Aromaticity of Annelated Borepins

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Significant C−C bond length alternation ($\Delta r = 0.047$ Å), very low aromatic stabilization energy (ASE = −5.1 kcal/mol), magnetic susceptibility anisotropy (χ_{anis} = −83.1 ppm cgs), and exaltation (Λ = −13.8 ppm cgs), as well as the nucleus-independent chemical shifts (NICS(0), −3.7 ppm) demonstrate borepin to be much less aromatic than the tropylium ion. The B3LYP/6-311+G** relative stabilities of annelated borepin positional isomers isoelectronic with azulene (**1a**) and the benzotropylium cation (**1b**), e.g., the boraazulene anion (**2c** > **2b** > **2a**) and the benzo-fused borepins (**5c** > **5b** > **5a**), are in accord with the topological charge stabilization rule. However, the aromaticity orderings (**2a** > **2b** > **2c**; **5a** > **5c** > **5b**) are opposite, as deduced from the Δr, χ_{anis}, and NICS values. All the aromaticity criteria support **4X** > **3X** ordering for the heterole-fused borepin positional isomers (**3X**, **4X**; X = NH, S, O), in agreement with their relative stabilities. The NICS(1) values (i.e., computed 1 Å above the ring centers) indicate both of the rings in **1**−**5** to exhibit diatropic ring currents. Nevertheless, the NICS(1) values of the seven-membered rings in **2b** (−5.1 ppm), **2c** (−4.7 ppm), **3X** (−2.4 for X = NH, −1.8 for X = S, and −1.3 ppm for X = O), **5b** (−4.6 ppm), and **5c** (−4.5 ppm) are smaller than that of borepin (−6.9 ppm) and indicate weak π-delocalization. In contrast, the NICS(0) and NICS(1) values suggest that both of the rings in **1a**, **1b**, **2a**, **4X**, and **5a** are delocalized significantly. NICS(1), which minimizes the local contribution from the C−C, C−X, C−H, and C−B σ-bonds, may be a better aromaticity index than NICS-(0). In view of the good agreement with the observed values, the computed ^{1}H, ^{11}B, and ^{13}C NMR chemical shifts should help characterize the unknown annelated borepin isomers.

Introduction

Borirene, the smallest 2π Hückel aromatic, possesses 70% of the resonance energy of the isoelectronic cyclopropenyl cation (69.5 kcal/mol).[1] In striking contrast, the 6-π-electron borepin is much less aromatic than benzene and the tropylium cation.[2] The empirical resonance energy of borepin (12.7 kcal/mol)[3] was computed to be only half of the benzene value (24.7 kcal/mol).[4] Schulman *et al.,*[5] noting the rather substantial C−C bond length alternation (0.106 Å at the STO-3G level), suggested that borepin possesses roughly 40% of the delocalization energy of the tropylium cation.

Borirene   Cyclopropenyl cation

Borepin   Tropylium cation
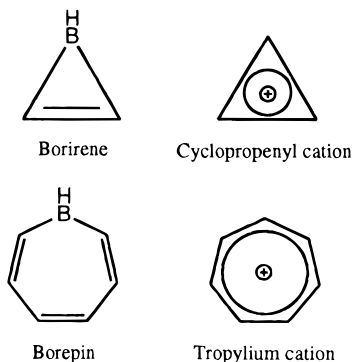
The π-delocalization in heptaphenylborepin was inferred from the UV spectrum (λ_{max} 412 nm) as compared to 405 nm for the heptaphenyltropylium salts.[6a] The downfield ^{1}H NMR chemical shifts of 1-substituted (hydrogen, methyl, mesityl, chloro, etc.) borepins[6g] also indicate the presence of diatropic ring currents. Enhanced delocalization in borepin complexed (η^7 coordination of 1-chloroborepin) to transition-metal fragments (e.g., Mo(CO)$_3$) was suggested by the reduced C−C bond length alternation (Δr = 0.023 Å, X-ray) and the downfield ^{1}H NMR chemical shifts as compared to the free ligand (Δr = 0.058 Å).[7]

Aromaticity[8] can be characterized by geometric (bond length alternation, bond order, and ring current indices),[9] energetic (stabilization energies),[10] and magnetic (^{1}H NMR chemical shifts, diamagnetic susceptibility anisotropy and exaltation, and most recently NICS) cri-

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Chart 1

1a   **1b**   **2c**

3X   (X = NH, S, O)   **4X**   **5c**
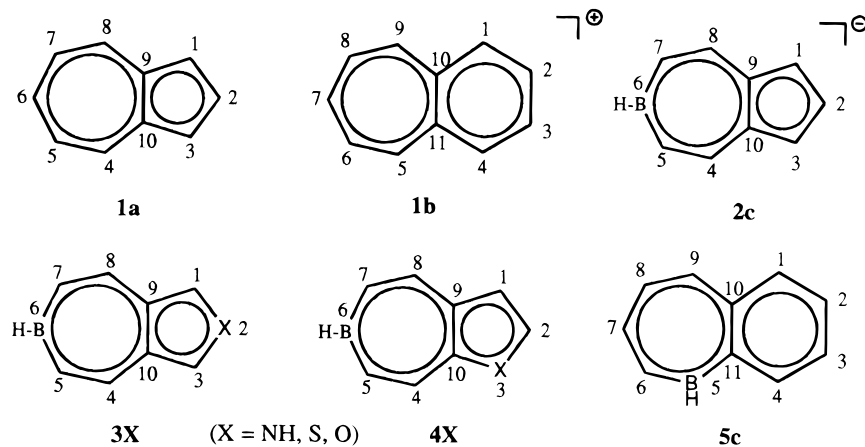
teria.[11,12] The direct quantitative relationships among these criteria were demonstrated for a wide-ranging set of five-membered aromatic and antiaromatic heterocycles.[12,13] However, such direct relationships among the above three criteria did not extend to more complicated systems, e.g., to [5,5]- and [5,6]-fused bicyclic compounds. Deviations were illustrated for furanofuran, thienothiophene, benzofuran, and benzothiophene positional isomers.[14] While enhanced thermodynamic stability[15] of molecules is a manifestation of aromaticity, aromatic stabilization energies are only 1−2% of the total energy

and may be dominated by other effects in more complex systems. Hence, direct relationships between the relative stability of isomers and their aromaticity need not exist.[8c,e] We now extend our systematic studies further to quantify the interrelationships among the various aromaticity criteria for [5,7]- and [6,7]-bicyclic molecules (Chart 1) and compare the aromaticity of azulene (**1a**), its isoelectronic boraazulene anions (**2a−c**), and heterole-fused borepins (**3X** and **4X**, X = NH, S, O), the 10-π-electron benzotropylium cation (**1b**), and the corresponding benzo-fused borepin isomers (**5a−c**). The related monocycles are included for reference.

In contrast to the extensive literature on azulene (**1a**),[16] heterole-fused borepins (**3X**, **4X**; X = NH, S, O) have only been characterized spectroscopically. ^{1}H, ^{11}B, and ^{13}C NMR chemical shifts of substituted (1-methyl or 1-phenyl) derivatives and *ab initio* (HF/3-21G) calculations on the unsubstituted molecules suggested pyrrolo[3,4-*d*]borepin (**3NH**) to be a polarized aromatic molecule.[17] On the basis of ^{1}H NMR data for thieno-[3,4-*d*]borepin (**3S**) and thieno[2,3-*d*]borepin (**4S**),[18] Sugihara *et al.* concluded that **3S** was conjugated "peripherally" and **4S** retained aromatic behavior similar to the component monocycles (borepin and thiophene).[18b] However, both **3S** and **4S** were suggested to be aromatic in a more recent paper.[18c] Our new magnetic criterion of aromaticity, NICS (nucleus-independent chemical shifts), along with diamagnetic susceptibility exaltation and anisotropy helps resolve the nature of **3S** and **4S**. Similarly, substituted derivatives of benzo-fused borepins, **5b**[19] and **5c**,[20] isoelectronic with the benzotropylium cation (**1b**),[21] have been identified spectroscopically (NMR) and the X-ray structure of a transition-metal carbonyl π-complex of **5b** is available. The purpose of this paper is to analyze the structural

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Table 1. Total (E_{tot}, hartrees) and Zero-Point Energies (ZPE, kcal/mol), Magnetic Susceptibilities (χ_M, ppm cgs), Magnetic Susceptibility Anisotropies (χ_{anis}, ppm cgs) and Exaltations (Λ, ppm cgs), Nucleus-Independent Chemical Shifts (NICS, ppm), and Dipole Moments (μ, D) for 1a,b, 3X, and 4X (X = NH, S, O) and Their Corresponding Monocycles

molecule	sym	E_{tot}	ZPE[a]	Δr[b]	χ_M[c]	χ_{anis}[c]	Λ[c]	NICS(0)[d]	NICS(1)[d]	μ[e]
$C_5H_5^-$	D_{5h}	−193.580 76	49.0	0.0	−50.3	−56.5	−18.9	−14.3	−10.6	0.0
C_4H_5N	C_{2v}	−210.230 52	51.6	0.047	−42.7	−44.5	−9.9	−15.0	−10.8	1.9
C_4H_4S	C_{2v}	−553.073 16	41.6	0.062	−50.5	−48.3	−11.9	−13.2	−10.5	0.5
C_4H_4O	C_{2v}	−230.087 85	43.7	0.077	−37.9	−37.5	−6.9	−12.3	−9.3	0.8
C_6H_6	D_{6h}	−232.311 27	62.8	0.0	−51.3	−72.3	−14.2	−9.7	−11.5	0.0
$C_7H_7^+$	D_{7h}	−270.740 26	74.3	0.0	−52.7	−100.0	−19.9	−7.6	−10.7	0.0
C_6H_7B	C_{2v}	−257.741 91	71.0	0.047	−52.1	−83.1	−13.8	−3.7	−6.9	2.2
1a	C_{2v}	−385.935 11	91.2	0.006 (0.002)	−88.3	−147.7	−37.2	−6.9 (−19.7)	−8.8 (−19.4)	1.1
1b	C_{2v}	−424.431 31	103.8	0.009 (0.036)	−89.7	−170.3	−39.3	−7.2 (−11.4)	−10.0 (−13.6)	1.2
3NH	C_{2v}	−389.351 27	89.4	0.073 (0.063)	−70.2	−94.6	−19.6	0.8 (−16.4)	−2.4 (−12.4)	5.6
4NH	C_s	−389.360 51	89.4	0.055 (0.062)	−76.6	−112.2	−24.8	−3.2 (−14.9)	−6.0 (−11.4)	4.6
3S	C_{2v}	−732.187 41	79.2	0.086 (0.074)	−77.1	−92.0	−20.7	1.9 (−14.2)	−1.8 (−11.6)	2.6
4S	C_s	−732.196 88	79.4	0.064 (0.080)	−82.5	−111.0	−25.3	−2.7 (−11.9)	−5.8 (−9.8)	2.8
3O	C_{2v}	−409.203 51	81.3	0.080 (0.086)	−63.3	−80.0	−14.5	2.0 (−13.5)	−1.3 (−10.5)	2.1
4O	C_s	−409.218 59	81.5	0.055 (0.086)	−72.5	−106.3	−22.9	−3.8 (−11.6)	−6.5 (−9.2)	2.9

[a] All structures correspond to minima at the Becke3LYP/6-311+G** level. [b] $\Delta r = r(C-C) - r(C=C)$ in Å. Δr values for the five-membered rings are given in parentheses. [c] At the CSGT-HF/6-31+G*//Becke3LYP/6-311+G** level. [d] Computed at the unweighted geometrical center (NICS(0)) and 1 Å above (NICS(1)) the seven-membered rings at the GIAO-HF/6-31+G*//Becke3LYP/6-311+G** level. The corresponding NICS values for the five-membered rings are given in parentheses. [e] At the Becke3LYP/6-311+G**//Becke3LYP/6-311+G** level.

and magnetic properties of [5,7]- and [6,7]-annelated borepins, **2−5**, and the corresponding monocycles (Figures 1−3) at a uniform level of theory to establish the interrelationships among the various criteria (stability, geometric, energetic and magnetic) of aromaticity.
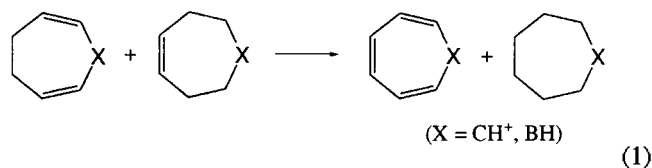
Computational Methods

Structures **1a,b**, **2a−c**, **3X** and **4X** (X = NH, S, O) and **5a−c** were optimized at the Becke3LYP/6-311+G** (B3LYP) level and characterized as energy minima by frequency analysis using the Gaussian 94 program.[22] The magnetic susceptibility anisotropies (χ_{anis}) and exaltations (Λ, CSGT-HF/6-31+G*[23]), the ^1H, ^{11}B, and ^{13}C NMR chemical shifts, and the NICS values (GIAO-HF/6-31+G*)[24] were evaluated for the B3LYP optimized geometries. The structural and magnetic properties of all the molecules are summarized in Tables 1−5 and Figures 1−3.

Results and Discussion

The aromaticity of the five-membered rings[8−13,25] have been established using the Julg index, aromatic stabilization energies (ASE), magnetic susceptibility exalta-

tion (Λ), and NICS.[12,13] All of these criteria, as well as the C−C bond length alternation, Δr (Table 1), as another geometrical measure of aromaticity, give the same $C_4H_4NH > C_4H_4S > C_4H_4O$ aromaticity ordering for the five-membered rings. Likewise, the C−C bond length alternation in borepin ($\Delta r = 0.047$ Å) is considerably smaller than that of the planar cycloheptatriene (C_{2v}; $\Delta r = 0.111$ Å) but significantly larger than in the symmetrical tropylium cation ($\Delta r = 0.0$ Å). Our Δr value for borepin is close to the X-ray data for 1-chloroborepin ($\Delta r = 0.057$ Å),[7b] and the MP2/6-31G* values ($\Delta r = 0.033$ Å for borepin and $\Delta r = 0.041$ Å for 1-chloroborepin).[5c] The ASE's (Becke3LYP/6-311+G**) for X = CH^+ and BH, computed using eq 1 (all species are computed in planar geometries to balance strain as much as possible), also indicate borepin to be a much weaker 6π aromatic (ASE = −5.1 kcal/mol), compared to the isoelectronic tropylium cation (ASE = −16.8 kcal/mol).

(X = CH+, BH)   (1)

Magnetic susceptibility anisotropies (χ_{anis}) and susceptibility exaltations (Λ)[11c−f] are manifestations of ring currents arising from cyclic electron delocalization. Generally, Λ is defined as the difference between the

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Table 2. B3LYP/6-311+G** Optimized Total Energies (E_{tot}, hartrees) and CSGT-HF/6-31+G*// B3LYP/6-311+G** Magnetic Susceptibilities (χ_M, ppm cgs) for All the Reference Molecules in the Conformations Used in Eqs 1–6

molecule	sym	E_{tot}	χ_M
C_2H_4	D_{2h}	−78.615 49	−15.3
C_4H_6	C_{2v}	−156.034 48	−26.8
$(C_2H_3)_2NH$	C_{2v}	−211.407 10	−36.6
$(C_2H_3)_2S$	C_{2v}	−554.240 32	−42.4
$(C_2H_3)_2O$	C_{2v}	−231.262 94	−34.8
$(C_2H_3)_2CH^-$	C_{2v}	−194.761 68	−42.3
$(C_2H_3)_2CH^+$	C_{2v}	−194.445 98	−22.5
$(C_2H_3)_2BH$	C_{2v}	−181.487 25	−28.0
C_6H_8 (1,3,5-hexatriene)	C_{2v}	−233.444 67	−40.9
C_6H_8	C_{2v}	−233.450 48	−37.5
C_6H_8NH	C_s	−288.822 52	−47.5
C_6H_8S	C_s	−631.654 83	−52.9
C_6H_8O	C_s	−308.680 97	−45.3
c-C_6H_8BH	C_{2v}	−258.929 29	−40.7
c-$C_6H_{10}BH$	C_{2v}	−260.145 92	−49.3
c-$C_6H_{12}BH$	C_{2v}	−261.341 49	−55.3
c-$C_6H_8CH^+$	C_{2v}	−271.912 50	−33.6
c-$C_6H_{10}CH^+$	C_{2v}	−273.097 83	−45.4
c-$C_6H_{12}CH^+$	C_{2v}	−274.296 90	−50.6
C_8H_{10}	C_{2h}	−310.855 76	−47.2
$(H_2C=CH)_2C_4H_4NH$	C_{2v}	−365.063 13	−61.6
$(H_2C=CH)_2C_4H_4NH$	C_s	−365.065 88	−63.5
$(H_2C=CH)_2C_4H_4S$	C_{2v}	−707.898 80	−69.7
$(H_2C=CH)_2C_4H_4S$	C_s	−707.901 31	−70.1
$(H_2C=CH)_2C_4H_4O$	C_{2v}	−384.920 03	−57.9
$(H_2C=CH)_2C_4H_4O$	C_s	−384.925 56	−59.9

bulk magnetic susceptibility (χ_M) of a compound and the susceptibility ($\chi_{M'}$) estimated from an increment system or from model compounds without cyclic conjugation. In this paper, Λ's are evaluated using eqs 2 and 3 for the five- and seven-membered monocycles (the χ_M values for all the reference species, computed in the planar conformations as shown, are given in Table 2).

$$(X = CH^-, NH, S, O) \quad (2)$$

$$(X = CH^+, BH) \quad (3)$$
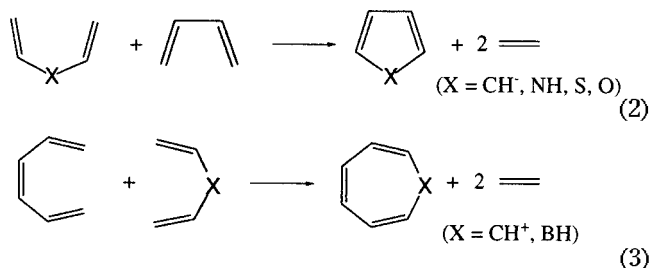
The computed Λ's (from eq 2; Table 1) indicate the $C_5H_5^- > C_4H_4S > C_4H_4NH > C_4H_4O$ aromaticity ordering for the five-membered rings.[26] Similarly, borepin is aromatic (Λ = −13.8 ppm cgs by eq 3; χ_{anis} = −83.1 ppm cgs), but less so than the tropylium cation (Λ = −19.9 ppm cgs by eq 3; χ_{anis} = −100.0 ppm cgs). This is also evident from the smaller downfield chemical shifts of the ring protons in borepin as compared to tropylium cation (Figure 1). The exaltations of borepin (−17.4 ppm cgs) and the tropylium cation (−24.3 ppm cgs), computed using eq 1, are in qualitative agreement with that obtained from eq 3. This supports our choice of open-chain reference molecules for the bicyclic mol-

Figure 1. Becke3LYP/6-311+G** optimized geometries (distances in Å), GIAO-HF/6-31+G*//Becke3LYP//6-311+G** ¹H NMR chemical shifts (ppm, given in italics; experimental values in parentheses) and NICS(0) values (ppm, given in boldface) at the geometrical center of individual rings.

ecules (**3X**, **4X**), rather than more arbitrary cyclic models. NICS, a new aromaticity criterion based on the absolute magnetic shieldings computed here at the geometrical center of the rings (NICS(0)) as well as 1 Å above (NICS(1)), provides an additional assessment of the ring current effects (Table 1). Accordingly, the NICS(0) and NICS(1) values of borepin (−3.7 and −6.9 ppm) are smaller than those of $C_7H_7^+$ (−7.6 and −10.7 ppm). The NICS trends for the five-membered rings (Table 1) follow those of Δr, Julg, and ASE indices. Since the computed NICS values in the molecular plane (NICS(0)) also are influenced by the local contributions[27] (for example, the C–C, C–X, and C–H σ bonds of the ring), we also report NICS(1) data, i.e., 1 Å above the plane (Table 1), since the local contributions are reduced relative to the π effects. The NICS(0) trends are maintained in the five- and seven-membered monocycles, although the NICS(1) differences are less. Thus, NICS(1) could prove to be an even better index than NICS(0) for the interpretation of π-ring currents. How does the aromaticity vary if the seven- and five-membered rings are fused?

Azulene (**1a**) is the [5,7]-fused ring prototype. The aromaticity of **1a** is indicated by the nearly equal C–C bond lengths (computed, X-ray,[28] and electron diffraction[29]), the stabilization energy (comparable to naphthalene),[30] the downfield ¹H NMR chemical shifts,[31] and the exalted diamagnetic susceptibility (nearly identical with that of naphthalene).[11b,d] The measured dipole moment of **1a** (0.796 D in the gas phase and 1.08 D in benzene)[32] indicates azulene to be polarized.[33] The

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(26) The reference structures are not computed in the most stable arrangements but were selected to be similar with the aromatic molecules considered. Also note that the formal connectivities of the non-hydrogen atoms are balanced on both sides of the equations. Although the thiophene and pyrrole ordering is reversed compared to Δr and NICS(0) as well as the criteria employed earlier,[13] the difference in their magnitudes are not very large and this justifies the present approach.
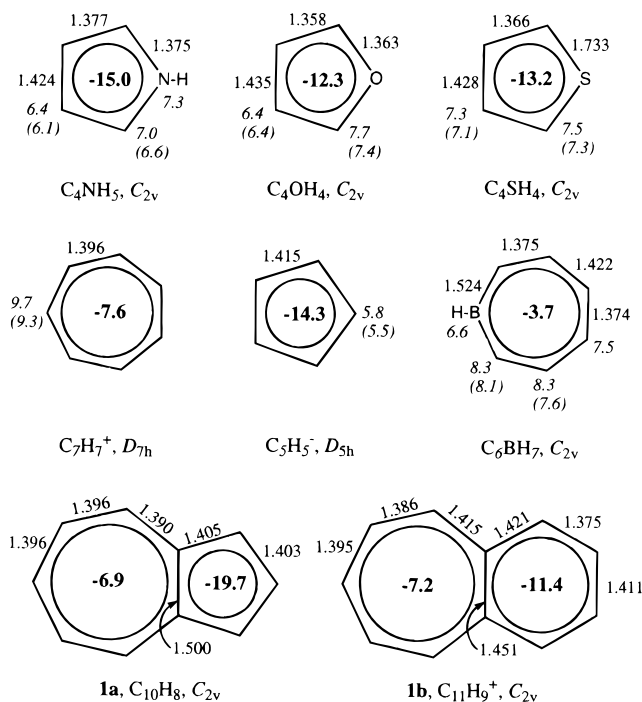
(27) Schleyer, P. v. R.; Hommes, N. J. v. E.; Jiao, H. Unpublished results. Also see ref 11f.
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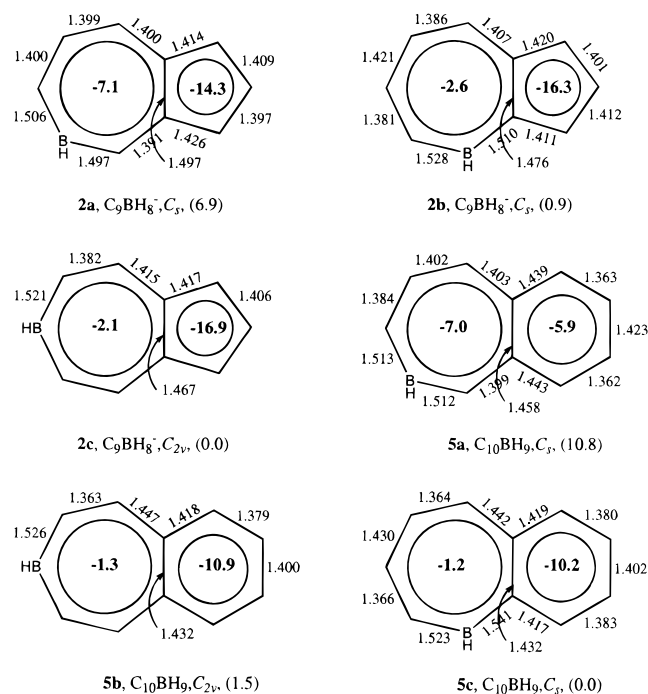(29) Bastiansen, O.; Derissen, J. L. *Acta Chem. Scand.* **1966**, *20*, 1319.

Figure 2. Becke3LYP/6-311+G** optimized geometries (distances in Å), relative energies (in parentheses, kcal/mol), and GIAO-HF/6-31+G*//Becke3LYP//6-311+G** NICS(0) values (ppm, in boldface) at the geometrical center of individual rings for annelated borepins **2a**−**c** and **5a**−**c**.

Figure 3. Becke3LYP/6-311+G** optimized geometries (distances in Å), relative energies (in parentheses, kcal/mol), and GIAO-HF/6-31+G*//Becke3LYP//6-311+G** NICS-(0) values (ppm, bold) at the geometrical center of individual rings for heterole-fused borepins, **3X** and **4X** (X = NH, S, O).

Chart 2

1a

calculated Δr, χ_{anis}, and Λ values of azulene (Table 1) also support the aromatic description quantitatively.

Although aromaticity is a global molecular property, the different contributions of individual rings in polycyclic molecules, long of interest, have been evaluated qualitatively in different ways.[34] The newly developed NICS characterizes the local aromaticity of each ring in polycyclic compounds[35] and serves as a simple and effective aromaticity criterion. The NICS(0) values for the seven (−6.9 ppm) and five-membered (−19.7 ppm) rings in azulene are similar to those of the constituent monocycles, the tropylium cation (−7.6 ppm) and the cyclopentadienyl anion (−14.3 ppm); hence, both rings
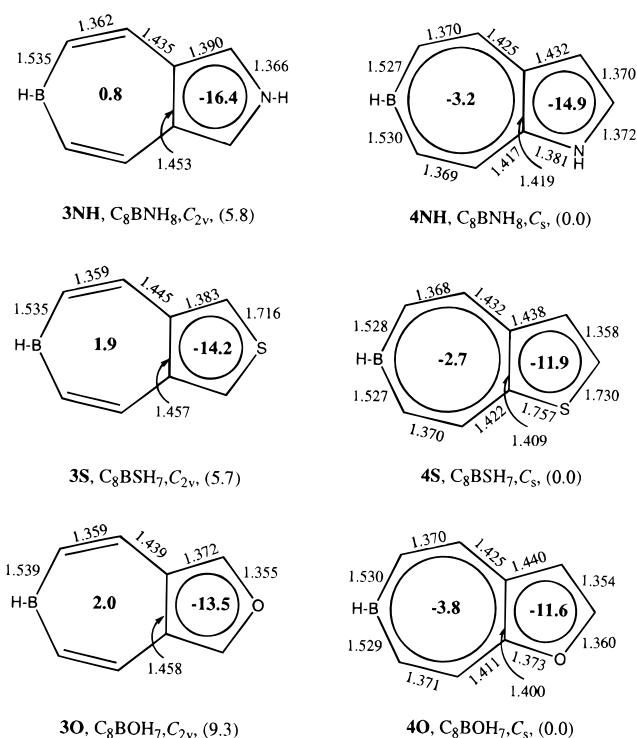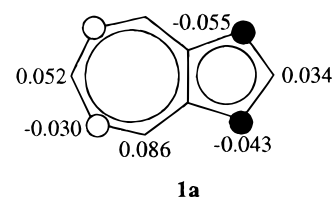
in azulene are aromatic. The stronger diatropic ring current of the five-membered ring, compared to that of the seven-membered ring, also is reflected by the NICS-(1) values (Table 1).

Borepin-fused cyclopentadienyl anions, isoelectronic with azulene (**1a**), have three positional isomers, **2a**−**c** (Figure 2). Similarly, two positional isomers (**3X**, **4X**; X = NH, S, O) are considered for heterole-fused borepins (Figure 3). According to the topological charge stabilization rule,[36] the relative stability of such positional isomers depends primarily on the placement of electronegative heteroatoms (for example N, S, and O) at positions with the largest charge density computed for an isoelectronic and isostructural reference skeleton (e.g., **1a**). The natural charges[37] of the carbon positions (including the hydrogen charges of CH groups) given in Chart 2 for azulene identify positions 1 and 3 (indicated by darkened circles; see Chart 1 for atom

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Table 3. Total (E_{tot}, hartrees) and Zero-Point Energies (ZPE, kcal/mol), Magnetic Susceptibilities (χ_M, ppm cgs), Magnetic Susceptibility Anisotropies (χ_{anis}, ppm cgs), Nucleus-Independent Chemical Shifts (NICS, ppm), and Dipole Moments (μ in D) for [5,7]- and [6,7]-Annelated Borepins

molecule	sym	$E_{tot}{}^a$	ZPE^b	$\chi_M{}^c$	$\chi_{anis}{}^c$	NICS(0)^d	NICS(1)^d	μ^e
2a	C_s	−372.737 17	87.8	−90.2	−143.6	−7.1 (−14.3)	−9.2 (−14.0)	3.0
2b	C_s	−372.747 21	88.1	−85.6	−127.9	−2.6 (−16.3)	−5.1 (−15.3)	2.6
2c	C_{2v}	−372.748 51	88.0	−83.7	−120.8	−2.1 (−16.9)	−4.7 (−14.7)	2.4
5a	C_s	−411.408 50	101.0	−87.6	−152.1	−7.0 (−5.9)	−9.8 (−8.5)	3.0
5b	C_{2v}	−411.423 62	101.2	−83.0	−136.4	−1.3 (−10.9)	−4.6 (−12.3)	2.9
5c	C_s	−411.426 13	101.3	−84.7	−142.1	−1.2 (−10.2)	−4.5 (−12.3)	1.9

^{a} Total energies for Becke3LYP/6-311+G** optimized geometries. ^{b} All structures correspond to minima at the Becke3LYP/6-31G* level. ^{c} At the CSGT-HF/6-31+G*//Becke3LYP/6-311+G** level. ^{d} Computed at the geometrical center (NICS(0)) and 1 Å above (NICS(1)) the seven-membered rings at the GIAO-HF/6-31+G*//Becke3LYP/6-311+G** level. NICS values for the corresponding five- and six-membered rings are given in parentheses. ^{e} At the Becke3LYP/6-311+G**//Becke3LYP/6-311+G** level.

Table 4. Computed ^{1}H, ^{11}B, and ^{13}C NMR Chemical Shifts for 2a−c and 5a−c^a

atom^b	1b	2a	2b	2c	5a	5b^c	5c^d
H-1	9.2	6.3	6.9	6.5	8.1	8.2	8.1
H-2	9.4	7.6	6.8	6.4	7.6	7.9	8.2
H-3	9.4	6.3	7.2	6.5	7.7	7.9	8.0
H-4	9.2	8.8	6.5	8.8	8.3	8.2	8.9
H-5	10.2	5.7	6.5	6.2	9.3	8.7 (8.2)	7.1
H-6	9.1	7.4	7.7	6.0	6.6	7.8 (7.7)	7.8
H-7	10.0	7.8	5.4	6.2	9.2	6.7	8.3
H-8	9.1	7.6	8.1	8.8	8.8	7.8 (7.7)	7.1 (7.0)
H-9	10.2				8.5	8.7 (8.2)	7.9
C-1	135.5	89.4	108.4	106.1	133.6	134.2	131.0
C-2	139.9	132.2	112.3	108.6	125.1	127.2	131.5
C-3	139.9	92.2	117.0	106.1	126.4	127.2	125.4
B(C)-4	135.5	145.7	40.2	152.6	133.8	134.2	145.1
B(C)-5	162.9	29.8	123.5	116.8	159.7	154.6 (154.0)	52.1 (53.6)
B(C)-6	133.4	133.8	146.4	40.2	38.7	136.0 (140.2)	137.2
B(C)-7	162.6	135.3	101.9	116.8	159.7	48.2 (49.5)	150.8
C-8	133.4	117.2	140.4	152.6	143.1	136.0 (140.2)	125.0
C-9	162.9	146.6	132.3	128.3	140.5	154.6 (154.0)	140.1
C-10	143.6	154.5	140.2	128.3	141.1	139.0 (138.4)	146.4
C-11	143.6				151.8	139.0 (138.4)	144.7

^{a} At the GIAO-HF/6-31+G*//Becke3LYP/6-311+G** level. Experimental values, where available, are given in parentheses. ^{b} See Chart 1 for atom numbering. ^{c} Experimental values from ref 19c for a phenyl derivative. ^{d} Experimental values from ref 20 for a substituted derivative.

numbering) as the preferred sites for electronegative heteroatom substitution.

The predicted **4X** > **3X** (X = NH, S, and O) stability ordering for heterole-fused borepins is confirmed by the relative energy of the isomers (Figure 3). As a corollary, electropositive elements, for example boron, should prefer sites with lower electron density (indicated by white circles in Chart 2). Consequently, positions 5 and 7 are unfavorable for boron, as is reflected by the **2c** > **2b** > **2a** relative thermodynamic stability ordering (Figure 2) for the boraazulene anion isomers.

The aromaticity of **2a−c** is demonstrated by the geometric and magnetic criteria. The B−C and C−C distances in the borepin moiety become shorter along the **2c** > **2b** > **2a** series, while the C−C bond lengths in the five-membered ring of **2a−c** show the opposite trend. Hence, the seven-membered ring in **2a** and the five-membered ring in **2c** are more delocalized than in **2b**. Indeed, the computed NICS(0) and NICS(1) values for the borepin moiety in **2a** (−7.1, −9.2 ppm) and, reasonably, the five-membered ring in **2c** (−16.9, −14.7 ppm) agree with the geometric features discussed above and, in addition, are larger than the corresponding monocycles. Although the NICS(0) and NICS(1) values

suggest both rings in **2a** to be aromatic, the borepin moieties in **2b** (−2.6, −5.1 ppm) and in **2c** (−2.1, −4.7 ppm) exhibit weaker diatropic ring currents as compared to borepin (−3.7, −6.9 ppm). Like the NICS(0) and NICS(1) descriptors, the χ_M and χ_{anis} (Table 3) data reveal the **2a** > **2b** > **2c** aromaticity trends opposite to the thermodynamic stability ordering (**2c** > **2b** > **2a**). The most stable isomer (**2c**) is *not* the most aromatic on the basis of the geometric and magnetic criteria! This supports and extends our earlier conclusion that thermodynamic stability and aromaticity need not be directly related in more complex systems.[14] The computed ^{1}H NMR chemical shifts in **2a−c** (Table 4) provide additional insight into the ring current effects. For example, the remote γ- proton of the borepin moiety in **2a** (7.6 ppm) is shifted downfield as compared to the corresponding proton in **2b** (5.4 ppm), in accord with our conclusion regarding the aromaticity.

The bond length alternations in heterole-fused borepins, **3X** and **4X**, do not provide much information (Figure 3). The Δr values between the C(7)=C(8) and C(8)−C(9) distances in **3X** are significantly larger than in borepin (Figures 1 and 3, Table 1). The corresponding Δr's for the seven-membered rings in **4X**, however,

are lower than in **3X**; the heterole moieties are relatively unaffected. This indicates **4X** to be more delocalized than its positional isomer, **3X**. Magnetic susceptibility (χ_M) and its anisotropies (χ_{anis}) reveal the consequences in cyclic delocalization due to these geometrical changes. Accordingly, the 3-hetero-substituted molecules **4X** (X = NH, S, O) are more aromatic than **3X**, since both χ_M and χ_{anis} are more negative (Table 1). Furthermore, the Λ's for **3X** (computed using eq 4), which are only

$$ \text{(4)} $$

3X (X = NH, S, O)

$$ \text{(5)} $$

4X (X = NH, S, O)

$$ \text{(6)} $$

1a
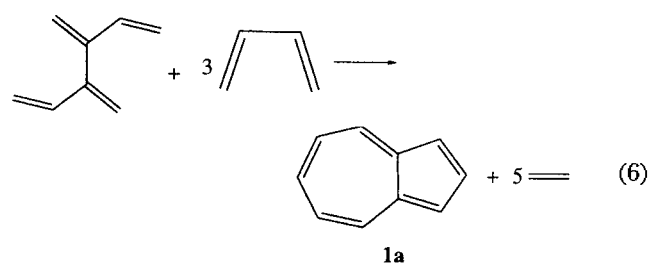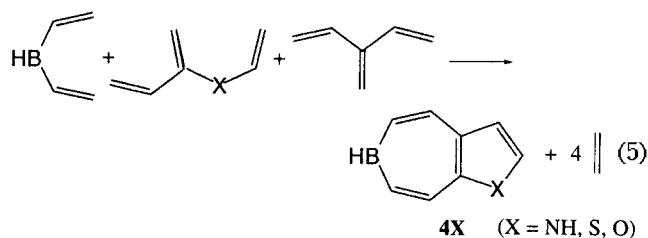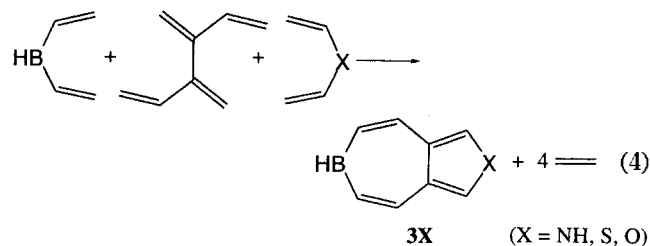
moderate (-19.6 for X = NH, -20.7 for X = S, and -14.5 ppm cgs for X = O) and are lower than for **4X** (computed using eq 5, Table 1), reflect the weak aromaticity in heterole-fused borepins (**3X**, **4X**) as compared to azulene (-37.2 ppm cgs, eq 6). However, the significantly negative Λ values clearly demonstrate that both **3X** and **4X** are indeed aromatic and resolve the contradicting descriptions provided by Sugihara *et al.* for **3S**.

The Λ aromaticity trends, **1a** > **4X** > **3X** (X = S > NH > O), follow that found similarly for the monocycles, with azulene (**1a**) having the largest exaltation and furano[3,4-*d*]borepin (**3O**) the weakest, among the isovalent, isostructural molecules considered. As also shown by the χ_M and χ_{anis} values (Table 1), the less symmetrical and more stable positional isomers (**3X**, Figure 3) are predicted to be more aromatic.

NICS evaluates the aromaticity contribution of the individual rings in **3X** and **4X**. Unlike the azulene NICS(0) values, which are similar to those for the corresponding monocycles (Figure 1), NICS(0) for the borepin moiety is increasingly positive along the pyrrolo-[3,4-*d*]borepin (**3NH**), thieno[3,4-*d*]borepin (**3S**), and furano[3,4-*d*]borepin (**3O**) series and is opposite in sign to that of borepin (Table 1, Figures 1 and 3). The NICS-(0) value for the five-membered rings in **3X** is slightly more negative than in the corresponding heteroles. This indicates the ring current to be more pronounced in the heterole rings of **3X**. Hence, the descriptions for **3X**

shown in Figure 3 seem more appropriate. In contrast, the NICS(0) values for the seven- and five-membered rings in **4X** resemble their aromatic monocyclic counterparts (borepin and heterole). The positive NICS(0) values in the seven-membered rings of **3X** and the correspondingly small negative values in **4X** are due to the local effects of the σ bonds. Thus, the NICS(1) values clearly indicate **3X** (Table 1) also to exhibit diatropic ring currents, but considerably less than **4X** and borepin itself. The exaltation of the borepin ring (Λ_b), estimated using eqs 7 and 8, for **3X** (-11.2 for X = NH, -10.2 for X = S, -8.0 ppm cgs for X = O) and its enhancement in **4X** (-15.7 for X = NH, -15.0 for X = S, -15.2 ppm cgs for X = O) and borepin (-13.8 ppm cgs, Table 1) further support the weak aromaticity of the seven-membered ring in **3X**.

$$ \text{(7)} $$

3X   X = NH, S, O

$$ \text{(8)} $$

4X   X = NH, S, O
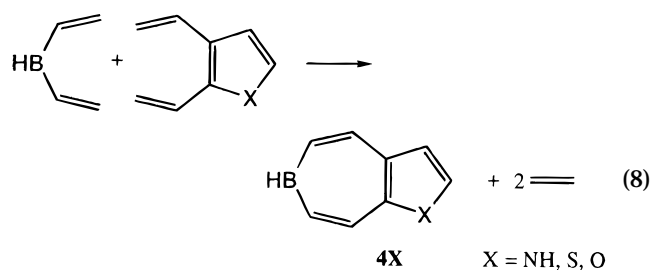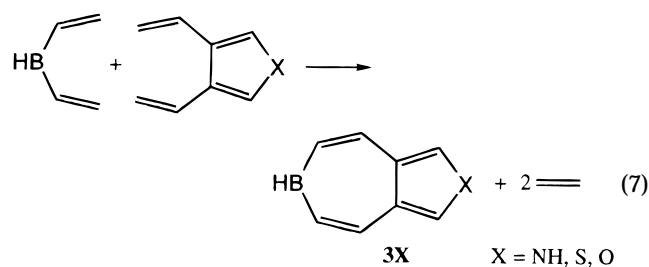
The relative ^{1}H NMR chemical shifts of **1a**, **3X**, and **4X** (Table 5) provide additional evidence for the ring current effects.[11a,b] In comparison to the corresponding monocyclic reference molecules (Figure 1), the protons on the α-carbon of the borepin moieties in the **3X** set are shielded, while the protons at positions 1 and 3 in the five-membered rings are deshielded. The chemical shifts of the other hydrogens in **3X** show only marginal deviations (Table 5). The downfield shifts of the hydrogens in **4X**, as compared to **3X**, reflect the greater diamagnetic ring current in the **4X** molecules. The close agreement between the computed and experimental chemical shifts (Table 4) should aid in the identification of the unknown species: **4NH**, **3O**, and **4O**.

The polarized nature of **1a**, **3X**, and **4X** is apparent from the dipole moments (Table 1). For example, the computed dipole moment of azulene is 1.1 D, while it is zero (because of symmetry) for the corresponding tropylium cation and cyclopentadienyl anion. Furthermore, the dipole moment points *away* from the heteroatom in borepin, furan, and thiophene but the direction is opposite in pyrrole. Similarly, the dipole moments point away from X (NH, S, O) in **3X**, but the direction is opposite in **1a**. This suggests a reversal of polarity between **1a** and **3X**. Again, the magnitudes of the dipole moments in heterole-fused borepins (**3X**, **4X**) are much larger than in azulene, and hence, **3X** and **4X** are strongly polarized aromatic systems (Table 1). Pyrrolo-[3,4-*d*]borepin (**3NH**) has the largest dipole moment (5.6

Table 5. Computed ^{1}H, ^{11}B, and ^{13}C NMR Chemical Shifts for 1a, 3X, and 4X^a

atom^b	1a^c	3NH^d	4NH	3S^e	4S^e	3O	4O
H-1	7.8 (7.4)	7.5 (7.1)	6.9	7.8 (7.8)	7.6 (7.5)	8.1	6.9
H-2	8.4 (7.9)	7.9	7.3		7.6 (7.6)		7.9
H-3	7.8 (7.4)	7.5 (7.1)	7.7	7.8 (7.8)		8.1	
H-4	9.1 (8.3)	8.4 (8.0)	8.4	8.4 (8.1)	8.7 (8.4)	8.1	8.8
H-5	7.4 (7.1)	7.0 (7.2)	7.8	7.1 (7.3)	7.9 (7.9)	6.9	8.1
H-6	8.3 (7.6)	6.6	6.6	6.6	6.7	6.6	6.6
H-7	7.4 (7.1)	7.0 (7.2)	7.7	7.1 (7.3)	8.1 (7.8)	6.9	8.0
H-8	9.1 (8.3)	8.4 (8.0)	8.8	8.4 (8.1)	8.8 (8.4)	8.1	8.7
C-1	112.4 (118.0)	119.6 (123.7)	108.0	137.8 (129.8)	127.3 (132.4)	144.7	109.3
X(C)-2	135.2 (136.9)		121.3		133.6 (127.6)		143.6
X(C)-3	112.4 (118.0)	119.6 (123.7)		137.8 (129.8)		144.7	
C-4	141.1 (136.4)	148.1 (145.1)	138.4	148.2 (145.7)	145.5 (145.9)	145.4	140.0
C-5	118.3 (122.6)	127.3 (132.3)	137.7	128.4 (134.7)	138.9 (140.8)	128.3	140.3
B(C)-6	140.9 (137.1)	49.8 (50.0)	45.1	50.9 (50.8)	46.0 (48.5)	51.8	45.1
C-7	118.3 (122.6)	127.3 (132.3)	134.0	128.4 (134.7)	140.1 (139.3)	128.3	139.6
C-8	141.1 (136.4)	148.1 (145.1)	148.2	148.2 (145.7)	147.2 (143.6)	145.4	144.8
C-9	136.0 (140.1)	124.0 (127.1)	128.4	138.9 (141.8)	140.7 (146.1)	124.2	129.3
C-10	136.0 (140.1)	124.0 (127.1)	136.6	138.9 (141.8)	152.5 (142.9)	124.2	156.5

^{a} At the GIAO-HF/6-31+G*//Becke3LYP/6-311+G** level. Experimental values, where available, are given in parentheses. ^{b} See Chart 1 for atom numbering. ^{c} Experimental values from ref 31. ^{d} Experimental values for substituted derivatives from ref 17. ^{e} Experimental values for substituted derivatives from ref 18b.

Chart 3

1b
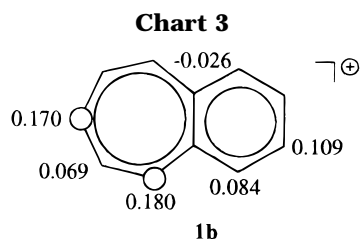
D) and is therefore a potential candidate for nonlinear optical materials.[38]

The aromaticity of the benzotropylium cation (**1b**, Figure 1), a [6,7]-fused bicyclic prototype, is characterized by the significant susceptibility anisotropy (−170.3 ppm cgs) and exaltation (−39.3 ppm cgs, Table 1). In addition, the NICS(0) values (Figure 1) indicate both the tropylium cation (−7.2 ppm) and the benzene (−11.4 ppm) moieties in **1b** to be diatropic, since these values are comparable to those of the monocyclic tropylium cation (−7.6 ppm) and benzene (−9.7 ppm), respectively. Of the three isomers (**5a−c**) considered for the benzo-fused borepins, **5c** is computed to be the most stable. The **5c** > **5b** > **5a** isomer stability ordering agrees with that predicted from the charge density patterns for **1b** (Chart 3, inclusive of C−H hydrogen charges), since boron favors the site with maximum positive charge (indicated by white circles in Chart 3). However, the variation of the C−C and C−B distances (Figure 2), the susceptibilities (χ_M), χ_{anis}, and the NICS(0) values (Table 3) suggest the *least stable* positional isomer, **5a**, to be the *most* aromatic. Furthermore, the NICS(0) values in **5b** and **5c** indicate the six-membered rings to be the major contributors to the ring-current effect (note that the small NICS(0) and NICS(1) values for the seven-membered rings in **5b** and **5c** are less than in borepin). However, the contribution of the borepin moiety dominates in **5a**. These results also emphasize the contrasts between the relative thermodynamic stability and aromaticity relationships of such sets of isomers. The computed ^{1}H, ^{11}B, and ^{13}C NMR chemical shifts for **5a−c** (Table 4) should help in identifying the unknown members in this series.

Conclusion

The geometries and the magnetic susceptibility anisotropies and exaltations, as well as the NICS values and ^{1}H NMR chemical shifts, reveal borepin to be weakly aromatic. The computed aromatic stabilization energy (ASE) of borepin (eq 1, −5.1 kcal/mol) is less than one-third of the ASE of the isoelectronic tropylium cation (−16.8 kcal/mol).

As judged by the geometric and magnetic criteria, the iso-π-electronic heterole-fused borepin (**3X**, **4X**) isomers of azulene (**1a**) are very weakly aromatic. The aromaticity of the individual rings, delineated from the NICS-(0) values, spans over the two rings in **1a** and **4X**, but only the heterole is involved in **3X**. However, the NICS-(1) values, which minimize the local contributions from the σ bonds, suggest both the rings in **3X** to have significant ring currents, although these are weaker than in **4X**. This conclusion resolves the rather inconclusive aromaticity description of **3S** and **4S** reported by Sugihara *et al.* Isomers **3X** are more polarized and have the dipole moment vectors opposite in direction than in azulene (**1a**).

The most aromatic heterole-fused borepin isomers (**3X**, **4X**; Figure 3) are also thermodynamically more stable. However, this aromaticity vs relative stability relationship does not extend to [5,7]- and [6,7]-annelated borepins (**2a−c**, **5a−c**; Figure 2), where the trends are opposite. The relationships among various aromaticity criteria (stability, geometric, energetic, and magnetic) depend highly on individual systems and are not parallel in complex systems. The NICS(0) and NICS(1) values suggest both the rings in **2a-c** and **5a-c** to be aromatic. The good agreement between the computed and measured ^{1}H, ^{11}B, and ^{13}C NMR chemical shifts (Tables 4 and 5) should help the characterization of the unknown annelated borepin isomers.

(38) Chemla, D. S.; Zyss, J. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic: Orlando, FL, 1987; Vols. 1 and 2.