Double Aromaticity in the 3,5-Dehydrophenyl Cation and in Cyclo[6]carbon

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Abstract: The presence of two ($4n+2$)-electron conjugated systems in perpendicular planes results in considerable aromatic stabilization. Despite having two fewer hydrogens, the 6πe-2oc 3,5-dehydrophenyl cation ($C_6H_3^+$, **1**) is 32.7 (CCSD(T)/6-31G**) and 35.2 kcal/mol (RMP4sdtq/6-31G*//RMP2(fu)/6-31G*) more stable than the phenyl cation (evaluated by an isodesmic reaction involving benzene and *m*-dehydrobenzene (**4**)). Cation **1**, the global $C_6H_3^+$ minimum, is 11.7, 24.2, 11.8, and 30.4 kcal/mol lower in energy than the 2,6- (**11**) and 3,4-dehydrophenyl (**12**) cations as well as the open-chain isomers **13** and **14** (RMP4sdtq/6-31G*//RMP2(fu)/6-31G* + ZPE(RMP2(fu)/6-31G*)). The stability of **1** is increased hyperconjugatively by 2,4,6-trisilyl substitution. The double aromaticity of **1** is indicated by the computed magnetic susceptibility exaltations (IGLO/II//RMP2(fu)/6-31G*) of -5.2, -6.8, -15, and -23.2 relative to **11**, **12**, **13**, and **14**, respectively. Thus, **1** fulfills the geometric, energetic, and magnetic criteria of aromaticity. The double aromaticity of the D_{6h} cyclo[6]carbon is apparent from the same criteria.

Introduction

Besides having the conventional 6π electron aromaticity, the 3,5-dehydrophenyl cation (**1**) is stabilized by three-center two-electron (3c-2e) bonding (**1a**) in the ring plane ("in-plane aromaticity").[1] This "doubly aromatic" cation (**1**), first conceived in 1979,[1] is a minimum at HF/STO-3G and was computed (isodesmic reaction 1) to be stabilized relative to the phenyl cation (**3**) and 1,3-dehydrobenzene (**4**) by 14.4 (HF/4-31G//HF/STO-3G) and 38.5 kcal/mol (MINDO/3).
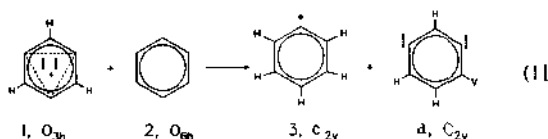
Occupied molecular orbitals resulting from in-phase overlap of three p (or sp^n) atomic orbitals stabilize molecules. The π-aromatic cyclopropenyl cation, $(CH)_3^+$ (**5**), with three parallel p(π) orbitals, is the best known example of 3c-2e bonding.[2] The three overlapping p orbitals are tilted inwards in the trishomocyclopropenium ion (**6**). In three-membered rings, a low-lying MO is comprised of three in-plane radial-type p (really sp) orbitals which overlap in the center (**7**) and result in 3c-2e σ-bonding. In cyclopropane, this "surface delocalization" contributed to "σ-aromaticity".[3–5]

Fukunaga et al.[6] suggested the possibility of analogous "trefoil" 3c-2e bonding in other systems with π perimeters. Stabilization can be expected when the σ centers are close together, e.g., in [5.5.5]trefoilene, C_9H_6 (**8**). A double aromatic 10 π electron structure with the trefoil 3c-2e bond might be achieved if one σ electron were shifted into the π system. Whereas MINDO/3 and MNDO calculations do show that the electronic structure of **8** conforms to this possibility and that the CC bond length alternation is small, the same calculations reveal that **8** is not a minimum and is highly unstable. The valence isomer of **8**, cyclonona-1,2,4,5,7,8-hexaene (**8a**), favors a nonplanar D_3 geometry and is nearly 100 kcal/mol lower in energy than **8**.[7]
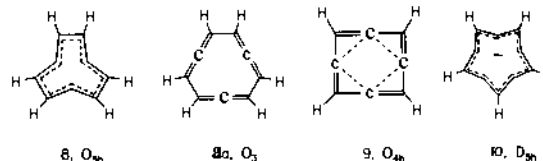
Our earlier computational searches for structures exhibiting double aromaticity due to homoconjugative overlap of radially oriented p_σ(sp^n) orbitals also did not succeed. For example, neither the D_{4h} form of the hypothetical C_8H_4 hydrocarbon **9** (which might have 10 π and 4c-2e σ central arrangement) nor the $C_{10}H_5^-$ D_{5h} anion **10** (with 10 π and 5c-6e σ systems) appears to be stabilized when examined computationally.[8]

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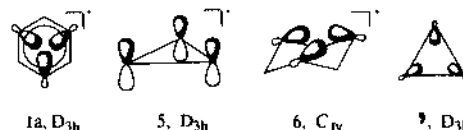⊗ Abstract published in *Advance ACS Abstracts*, August 15, 1994.
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Table 1. Total (–au) and Relative (kcal/mol) Energies of the $C_6H_3^+$ Isomers **1**, **11–14**, and **18–22** Calculated at Various Computational Levels

no.	symmetry	RHF/6-31G* E_{tot}	RMP2(fu)/6-31G* E_{tot}	MP4SDTQ/6-31G*//RMP2/6-31G* E_{tot}^e	E_{rel}
1	D_{3h}	228.471 03	229.278 04 (0, 39.0)^a	229.312 56 (229.34393)	0.0
11	C_{2v}	228.480 83	229.254 74 (0, 40.1)	229.295 44	10.7 (11.7)^b
12	C_s	228.456 85	229.237 23 (0, 39.4)	229.274 54	23.9 (24.2)
13	C_s	228.491 79	229.243 78 (0, 36.5)	229.290 16	14.1 (11.8)
14	C_s	228.467 65	229.213 69 (0, 36.1)	229.259 99	33.0 (30.4)
2	D_{6h}	230.703 14	231.487 19	231.531 74 (231.61090)	
3	C_{2v}	229.758 39	230.522 15	230.568 10 (230.63468)	
4	C_{2v}	229.386 85	230.191 92	230.220 05 (230.26807)	
21	D_{3h}	226.803 06	227.558 12 (0, 16.2)^c	227.624 12	0.0
22	D_{6h}	226.729 98	227.565 90 (0, 18.3)^c	227.628 20	–2.6 (–0.5)^d
18	C_{3v}	1098.733 82			
19	C_s	1100.025 27			
20	C_s	1100.934 27			

^{a} The numbers of imaginary frequencies (NIMAGs) and zero-point vibrational energies (ZPEs) are given in parentheses. ^{b} Relative energies with ZPE(RMP2(fu)/6-31G*) corrections are given in parentheses. ^{c} RMP2(fc)/6-31G* values. ^{d} At RMP4SDTQ(fc)/6-31G*//RMP2(fc)/6-31G* + ZPE(RMP2(fc)/6-31G*). ^{e} The CCSD(T)/6-31G**//CCSD(T)/6-31G** energies are given in parentheses.

The possible experimental detection of **1**[9] has encouraged us to report this reexamination at more sophisticated *ab initio* levels. Is **1** a minimum? What is its stabilization energy? Is **1** more stable than other $C_6H_3^+$ cyclic and open-chain isomers, e.g., **11–14**? Does **1** have double aromatic character? How can this be demonstrated?
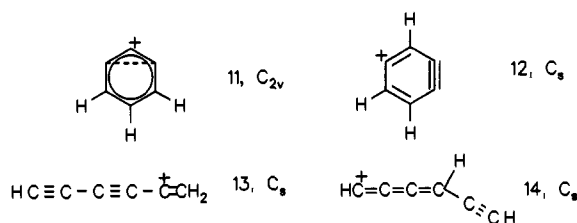
Calculation Methods

Using the GAUSSIAN 92 program,[10a] the geometries of **1–4** and **11–14** were optimized at RMP2(fu)/6-31G*. The larger, silyl-substituted systems **18** and **19** (discussed later) were optimized only at RHF/6-31G* and **21–24** at RMP2(fc)/6-31G*.[11,12] Single-point energies were computed at RMP4sdtq(fc)/6-31G*[13] using the RMP2(fu)/6-31G* geometries. Analytical second derivatives established the nature of all stationary points at the RMP2(fu)/6-31G* level (**18** and **19** at RHF/

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Table 2. Calculated Wiberg Bond Indexes (WBIs) for Benzene, **1**, **21**, and **22** (RHF/6-31G*//RMP2/6-31G*)

species	symmetry	C1C2	C1C3	C1C4
1^a	D_{3h}	1.447 (1.444)	0.376 (0.392)	0.128 (0.125)
C_6H_6 (**2**)	D_{6h}	1.440	0.113	0.012
21	D_{3h}	1.638	0.102	0.156
22	D_{6h}	1.870	0.024	0.229

^{a} The Becke3LYP/6-31G* values are given in parentheses.

Table 3. IGLO/II/RMP2(fu)6-31G* Calculated Magnetic Susceptibility Anisotropy (χ_{anis}),^{a} Magnetic Susceptibility (χ_{tot}),^{b} and Magnetic Susceptibility Exaltation (Λ) (ppm cgs) for **1**, **11–14**, and **21–24**

isomers	symmetry	χ_{anis}	χ_{tot}	Λ
1	D_{3h}	–94.2	–61.5	0.0
11	C_{2v}	–47.8	–56.3	–5.2
12	C_s	–41.6	–54.7	–6.8
13	C_s	–20.5	–46.5	–15.0
14	C_s	–37.0	–38.3	–23.2
22	D_{6h}	–38.9	–64.2	0.0
21	D_{3h}	–15.4	–53.3	–10.9
24	C_{6v}	–43.1	–62.0	0.0
23	C_{3v}	–21.9	–52.6	–9.4

^{a} $\chi_{anis} = \chi(11) - {}^1/_2[\chi(22) + \chi(33)]$, where $\chi(11)$ is the out-of-plane component and $\chi(22)$ and $\chi(33)$ are the in-plane components. ^{b} $\chi_{tot} = {}^1/_3[\chi(11) + \chi(22) + \chi(33)]$.

6-31G*).[14] These are indicated by the number of imaginary frequencies (NIMAG), e.g., NIMAG = 0 for minima and NIMAG = 1 for transition states.[12] Zero-point vibrational energies (ZPEs), all scaled by the average factor 0.91,[15] are used to correct the relative energies (Table 1). Natural population analysis (NPA)[16] was used to probe the electronic structure of **1** (Table 2). The "doubly aromatic" character of **1** was assessed by comparing its magnetic susceptibility, computed with the IGLO method using the standard II basis set[17] and the correlated geometries (IGLO/II/RMP2(fu)/6-31G*), with those of the other $C_6H_3^+$ isomers, **11–14** (Table 3). In selected cases, CCSD(T)/6-31G**[13b] calculations have been carried out with the ACES II program[10b] to test the reliability of the MP4 results. MP4 is known to overestimate triple effects because of the absence of TT coupling terms as this level of theory.[13c,d] CCSD(T) includes a number of these terms at MP6 and higher levels and, therefore, gives a balanced account of T correlation effects. Also, it covers a significant part of multireference effects and, accordingly, is more reliable than MP4. By computing the singlet–triplet splitting in **1**, **11**, and **12**, the calculations were carried out at the Becke3LYP/6-31G* level of the

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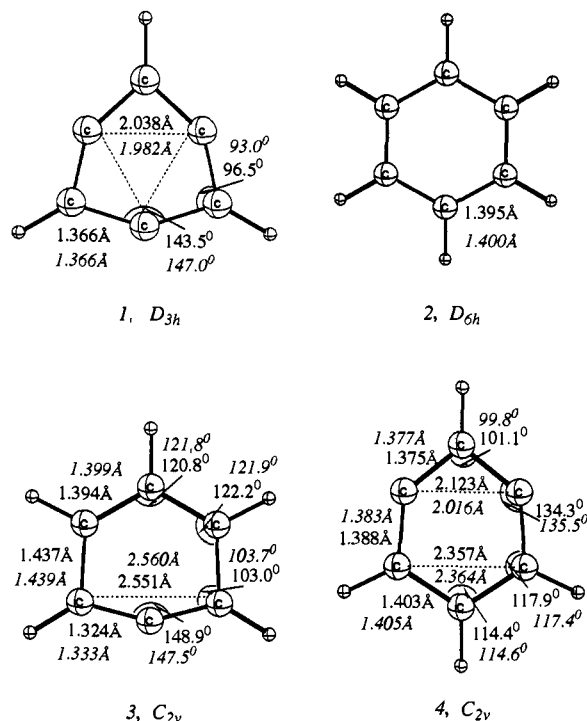
Figure 1. RMP2(fu)/6-31G* geometries of **1** (3,5-dehydrophenyl cation), **2** (benzene), **3** (phenyl cation), and **4** (1,3-dehydrobenzene) (the CCSD-(T)/6-31G** values are given in italics).

density functional theory using the G92/DFT program.[10c] Although from our experience the structure parameters from the MP2 and Becke3LYP levels are usually quite similar, the Becke3LYP-DFT includes the effects of both dynamic and nondynamic correlation to some extent, and the calculated vibrational frequencies are in good agreement with the measured values. Thus, no scalation is necessary for the ZPE estimations.

Results and Discussion

The D_{3h} structure **1** is a minimum at RMP2(fu)/6-31G* (the lowest frequency, $v(a_2'') = 433$ cm⁻¹, is quite large). The CC ring bond lengths (all 1.366 Å) at both MP2 and CCSD(T) are substantially shorter than those in benzene (1.395 (MP2) and 1.400 Å (CCDS(T), Figure 1 in italics). The bare carbons, C1, C3, and C5, are closer to the center of the ring (1.177 Å) than the CH carbons (1.498 Å) (Figure 1). The MP2 central C1C3, C3C5, and C1C5 distances, 2.038 Å (cf. the MINDO/3 value, 2.020 Å),[1] are longer than the CCSD(T) values of 1.933 Å. This seems to indicate somewhat stronger through-space 1,3-interaction at the CCSD(T) level than at the MP2 level.

The cyclic isomers **11** and **12** also are minima but are 11.7 and 24.2 kcal/mol higher in energy than **1**, respectively (RMP4sdtq/6-31G*//RMP2(fu)/6-31G* + ZPE(RMP2(fu)/6-31G*). At the same level, the open-chain isomers **13** and **14** (Figure 2) are 11.8 and 30.4 kcal/mol higher in energy than **1**, respectively (Table 1). Thus, **1** appears to be the $C_6H_3^+$ global minimum.

The isodesmic[12] reaction energy (eq 1), 32.7 kcal/mol at CCSD-(T)/6-31G** and 35.2 kcal/mol at RMP4sdtq/6-31G*//MP2/6-31G*, is closer to the earlier MINDO/3 value (38.5 kcal/mol) and larger than that computed at STO-3G.[1] All the molecules, **1–4**, in eq 1 are 6 π electron systems. The shortest 1,3-CC distances are 2.436 Å in the phenyl cation (**3**) and 2.106 Å (C1C3) in *m*-benzyne (**4**) at CCSD(T)/6-31G** (2.423 and 2.123 Å, respectively, at MP2).[8a] The average CC bond lengths (1.390 and 1.388 Å at CCSD(T), 1.385 at MP2) in **3** and **4** are longer than the CC bond length in **1** (1.366 Å at both CCSD(T) and MP2) but are closer to the benzene value (1.400 Å at CCSD(T), 1.395 Å at MP2) (Figure 1). Reaction (eq 1) provides a basis to estimate the heat of formation for cation **1**. Using the heat
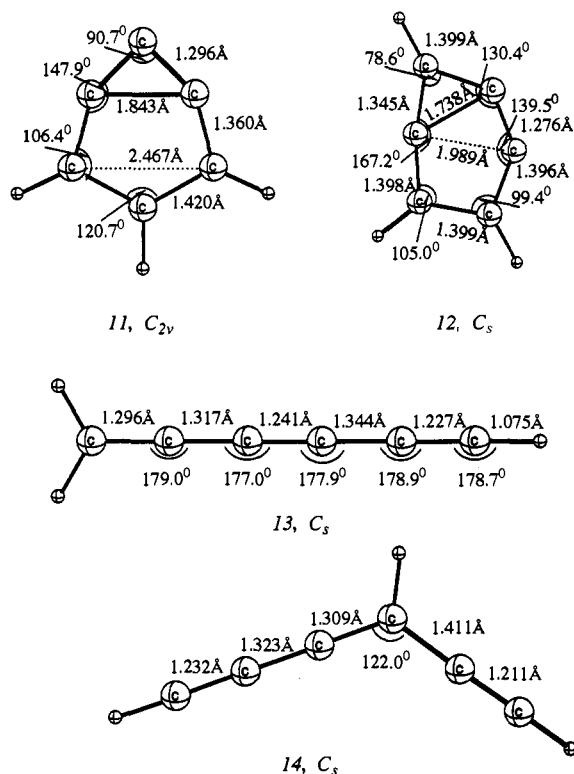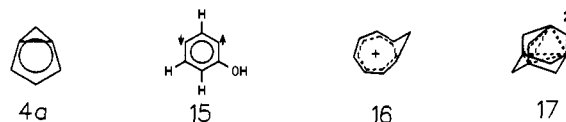

Figure 2. RMP2(fu)/6-31G* geometries of the cyclic (**11, 12**) and open-chain (**13, 14**) isomers of C_6H_3 cation.

of formation for **2** (19.8 kcal/mol),[18f] **3** (273 ± 2 kcal/mol), and **4** (122.8 kcal/mol),[18a,e] the $\Delta H_f°(298)$ evaluated for **1** is 343.9 kcal/mol.

The preferred structure of *m*-benzyne (**4**) deserves a more detailed comment.[18] The bicyclic geometry **4a** (claimed on the basis of MNDO calculations to be a separate minimum with a 1.628 Å C1C3 distance, 5.7 kcal/mol higher in energy than **4**)[18b] is also calculated at HF/6-31G* (erroneously) to be a minimum with a 1.483 Å C1C3 distance. However, in accord with GVB and MP2/6-31G** calculations on 2,4-didehydrophenol (**15**),[19] bicyclic **4a** does not survive GVB, MP2, or MP4/6-31G** [18e] optimizations and is converted into 1,3-dehydrobenzene (*m*-benzyne) (**4**) (the C1C3 distance elongates to 2.106 Å) (Figure 1). TCSCF and MCSCF calculations by Borden et al.[18c] and by Squires et al.[18d] gave similar results: **4a** is 12–15 kcal/mol higher in energy than **4** (TCSCF/6-31G* and MCSCF(2,2)/6-31G* using the RHF geometries). TCSCF and MCSCF optimizations, starting from the RHF geometries for **4a**, both led back to **4**.

Equal or nearly equal ring bond lengths—the geometric criterion of aromaticity—is one of the characteristics of an aromatic molecule.[20–23] On this basis, **1**, with a CC bond length

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of 1.366 Å, should possess greater aromatic character than **3** and **4** with nonequal CC bond lengths.[20-23] The Wiberg bond indexes (WBIs[24]) for C1C2 and C1C3 in **1** are 1.447 and 0.376, respectively; these may be compared with the benzene values of 1.440 and 0.113 (Table 2). Hence, electron delocalization embracing the C1C3C5 triangle is present in **1**, notwithstanding the rather long C1C3, C3C5, and C1C5 distances. Such electron delocalization, resulting from orbital overlap without supporting the CC bond, is exemplified by the homotropylium cation (**16**), with a C1C7 distance of 1.906 Å at RMP2(fu)/6-31G* [25] (2.031 Å at RMP4sdq//RMP2(fu)/6-31G*)[26] and by the 1,3-dehydroadamant-5,7-diyl dication (**17**), with its 2.084 Å C1C3 distance at RMP2(fu)/6-31G*,[25] as well as by the trishomocyclopropenium ion (**6**), with its C1C3 distance of 1.842 Å at RMP2(fu)/6-31G*.[25] Apart from stabilizing through-space interactions and resulting 2-electron delocalization, cation **1** can also benefit from through-bond interactions involving the radially oriented σ orbitals at C1, C3, and C5 and the σ^* orbitals of the six-membered ring. Such interactions have been found to be stabilizing factors in *m*-benzyne, where they lead to additional electron pairing possibilities for the singlet biradical.[18a,d,e]

The C2, C4, and C6 carbons in **1** bear negative natural charges (-0.323) which are counterbalanced by the positive hydrogen charges (0.336) according to NBO analysis.[16] The bare carbons, C1, C3, and C5, involved in the three-center interaction share the remaining net positive charge (+0.321 each). This charge alternation on the carbons may lead to additional stabilization.[27] While the D_{3h} symmetric 3,5-dehydrophenyl cation (**1**) fulfills the geometric and energetic criteria of aromaticity, these characteristics are absent and not well in **11, 12, 13**, and **14**, since **11** and **12** are 11.7 and 24.2 kcal/mol less stable than **1** at the RMP4sdtq/6-31G*//RMP2(fu)/6-31G* + ZPE(RMP2/6-31G*) level.

About 25 years ago, Dauben et al.[28] used the exaltation of magnetic susceptibility to characterize aromatic systems. Exaltation of the magnetic susceptibility (Λ) characterizes an "aromatic" compound. This magnetic susceptibility exaltation has been attributed to the presence of cyclic delocalization of electrons ("ring current"). Cremer et al.[26,29] used this magnetic criterion to characterize the homo- and bishomoaromaticity in the homo- and bishomotropenylium cations as well as in the barbaralyl cation. Our group[30,31] has used the same criterion to demonstrate the aromaticity of pericyclic transition states. Generally, Λ is defined as the difference between the measured bulk magnetic susceptibility value and the susceptibility evaluated on the basis of an increment system ($\Lambda = \chi_M - \chi_{M'}$). In this paper, the magnetic susceptibility exaltation values are the differences between the IGLO calculated magnetic susceptibilities for isomers.

We now characterize the double aromaticity in **1** by evaluating the magnetic susceptibility exaltation (Λ). With IGLO/II//RMP2(fu)/6-31G*,[17] the calculated magnetic susceptibilities (χ_{tot}, ppm cgs) are **1**, -61.5; **11**, -56.3; and **12**, -54.7. For the

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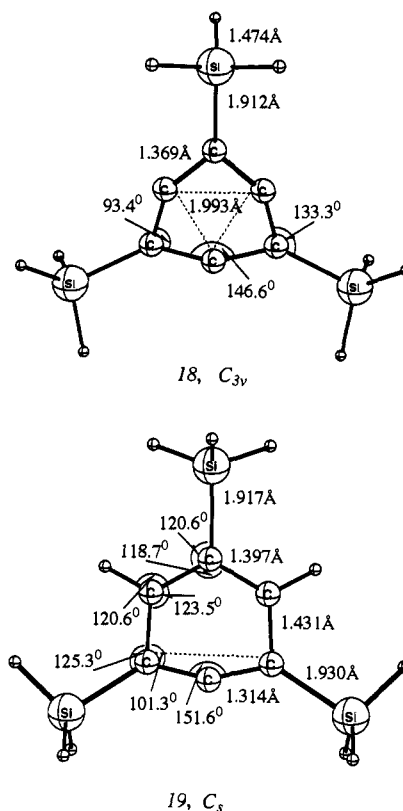
Figure 3. RHF/6-31G* geometries of **18** (2,4,6-trisilyl-3,5-dehydrophenyl cation) and **19** (2,4,6-trisilylphenyl cation).

open-chain isomers **13** and **14**, the χ_{tot} values are -46.5 and -38.3, respectively. Thus, the magnetic susceptibility exaltations for **1** are -5.2 and -6.8, in comparison with the cyclic isomers **11** and **12** (which have 6-π-electron systems). Larger values, -15.0 and -23.2, are found for the acyclic isomers **13** and **14**. Hence, the 3,5-dehydrophenyl cation (**1**) fulfills the magnetic as well as the geometric and energetic criteria of aromaticity. In comparison with the open-chain isomers **13** and **14**, the cyclic isomers **11** and **12** should have partial aromatic character from the same criterion. Even the more negative magnetic susceptibility anisotropies, -94.2 (**1**), -47.8 (**11**), -41.6 (**12**), -20.5 (**13**), and -37.0 (**14**), indicate the aromaticity of **1** and partial aromaticity of **11** and **12** (Table 3). The larger magnetic susceptibility anisotropy (-94.2) and magnetic susceptibility exaltation (-23.2, relative to **14**) in **1**, compared to the benzene values (χ_{anis} = -62.9 and Λ = -13.4), clearly reveal the doubly aromatic nature of **1**. The calculated ^{1}H chemical shift is 9.2 ppm, and δ(^{13}C) is 206.2 for the bare carbon and 54.7 for the other carbons (C-H).

Observation of 3,5-Dehydrophenyl Cations. While $C_6H_3^+$ ions have been detected mass spectrometrically,[9] their structures are unknown. Ongoing gas phase experiments may provide more decisive evidence.[9] Can 3,5-dehydrophenyl cations be observed in solution? While the parent ion, **1**, is appreciably more stable than the phenyl cation, detection in nonnucleophilic "superacid" media seems unlikely. However, appropriately substituted systems may be more promising.

Attempts to generate phenyl cations by solvolysis failed until it was appreciated that the β-silicon effect[32] would lead to substantial Si-C hyperconjugative stabilization, e.g., in the 2,6-di-SiR$_3$ phenyl cation.[33] This β-Si effect might also stabilize **1**, e.g., by 2,4,6-trisilyl substitution (**18**) (Figure 3). Indeed, the HF/6-31G* energies of isodesmic reactions 2 and 3 indicate

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Double Aromaticity in Two Compounds

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Table 4. Total (–au) and Relative (kcal/mol) Energies for the $C_6H_3{}^+$ Cyclic Isomers of Singlet and Triplet States

| no.	symmetry	Becke3LYP/ 6-31G*	ZPE (NIMAG)	$\Delta E_{ST}{}^a$	E_{rel} (S)^b	E_{rel} (T)^c
1S	D_{3h}	229.955 13	38.5 (0)	0.0	0.0	
1T	D_{3h}	229.863 21	35.5 (2)	54.7		25.1
1TG	C_2	299.880 69	36.9 (0)	45.1		15.5
11S	C_{2v}	299.953 36	39.7 (0)	0.0	2.3	
11TG	C_{2v}	229.908 23	38.7 (0)	27.3		0.0
12S	C_s	229.931 28	39.1 (0)	0.0		
12TG	C_s	229.887 69	37.0 (0)	25.3	8.6	11.2

^{a} The singlet–triplet energy gaps (Becke3LYP/6-31G* + ZPE-(Becke3LYP/6-31G*)). ^{b} Relative energies of the singlet states (Becke3LYP/6-31G* + ZPE(BEcke3LYP/6-31G*)). ^{c} Relative energies of the triplet states (Becke3LYP/6-31G* + ZPE(Becke3LYP/6-31G*)).

cation **18** to have a stabilization energy (–19.9 kcal/mol) similar to that of the trisilyl-substituted phenyl cation (–22.4 kcal/mol) **19** (Figure 3, X = SiH_3).

(2)

18   2   1   20

(3)

19   2   3   20
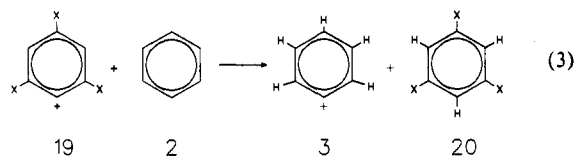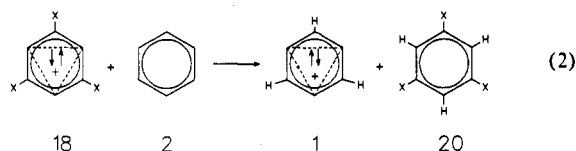
Singlet–Triplet Splittings. Due to the pronounced biradical character of dehydrobenzene isomers,[18a,d,e] it would be interesting to test the singlet–triplet splittings in **1**, **11**, and **12**. For example, how high in energy is the degenerate pair of unoccupied antisymmetric σ orbitals in **1**? To what extent would the triplet state of **1** undergo Jahn–Teller distortion from D_{3h} symmetry, etc.? Geometry optimizations and energy calculations as well as characterizations of the singlet and triplet states for **1**, **11**, and **12** were carried out using the G920/DFT program at the Becke3LYP/6-31G* level of density functional theory (DFT).[10c] The optimized geometries are given in Figure 4, and the energies are given in Table 4. As given in Figure 4, the Becke3LYP/6-31G* CC separations (1.3-, 1.933; 1,2-, 1.358 Å) for singlet **1** (**1S**) are shorter than those at RMP2/6-31G* (2.038 and 1.366 Å) and at CCSD(T)/6-31G** (1.982 and 1.366 Å, Figure 1). Hence, a stronger C1C3C5 triangle interaction in **1** is favored at Becke3LYP/6-31G* than at MP2/6-31G* or at CCSD(T)/6-31G**. The D_{3h} symmetric triplet **1T** is *not* an energy minimum rather than a transition state with two imaginary frequencies. The first frequency (–3551 cm^{-1}) involves the carbon skeleton stretching to C_{2v} symmetry, and the second (–321 cm^{-1}) pertains to ring twisting from C_{2v} to C_2. Indeed, C_2 symmetric **1TG** is the triplet 3,5-dehydrophenyl cation ground state. At Becke3LYP/6-31G* + ZPE(Becke3LYP/6-31G*), **1T** is 54.7 kcal/mol higher in energy than **1S**, and the singlet–triplet energy gap (ΔE_{ST}) between **1S** and **1TG** is 45.1 kcal/mol (Table 4). This is much larger than the 34.4 kcal/mol *p*-benzyne value of Borden et al.[18c] and ca. 36 kcal/mol of Squires et al.[18d] computed at various levels.

At Becke3LYP/6-31G*, both the singlet and triplet states of **11** (**11S** and **11TG**, C_{2v}) and **12** (**12S** and **12TG**, C_s) are energy minima. The large changes of the geometries are shown in Figure 4. The calculated ΔE_{ST} values for **11S → 11TG** (27.3 kcal/mol) and for **12S → 12TG** (25.3 kcal/mol) are smaller than the values for **1S → 1TG**. The energy differences between the singlet **1S** and **11S** and **12S** are 2.3 and 15.6 kcal/mol (Table 4), which are 9.4 and 8.6 kcal/mol lower than the MP4 values (Table 1). On

1 S, D_{3h}   *1 TG, D_{3h}*

1 TG, C_2

11 S, C_{2v}   *11 TG, C_{2v}*

12 S, C_s   *12 TG, C_s*
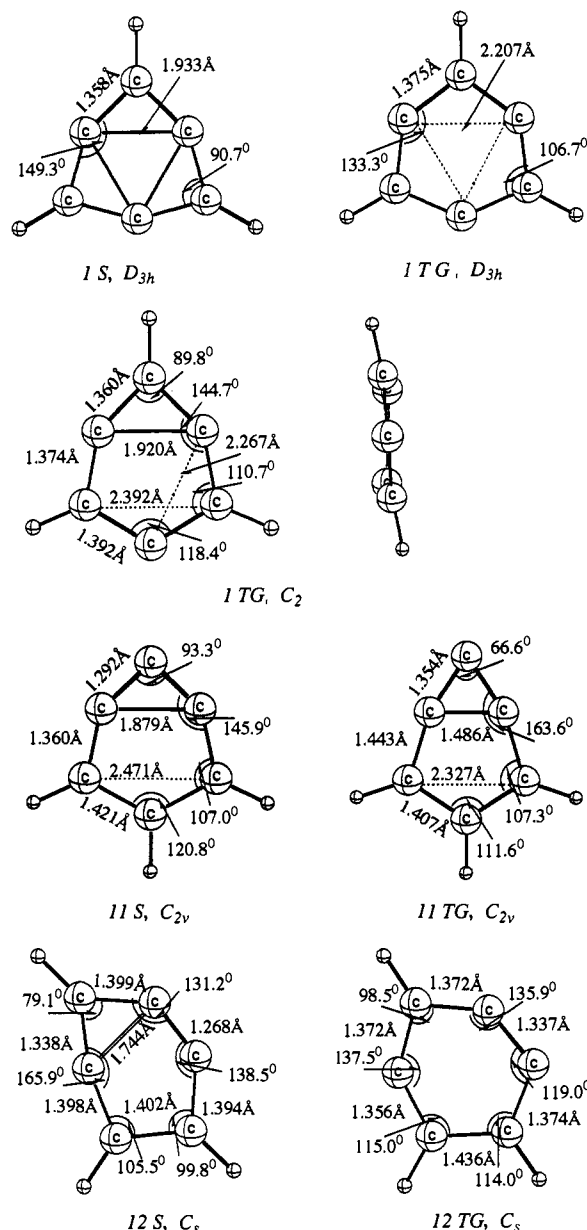
Figure 4. Becke3LYP/6-31G* geometries for the singlet (**1S**, **11S**, **12S**) and triplet (**1T**, **1TG**, **11TG**, **12TG**) states of the $C_6H_3{}^+$ isomers.

the other hand, the triplet **11TG** is lower in energy than both **1TG** (15.5 kcal/mol) and **12TG** (11.2 kcal/mol).

Double Aromaticity of Cyclo[6]carbon. Cyclo[6]carbon[34] is another molecule with potential doubly aromatic character. Two pertinent isomers are possible, namely **21** (D_{3h}) and **22** (D_{6h}). As shown in Figure 5, the D_{3h} **21**, like **1**, has in-plane three-center bonding with 1.333 and 1.809 Å CC bond lengths, whereas the D_{6h} **22** has only one CC bond length of 1.324 Å. At RMP4SDTQ/6-31G*//RMP2/6-31G* + ZPE(RMP2/6-31G*), **22** is 0.5 kcal/mol (2.6 kcal/mol without ZPE correction) more stable than **21**. This means the three-center in-plane bonding stabilization, as in **1**, does not compensate for the greater strain. In contrast to the earlier *ab initio* calculation[34a] and the recent DFT result[34d] that **22** is a saddle point on the energy surface and higher in energy than **21**, our calculations indicate that both **21** and **22** are energy minima (NIMAG = 0, RMP2/6-31G*) and are nearly isoenergetic. This agrees well with the CASSCF/MRCI

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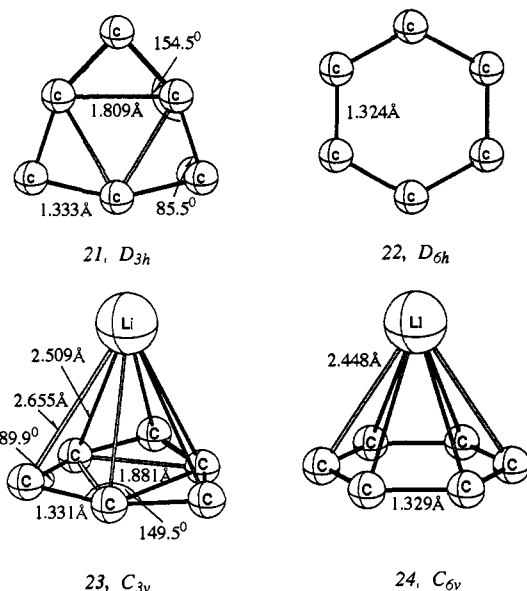
Figure 5. RMP2(fc)/6-31G* geomtries of cyclo[6]carbon in D_{3h} (**21**) and D_{6h} (**22**) symmetries as well as their Li⁺ complexes **23** (C_{3v}) and **24** (C_{6v}).

calculations.[34e] The strong in-plane bonding of **22** is indicated by the Wiberg bond indexes (WBIs, Table 2). The C1C2 and C1C4 WBIs of **22** (1.870 and 0.229) are larger than those for **21** (1.638 and 0.156) and for benzene (1.440 and 0.012). On the other hand, the calculated magnetic susceptibility and the magnetic susceptibility anisotropy for **22** (−64.2 and −38.9, respectively) are larger in magnitude than those for **21** (−53.3 and −15.4). Hence, **22** is more "aromatic" than **21**. Thus, **22** is the more favorable form of the cyclo[6]carbon according to the geometric, energetic, and magnetic criteria of aromaticity.[20,22] The greater aromaticity of **22** relative to **21** is also indicated by the computed Li⁺ upfield chemical shifts in the corresponding complexes **23** and **24**. The delocalization in the carbon ring **24** leads to an upfield shift of the Li⁺ cap (−7.4 vs −4.2 in **23**).[35]

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Conclusions

The 3,5-dehydrophenyl cation (**1**) is 11.7, 24.2, 11.8, and 30.4 kcal/mol lower in energy respectively than its cyclic isomers, the 3,4- and 2,3-dehydrophenyl cations **11** and **12**, and its open-chain isomers, **13** and **14** (RMP4sdtq/6-31G*//RMP2(fu)/6-31G* + ZPE(RMP2(fu)/6-31G*)). The effectiveness of the 1,3-stabilizing interactions in **1**, despite the rather long distances in the C1C3C5 triangle, is shown by the energy of isodesmic reaction, eq 1: the 3,5-dehydrophenyl cation (**1**) and benzene are 32.7 kcal/mol more stable than the phenyl cation (**3**) and *m*-benzyne (**4**) (CCSD(T)/6-31G**). The heat of formation of cation **1** is predicted to be 343.9 kcal/mol. While the term "aromaticity" may be overused,[3,4,21,22,36] it is appropriate to consider **1** to be a "doubly aromatic" species. In addition to the geometric and energetic criteria, the "double aromaticity" in **1** is demonstrated by the magnetic susceptibility exaltations of −5.2 and −6.8, compared with its cyclic isomers **11** and **12**, respectively (which also have cyclic 6 π electron systems), as well as −15 and −23.2, compared with the open-chain isomers **13** and **14**, respectively. The very large singlet–triplet energy gaps for the $C_6H_3^+$ cyclic isomers reveal that there are non singlet–triplet competitions. The greater aromaticity of the D_{6h} over the D_{3h} form of cyclo[6]carbon is indicated by the same criteria.

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