T_d B(BO)$_4^-$: A Tetrahedral Boron Oxide Cluster Analogous to Boron Hydride T_d BH$_4^-$

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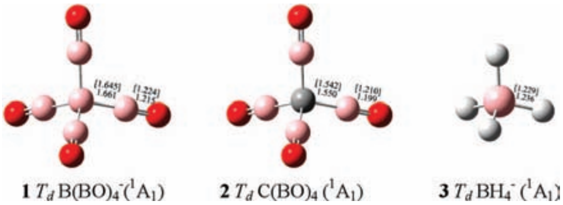
A density functional theory and wave function theory investigation on the geometrical and electronic structures of $B_5O_4^{0/-}$ clusters has been performed in this work. $B_5O_4^-$ anion proves to possess a perfect tetrahedral ground state of T_d B(BO)$_4^-$ ($^1A_1$) analogous to BH$_4^-$ with four equivalent −BO terminals around the B center, while B_5O_4 neutral favors a slightly off-planed C_s B(BO)$_4$ ($^2A'$) which contains three −BO terminals and one −O− bridge. An intramolecular BO radical transfer occurs from T_d B(BO)$_4^-$ to C_s B(BO)$_4$ when one electron is detached from the anion. The one-electron detachment energies of the anion and characteristic stretching vibrational frequencies of −B═O groups at about 2000 cm^{-1} have been calculated to facilitate future experimental characterization of these clusters.

1. Introduction

Combining photoelectron spectroscopy (PES) and *ab initio* calculations, in two recent papers, Zhai, Li, and Wang[1,2] produced and characterized a series of novel boron oxide clusters B$_m$(BO)$_n$ including the linear $D_{\infty h}$ B(BO)$_2^{0/-}$, triangular D_{3h} B(BO)$_3^{0/-}$.[1] and linear $D_{\infty h}$ B$_2$(BO)$_2^{0/-/2-}$.[2] These interesting small boron oxide clusters with two or three −BO groups bonded to a B$_m$ core (m = 1, 2) turned out to be analogues of the well-known boron hydride molecules BH$_2$, BH$_3$, and B$_2$H$_2$, respectively, revealing an isolabal relationship between the BO radical (boronyl)[3−5] and H atom and establishing an interesting link between boron oxides and boron hydrides. The BO/H analogy provides a new way to design boron oxide clusters. However, in the B(BO)$_n^{0/-}$ series (n = 2−4), two crucial species in the formula of B(BO)$_4^{0/-}$ ($B_5O_4^{0/-}$) still remain uncharacterized so far. Whether B(BO)$_4^{0/-}$ clusters with four BO groups follow the boronyl pattern and possess perfect tetrahedral structures analogous to T_d BH$_4^-$ is the main question we aim to answer in this work at density functional theory (DFT) and wave function theory levels. The $B_5O_4^-$ anion was experimentally observed in the mass spectrum of boron oxides, but its PES spectrum could not be measured with the detachment energies of 266 and 193 nm.[1,6] To facilitate future experiments, we present here a detailed theoretical investigation on $B_5O_4^{0/-}$ clusters to predict their ground and low-lying excited states. The results obtained in this work indicate that the ground state of $B_5O_4^-$ anion is indeed a perfect singlet tetrahedron T_d B(BO)$_4^-$ (**1**) analogous to T_d BH$_4^-$ (**3**), while its neutral B_5O_4 prefers a slightly off-planed C_s B(BO)$_4$ **(12)** (see Figures 1 and 4). The structural change from $D_{\infty h}$ B(BO)$_2$, D_{3h} B(BO)$_3$, and D_{3h} B(BO)$_3^{-1}$ to T_d B(BO)$_4^-$ and C_s B(BO)$_4$ can be rationalized in the following scheme (Scheme 1)in which D_{3h} B(BO)$_3$ is formed when the singly occupied π-HOMO of $D_{\infty h}$ B(BO)$_2$ (π_u, mainly from B 2p$_z$)[1] overlaps with the singly occupied σ-HOMO of the third BO radical (σ, mainly from B 2s),[3] while the tetrahedral T_d B(BO)$_4^-$ (**1**) is produced when the extra electron in the π-HOMO of D_{3h} B(BO)$_3^-$ (a_2'', also mainly from B 2p$_z$)[1] is paired by the unpaired electron of the fourth BO radical. An intramolecular BO radical transfer occurs from T_d B(BO)$_4^-$ (**1**) to C_s B(BO)$_4$ (**12**) when one electron is detached from the anion through a C_s B(BO)$_4$ transition state (**21**) (see Figure 5) with a bridging BO group. $B_5O_4^{0/-}$ are the first boron oxide clusters reported so far with more than three O atoms.[7] The experimentally characterized gold boronyls Au$_n$BO (n = 1−3) by Zubarev et al.[8] and the theoretically investigated carbon boronyls C$_n$(BO)$_n$ (n = 3−7) and C$_2$(BO)$_m$H$_n$ by our group[9,10] provide further evidence that BO groups do serve as robust σ-radicals in a wide range of inorganic and organic compounds.



1 T_d B(BO)$_4^-$ ($^1A_1$) **2** T_d C(BO)$_4$ ($^1A_1$) **3** T_d BH$_4^-$ ($^1A_1$)

Figure 1. Ground-state structures of T_d B(BO)$_4^-$ anion compared with those of T_d C(BO)$_4$ and T_d BH$_4^-$ with bond lengths indicated at both B3LYP and [MP2] levels in angstroms.

2. Theoretical Approach

Full structural optimizations, frequency analyzes, and natural bonding orbital analyses were performed at two theoretical levels, DFT-B3LYP[11] and MP2(full),[12] starting from initial structures either arbitrarily constructed with specific symmetries or obtained by employing the Gradient Embedded Genetic Algorithm (GEGA) procedure.[13] Figure 1 depicts the ground state of T_d B(BO)$_4^-$ ($^1A_1$) compared with those of T_d C(BO)$_4$ ($^1A_1$) and T_d BH$_4^-$ ($^1A_1$). Figure 2 shows the eight low-lying or especially concerned isomers of $B_5O_4^-$. Figure 3 presents the pictures of four characteristic molecular orbitals (MOs) of T_d B(BO)$_4^-$ compared with those of T_d BH$_4^-$. Figure 4 shows the ground state of C_s B(BO)$_4$ compared with planar C_{2v} B(BO)$_4$, and Figure 5 illustrates the eight low-lying isomers obtained for B_5O_4. Adiabatic detachment energies (ADEs) were calculated as the energy differences between the ground states of the anion

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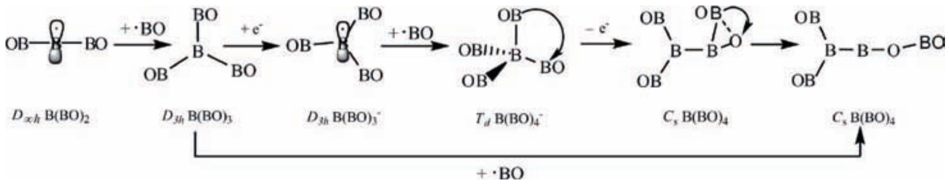
SCHEME 1



(**1**) and the corresponding minima of the neutral (**20**) lying closest to the anionic ground states, while vertical detachment energies (VDEs) were calculated as the energy differences between the anion and the neutral at the ground-state structures of the anion (**1**). ADEs and VDEs are further refined at the CCSD(T) level[14] at both B3LYP and MP2(full) structures. VDEs corresponding to the low-lying excited states of the neutrals at anionic structures were approximated using the OVGF(full) procedure[15] at both B3LYP and MP2(full) anionic geometries. All the calculations in this work were performed using the Gaussian 03 program[16] with the augmented Dunning's all-electron basis sets (aug-cc-pvtz).[17] Structural optimizations were achieved with the default convergence criteria of the program employed.[16] The calculated electronic and vibrational properties of T_d B(BO)$_4^-$, T_d C(BO)$_4$, C_s B(BO)$_4$, and C_{2v} B(BO)$_4$ are summarized in Table 1, and the predicted ADE and VDE values for T_d B(BO)$_4^-$ are tabulated in Table 2.

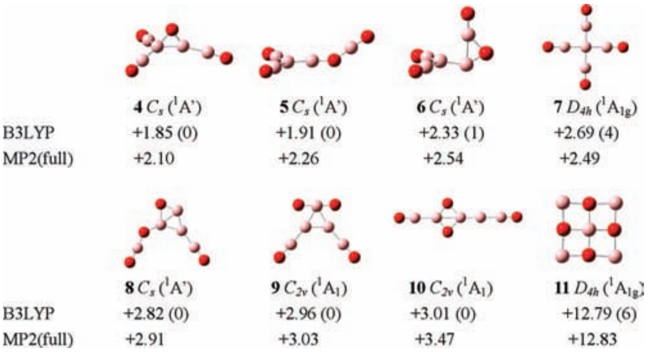


Figure 2. Low-lying isomers of $B_5O_4^-$ anion at B3LYP and MP2(full) levels with energies relative to T_d B(BO)$_4^-$ (**1**) indicated in eV. The numbers in parentheses represent the numbers of imaginary frequencies for each optimized structure at B3LYP.

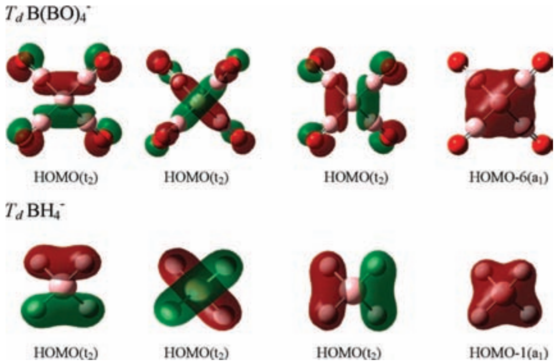
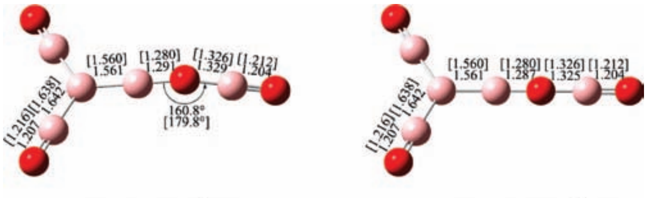


Figure 3. Comparison of the four MOs responsible for the four tetrahedral σ-bonds in T_d B(BO)$_4^-$(^{1}A$_1$) and T_d BH$_4^-$(^{1}A$_1$) at B3LYP.



12. C_s B(BO)$_4$ (^{2}A') **13.** C_{2v} B(BO)$_4$ (^{2}B$_1$)

Figure 4. Ground-state structure of C_s B(BO)$_4$ (**12**, ^{2}A′) compared with its almost isoenergetic isomer of C_{2v} B(BO)$_4$ (**13**, ^{2}B$_1$).

3. Results and Discussion

As expected from chemical intuition and indicated in Figures 1 and 2, $B_5O_4^-$ anion possesses a perfect tetrahedral ground state of T_d B(BO)$_4^-$ (**1**,^{1}A$_1$) with four equivalent −BO terminals singly bonded to the central B. The parent D_{3h} B(BO)$_3^-$ has a singly occupied π-HOMO (a$_2''$) perpendicular to the molecular plane at the center[1] which plays a dominating role in forming the tetrahedral T_d B(BO)$_4^-$ when the fourth BO radical approaches the triangular unit in a vertical direction (see Scheme 1). B3LYP and MP2(full) methods produced close bond parameters and similar relative energies for all the low-lying isomers of the anion (see Figure 2). We will mainly focus on B3LYP results in the following discussion.

Extensive searches indicate that T_d B(BO)$_4^-$ (**1**) with a tetrahedral B center is the true global minimum of $B_5O_4^-$, which lies at least 1.85 eV lower in energy than all the other 2D or 3D isomers (**4**−**11**). Although $Al_5O_4^-$ was recently confirmed to have a D_{4h} ground state containing a planar tetracoordinate Al at the center,[18] planar squared D_{4h} $B_5O_4^-$ (**11**) was found to be a sixth-order stationary point lying about 12.8 eV higher in energy than the tetrahedral ground state (**1**). A potential energy surface scanning indicates that C_s B(BO)$_4^-$ (**6**, ^{1}A′) with a bridging BO group serves as the transition state (with one imaginary frequency at −154i cm^{-1}) between T_d B(BO)$_4^-$ (**1**) and C_s B(BO)$_4^-$ (**5**); i.e., there exits a **1** → **6** → **5** intramolecular BO-radical transfer. The four −BO terminals turn out to be singly σ-bound to central B in T_d B(BO)$_4^-$ (**1**), with the bond lengths of $r_{B-B} = 1.66$ Å and $r_{B=O} = 1.22$ Å and the Wiberg bond indexes of $WBI_{B-B} = 0.96$ and $WBI_{B=O} = 1.80$. The central B has the total bond order of $WBI_B = 3.90$ and natural atomic charge of $q_B = -1.60$ |e|, well following the octet rule.

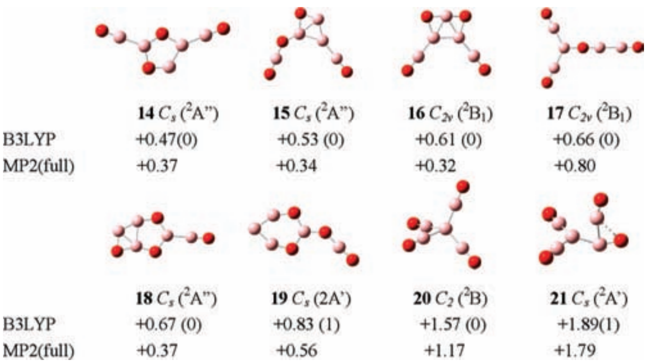


Figure 5. Low-lying isomers of B_5O_4 neutral at B3LYP and MP2(full) levels with energies relative to C_s B(BO)$_4^-$ (**12**) indicated in eV. The numbers in parentheses represent the numbers of imaginary frequencies for each isomer optimized at B3LYP.

TABLE 1: Calculated Natural Atomic Charges (q_X/|e|) and Total Wiberg Bond Indexes (WBI_X) of the Central X Atoms, Bond Orders between X and Surrounding B Atoms (WBI_{X-B}), Bond Orders of the B=O Double Bonds ($WBI_{B=O}$), and Vibrational Frequencies (cm^{-1}) of T_d $B(BO)_4^-$, T_d $C(BO)_4$, C_s $B(BO)_4$, and C_{2v} $B(BO)_4$ at the B3LYP Level[a]

	state	q_X	WBI_X	WBI_{X-B}	$WBI_{B=O}$	vibrational frequency
1 T_d $B(BO)_4^-$	$^1A_1$	−1.60	3.90	0.96	1.80	79(e), 102(t_2), 370(t_1), 401(a_1), 476(t_2), 558(e), 888(t_2), 1922(t_2), 1938(a_1)
2 T_d $C(BO)_4$	$^1A_1$	−1.56	3.39	0.81	2.71	86(e), 115(t_2), 359(t_1), 489(a_1), 509(t_2), 563(e), 985(t_2), 2038(t_2), 2063(a_1)
12 C_s $B(BO)_4$	$^2A'$	−0.84	3.30	1.00, 1.26	1.89, 1.91	27(a″), 34(a′), 73(a″), 79(a′), 122(a′), 330(a′), 344(a″), 347(a″), 389(a′), 464(a′), 468(a″), 474(a′), 498(a″), 506(a′), 796(a′), 952(a″), 1113(a′), 1690(a′), 1968(a′), 1969(a″), 2108(a′)
13 C_{2v} $B(BO)_4$	$^2B_1$	−0.84	3.30	1.00, 1.26	1.89, 1.90	−26i(b_1), 24(b_2), 67(b_2), 78(a_1), 115(b_1), 323(b_1), 343(b_2), 347(a_2), 384(a_1), 453(b_1), 467(b_2), 470(a_1), 493(b_2), 505(b_1), 790(a_1), 952(b_2), 1120(a_1), 1706(a_1), 1967(a_1), 1969(b_2), 2112(a_1)

[a] X stands for the central B and C in **1** and **2** and the planar tricoordinate B atom in **12** and **13**.

TABLE 2: Calculated One-Electron Detachment Energies ADEs/eV and VDEs/eV of T_d $B(BO)_4^-$ at Various Theoretical Levels with the Pole Strengths Indicated in Parentheses

		B3LYP			MP2(full)		
	transition	B3LYP	OVGF(full)	CCSD(T)	MP2(full)	OVGF(full)	CCSD(T)
ADE	$^2A' \leftarrow A_1$	6.79		6.94	6.87		6.94
VDE	$^2T_2 \leftarrow {}^1A_1$	7.32	7.99(0.89)	7.84	7.76	8.03(0.89)	7.85
A	$^2T_1 \leftarrow {}^1A_1$		9.34(0.89)			9.28(0.89)	
B	$^2E \leftarrow {}^1A_1$		9.60(0.89)			9.56(0.89)	
C	$^2T_2 \leftarrow {}^1A_1$		9.95(0.89)			9.95(0.90)	

Replacing the B center in **1** with a C atom produces its isoelectronic neutral of T_d $C(BO)_4$ (**2**) which is a carbon tetraboronyl with $r_{C-B} = 1.55$ Å, $r_{B=O} = 1.20$ Å, $WBI_C = 3.39$, and $q_C = -1.56$ |e| at the same theoretical level. Obviously, the B center carrying a negative charge in **1** behaves similar to the C center in **2**. It should also be noticed that, in both **1** and **2**, the B=O bond lengths vary within the range of $r_{B=O} = 1.20 \sim 1.23$ Å, very close to the B=O distances of $r_{B=O} = 1.20$ Å in free BO radical[3] and $r_{B=O} = 1.20 \sim 1.24$ Å in $D_{\infty h}$ $B(BO)_2^{0/-}$, D_{3h} $B(BO)_3^{0/-}$ [1], and $D_{\infty h}$ $B_2(BO)_2^{0/-/2-}$,[2] indicating that the integrity of B=O groups in both **1** and **2** has been well preserved. In fact, the four robust BO groups around the sp^3 hybridized B or C center dominate the structures and stabilities of T_d $B(BO)_4^-$ (**1**) and T_d $C(BO)_4$ (**2**).

Molecular orbital analyses help to interpret the bonding nature of the anion. As clearly shown in Figure 3, T_d $B(BO)_4^-$ (**1**) has a bonding pattern very similar to that of T_d BH_4^- (**3**): both of them contain an sp^3 hybridized B center surrounded by four σ-radicals (BO in **1** and H in **3**) to form three triply degenerate t_2 MOs (HOMOs) and one a_1 MO (HOMO-6 for **1** and HOMO-1 for **3**). T_d $C(BO)_4$ (**2**) has very similar MOs as T_d $B(BO)_4^-$ (**1**). The four MOs result in the four equivalent σ single bonds around the B center in these T_d structures. B center in T_d $B(BO)_4^-$ has the valence orbital occupation of B $2s^{1.00}2p^{3.59}$, similar to the situations of C $2s^{1.16}2p^{3.65}$ in T_d CH_4, C $2s^{1.26}2p^{4.28}$ in T_d $C(BO)_4$, and B $2s^{0.89}2p^{2.82}$ in T_d BH_4^- at the same theoretical level. All the other valence MOs of T_d $B(BO)_4^-$ belong to the localized B=O interactions within the BO groups.[1−3]

However, the global minimum of B_5O_4 neutral turned out to be the slightly off-planed C_s $B(BO)_4$ (**12**, $^2A'$) which contains a slightly bent O−B−O bridge. The perfect planar C_{2v} $B(BO)_4$ (**13**, $^2B_1$) proves to be a transition state with a small imaginary frequency of −26i cm^{-1} at B3LYP. However, C_{2v} **13** lies only slightly higher (less than 0.003 eV) than C_s **12** at B3LYP, MP2(full), and CCSD(T) levels, and the two isomers have practically the same calculated bond parameters and electronic properties (see Figure 4 and Table 1). They are expected to be undistinguishable in experiments. It is interesting to notice that a transition state C_s $B(BO)_4$ (**21**, $^2A'$) with an imaginary frequency of −296i cm^{-1} was located between T_d $B(BO)_4$ (**1**) and C_s $B(BO)_4$ (**12**). C_s **21** is similar to the anionic transition state of C_s **6** in geometry, and both of them contain a BO bridge.

We propose the following structural relaxation from T_d $B(BO)_4^-$ (**1**) to C_s $B(BO)_4$ (**12**) at their ground states: T_d $B(BO)_4^-$ (**1**) − e^- → T_d $B(BO)_4$ (**1**) → C_s $B(BO)_4$ (**21**) → C_s $B(BO)_4$ (**12**).

In experiments, the first step from T_d $B(BO)_4^-$ (**1**) to T_d $B(BO)_4$ (**1**) is a vertical one-electron detachment process at the anionic structure. The $(OB)_2BB-O-BO$ bridge in **12** has the single bond lengths of $r_{B-O} = 1.29$ Å and $r_{O-B} = 1.33$ Å and the corresponding bond orders of 0.96 and 0.82, while the three −BO terminals have the typical B=O double bond lengths between 1.20 and 1.22 Å and the bond orders between 1.89 and 1.90. In MO theory, the sp^2 hybridized B center of the singlet D_{3h} $B(BO)_3$ ($^1A_1'$)[1] (see Scheme 1) has no singly occupied orbital to form another σ-bond with the fourth BO radical which, instead, is bonded to the $B(BO)_3$ unit through a −BO terminal, giving rise to the ground state of C_s **12** which contains three −BO terminals and one −O− bridge.

Frequency analyses (see Table 1) help to characterize these tetraboronyl boron oxide clusters in future experiments. The asymmetrical B=O stretching vibrations at 1922 cm^{-1} (t_2) and symmetric B=O stretching vibration at 1938 cm^{-1} (a_1) in T_d $B(BO)_4^-$ (**1**) have been split into three B=O stretching modes at 2108 cm^{-1} (a′), 1969 cm^{-1} (a″), and 1968 cm^{-1} (a′) and one B−O−B stretching mode at 1690 cm^{-1} (a′) in C_s $B(BO)_4$ (**12**). C_{2v} $B(BO)_4$ (**13**) possesses practically the same corresponding vibrational frequencies at 2112 cm^{-1} (a_1), 1969 cm^{-1} (b_2), 1967 cm^{-1} (a_1), and 1706 cm^{-1} (a_1), respectively. These characteristic B=O related vibrational frequencies are expect to be observed in future IR or PES measurements.

As shown in Table 2, T_d $B(BO)_4^-$ anion has the calculated one-electron detachment energies of ADE = 6.94 eV and VDE = 7.84 eV at the CCSD(T)//B3LYP level. CCSD(T)//MP2(full) approach produces almost the same values with ADE = 6.94 eV and VDE = 7.85 eV. Both MP2(full) and OVGF(full) approaches produced close ADE and VDE values with CCSD(T). The biggest discrepancy occurs at B3LYP, which produces a too low VDE at 7.32 eV. The extremely high electron detachment energies of T_d $B(BO)_4^-$ indicate that $B(BO)_4$ neutrals lie considerably higher than $B(BO)_4^-$ anions in energy, while the big ADE − VDE differences (0.53∼0.90 eV) agree with the considerable structural relaxation from the T_d anion (**1**) and its closely related C_2 neutral (**20**). The first ($^2T_1$), second (^2E), and the third ($^2T_2$) excited states of the neutral at the T_d anionic structure are predicted to have the VDEs at about 9.3, 9.6, and 10.0 eV, respectively. The high pole strengths (≈0.89) of these electron detaching channels suggest that multireference interactions would be most likely negligible for $B_5O_4^{0/-}$ clusters.

4. Summary

We have presented a geometrical and electronic structure analysis for $B_5O_4^{0/-}$ clusters at both DFT and wave function theory levels. $B_5O_4^-$ anion is predicted to possess the perfect tetrahedral ground state of T_d $B(BO)_4^-$ analogous to T_d BH_4^-, while its neutral B_5O_4 favors the slightly off-planed C_s $B(BO)_4$, which contains a slightly bent −O− bridge. The huge structural relaxation from the anion to its neutral involves a BO radical transfer within the molecule. Extremely high one-electron detachment energies are predicted for $B_5O_4^-$ with ADE ≈ 6.94 eV and VDE ≈ 7.84 eV at *ab initio* levels, the highest in the $B_m(BO)_n^-$ series reported so far.[1,2] The characteristic stretching vibrational frequencies of B=O groups at about 2000 cm^{-1} have also been obtained for $B(BO)_4^{0/-}$. These predictions need to be confirmed in future experiments to complete the simplest boron boronyl series of $B_m(BO)_n^{0/-}$ ($m = 1$; $n = 2-4$).

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