) in freshly dist. CCl₄ (3.7 ml) was added *N*-bromosuccinimide (NBS; 0.61 g, 3.43 mmol). The resulting soln. was heated to reflux under N₂ and irradiated with direct light from a 200 W light bulb for 5.5 h. The mixture was cooled to r.t., the precipitated succinimide filtered off, and the filtrate evaporated at 0° to afford 720 mg (96%) of a yellowish oil. The oil was subjected to CC (jacketed column, SiO₂ (30 g, 230–400 mesh) wet-packed at 0° under N₂; the column temp. was lowered to –20° before elution with Et₂O/PE 5:95. Three fractions (20 ml), each collected at 0° and under N₂ were combined and evaporated at 0°: **13** (597 mg, 83%). Colorless oil. ¹H-NMR (90 MHz, CDCl₃): 2.24 (*m*, 2 H); 4.20 (*m*, 1 H); 4.50 (*m*, 1 H); 5.02 (*m*, 1 H); 5.96 (*dd*, *J* = 12.2, 5.1, 1 H); 6.27 (*d*, *J* = 12.2, 1 H); 7.1 (*m*, 4 H). ¹³C-NMR (22.5 MHz, CDCl₃): 33.3 (*t*, *J* = 131.7); 49.8 (*d*, *J* = 150.2); 70.9 (*t*, *J* = 144.5); 122.4 (*d*, *J* = 166.0); 123.7 (*d*, *J* = 168.4); 125.6 (*d*, *J* = 157.5); 128.1(*s*); 129.8 (*d*, *J* = 168.4); 131.0 (*d*, *J* = 167.2); 131.8 (*d*, *J* = 166.0); 154.9 (*s*).

2H-1-Benzoxocin (7c). A mixture of **13** (180 mg, 0.75 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 230 mg, 1.51 mmol), and NaI (900 mg, 6.0 mmol) in freshly dist. MeCN (11 ml) was stirred at 0° under N₂ for 8 h. H₂O (20 ml) was added to the resulting mixture, the aq. layer extracted with Et₂O (2 × 15 ml), the combined Et₂O layer successively washed with 5% H₂SO₄ soln. (15 ml), 5% NaHCO₃ soln. (15 ml), aq. sat. NaCl soln. (15 ml), and H₂O (15 ml), dried (MgSO₄), and concentrated at 0°: 80 mg (67%) of a yellow oil. The crude oil was subjected to CC (jacketed column, SiO₂ (25 g, 230–400 mesh) wet-packed with Et₂O/PE 5:95 at 0° under N₂ and eluted with the same solvent at –20°: **7c** (40 mg, 34%). Colorless oil. ¹H-NMR (500 MHz, CDCl₃): 4.72 (*d*, *J* = 3, 2 H); 5.62 (*dt*, *J* = 11.6, 3, 1 H); 5.81 (*dd*, *J* = 11.6, 6.1, 1 H); 5.94 (*dd*, *J* = 12.2, 6.1, 1 H); 6.25 (*d*, *J* = 12.2, 1 H); 6.95 (*d*, *J* = 6.7, 1 H); 6.96 (*dd*, *J* = 6.7, 7.3, 1 H); 7.05 (*d*, *J* = 7.9, 1 H); 7.13 (*dd*, *J* = 7.9, 7.3, 1 H). ¹³C-NMR (125 MHz, CDCl₃): 75.7 (1 C); 116.1 (1 C); 116.4 (1 C); 120.2 (1 C); 121.2 (1 C); 123.9 (1 C); 124.3 (1 C); 126.6 (1 C); 129.3 (1 C); 136.6 (1 C); 153.1 (1 C). MS: 158 (100, *M*⁺).

Generation of Anion 3d. A medium-wall 9 in. NMR tube containing KNH₂ in liq. NH₃ (prepared from K (80 mg, 2.0 mmol), liq. NH₃ (0.5 ml), and a small crystal of FeCl₃) maintained at –78° was charged with a soln. of **7c** (90 mg, 0.57 mmol) in (D₈)THF (*ca.* 0.5 ml). A glass-wool plug was pushed about half way down into the tube, and the tube was carefully sealed under room pressure. The tube then was placed in a dry ice/acetone bath at –30° for a few minutes, and then it was inverted into a –78° bath, allowing the dark soln. to filter through the glass-wool plug. The tube was warmed to *ca.* 35° for *ca.* 5 min and then placed in an ice-bath for 5 min and then the NMR spectrum recorded immediately at the probe temp. ¹H-NMR (90 MHz, liq. NH₃): 3.72 (*dd*, *J* = 11.2, 8.1, 1 H); 4.41 (*d*, *J* = 11.2, 1 H); 5.51 (*dd*, *J* = 8.1, 5.2, 1 H); 5.72 (*t*, *J* = 11.2, 1 H); 6.20 (*d*, *J* = 5.2, 1 H); 6.18 and 6.68 (*m*, 4 H).

Water-Quench Product of the Rearranged Anion: 2-(Penta-1,3,4-trien-1-yl)phenol (15). The NMR tube containing anion **7c** in liq. NH₃ (prepared from 90 mg of **8c** as described above), was warmed to r.t. and then to –35° and cut open. The contents were poured into a degassed mixture of Et₂O (100 ml) and H₂O (30 ml) at 0° under N₂. The mixture was stirred for 0.5 h, the org. layer washed with H₂O (2 × 25 ml) and sat. NaCl soln. (2 × 20 ml), dried (anh. MgSO₄), and concentrated at 0°, and the crude yellow oil (80 mg, 89%) subjected to CC (SiO₂ (25 g, 230–400 mesh), wet-packed with PE, elution with Et₂O/PE 20:80): **15** (30 mg, 43%). Pale solid. M.p. 119–121°. IR (KBr): 3369s (OH), 1928s (C=C=C stretching), 969s (*trans* CH=CH), 858m (=CH₂ bending). ¹H-NMR (90 MHz, CDCl₃): 4.80 (*d*, overlapping OH signal, *J* = 6.6, 2 H–C_e, OH); 5.85–6.25 (*m*, H–C_e); 6.49–7.56 (*m*, H–C_a, H–C_b, 4 arom. H). ¹³C-NMR (22.5 MHz, CDCl₃): 77.36 (*t*, *J* = 126.8, C_e); 95.15 (*d*, *J* = 166.0, C_e); 116.50 (*d*, *J* = 155.8, 1 C); 121.83 (*d*,

$J = 156.3$, 1 C); 125.39 (d , $J = 156.2$, 1 C); 126.28 (d , $J = 156.3$, 1 C); 128.06 (d , $J = 156.3$, 1 C); 128.95 (d , $J = 161.2$, 1 C); 131.17 (s , 1 C), 153.85 (s , 1 C); 214.76 (s , C_d). MS: 158 (93, M^+), 141 (47, $[M - 17]^+$), 77 (100, $[M - 18]^+$).

2-(1*H*-Inden-2-yl)phenol (**18**). To a soln. of KNH_2 in liq. NH_3 prepared from K (180 mg, 4.0 mmol), a few crystals of FeCl_3 , and liq. NH_3 (30 ml) was added at -78° under N_2 a soln. of 6*H*-dibenz[*b,f*]oxocin (**8**; 208 mg, 1.0 mmol) in anh. THF (7 ml). The resulting soln. was gradually warmed to -35° and stirred at -35° for 1 h. A mixture of MeOH (30 ml) and Et_2O (100 ml) was added dropwise to the mixture. The org. layer was washed with H_2O (2×25 ml) and sat. NaCl soln. (2×20 ml), dried (anh. MgSO_4), and concentrated at 0° . The obtained yellow oil (190 mg, 91%) was subjected to CC (SiO_2 (25 g, 230–400 mesh), $\text{Et}_2\text{O}/\text{PE}$ 20:80): **18** (40 mg, 21%). Yellow solid. M.p. $170\text{--}173^\circ$. IR (CHCl_3): 3519 (OH), 2922 (CH_2). ^1H -NMR (90 MHz, CDCl_3): 3.86 (s , 2 H); 5.14–5.56 (m , 1 H); 6.79–7.55 ($br.$, 9 H). ^{13}C -NMR (22.5 MHz, CDCl_3): 42.36 (1 C); 117.2 (1 C); 121.8 (1 C); 122.1 (1 C); 124.5 (1 C); 125.9 (1 C); 127.6 (1 C); 129.5 (1 C); 129.7 (1 C); 130.9 (1 C); 131.9 (1 C); 143.7 (1 C); 144.0 (1 C); 146.3 (1 C); 154.2 (1 C). MS: 208 (100, M^+); 115 (46, $[M - 93]^+$).

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Received December 2, 2009