



The enhanced structural carborane effect



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Dedicated to Professor Michael Mingos with very best wishes on the occasion of his 70th birthday and in recognition of his many outstanding contributions to inorganic and organometallic chemistry.

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ABSTRACT

The structures of 1,2- μ -(C₄H₆)-1,2-*closo*-C₂B₁₀H₁₀ (“dihydrobenzocarborane”) and 1,2- μ -(C₄H₄)-1,2-*closo*-C₂B₁₀H₁₀ (“benzocarborane”) determined previously (Wade et al., 1996) are analysed. This provides evidence for an *enhanced structural carborane effect*, whereby the cage carbon atoms in the latter bond less strongly with B3 and B6, presumably because their p_{π} orbitals are associated to some degree with the exopolyhedral C₆ ring, affording it a small degree of aromaticity. The corresponding cobaltacarboranes 3-Cp-1,2- μ -(C₄H₆)-1,2-*closo*-CoC₂B₉H₉ (**1**) and 3-Cp-1,2- μ -(C₄H₄)-1,2-*closo*-CoC₂B₉H₉ (**2**) are synthesised, fully characterised by spectroscopic methods and studied crystallographically. Comparison of their molecular structures affords further evidence for the enhanced structural carborane effect in that the C_{cage}–Co3 and C_{cage}–B6 distances in the latter are both significantly longer than those in the former, whilst at the same time the C1–C2 distance significantly decreases on moving from **1** to **2**.

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Introduction

When an indenyl ligand is η^5 -bonded to a transition metal the metal to ring junction carbon atom bonds are weaker than those to the non-junction carbon atoms because the p_{π} atomic orbitals of the junction C atoms are part of both the η^5 -bonded C₅ ring and the free C₆ ring. This gives rise to both a *kinetic indenyl effect* [1] in which rates of ligand substitution in indenyl compounds are orders of magnitude faster than those in analogous Cp compounds, and also a *structural indenyl effect* in which the metal to ring junction C atom distances are measurably longer than those to the non-junction atoms [2] and distinct molecular conformations are adopted [3]. Closely related phenomena are the *kinetic naphthalene effect* [4] and the *structural naphthalene effect* [5].

In 3,1,2-*closo*-MC₂B₉ metallacarboranes the η^5 -bonded carborane ligand face also contains two adjacent atoms that are relatively weakly bound to the metal atom, specifically the cage carbon atoms. This arises because, as Mingos showed many years ago, the

frontier molecular orbitals of a carborane ligand are relatively concentrated on the boron atoms in the ligand face [6]. However, because the atomic radius of C is less than that of B, the C atoms lie closer to the polyhedral centroid [7] and, everything else being equal, M–C distances are actually *shorter* than M–B distances, in spite of the C atoms being less strongly bound. Thus, in the archetypal species 3-Cp-3,1,2-*closo*-CoC₂B₉H₁₁ Co–C distances are 2.005 (2) and 2.009 (2) Å whilst Co–B distances are 2.069(2), 2.106(2) and 2.076 (2) Å [8]. This means that a *structural carborane effect* cannot be measured directly, i.e. by metal–carborane distances. Nevertheless, clear evidence for this effect is available by consideration of metal–exopolyhedral ligand distances and exopolyhedral ligand orientations since the structural trans effect (trans influence) of cage C is less than that of cage B [7].

Given that fusing a {C₄H₄} diene fragment onto a Cp ligand (affording an indenyl ligand) transforms an otherwise evenly bound ligand (in terms of the strength of the M–C links) into an unevenly bound one (the structural indenyl effect) and fusing the same fragment onto a η^6 -C₆H₆ ligand has an analogous result (the structural naphthalene effect) we became interested in the consequences of fusing an exopolyhedral {C₄H₄} fragment onto the C atoms of an MC₂B₉ species. Would this make the cage C atoms even

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less strongly-bonded to the metal atom, resulting in what could be described as an *enhanced structural carborane effect*? In this communication we describe our preliminary results in pursuit of the answer to this question.

Results and discussion

The 1,2-*closo*-C₂B₁₀ carborane with a {C₄H₄} diene fragment fused onto the cage C atoms is the well-known species 1,2- μ -(C₄H₄)-1,2-*closo*-C₂B₁₀H₁₀, generally known as “benzocarborane” (**I**) (Fig. 1) and first prepared by Matteson [9] and studied crystallographically by Wade et al. [10] A fundamental question concerning **I** is the degree of aromatic character associated with the exopolyhedral C₆ ring. Based primarily on ¹H NMR spectroscopy Matteson concluded that the ring has little aromatic character, a view echoed by Wade et al. from their analysis of C–C distances and calculated π -bond orders. Any such aromatic character would require involvement of the *p* π orbitals of the cage carbon atoms which in turn would lead to an enhanced structural carborane effect. Therefore, if we were able to establish such an effect we would at the same time be able to contribute to the ongoing debate about aromaticity in benzocarborane.

To probe the possibility of an enhanced structural carborane effect in **II**, a metallacarborane derivative of benzocarborane, it is necessary to compare the C_{cage}–M3 distances in **II** with those of a sterically-comparable molecule in which delocalisation in the appended C₄ ring is denied. Such a compound would be **H2-II**, the dihydro analogue. This is a derivative of 1,2- μ -(C₄H₆)-1,2-*closo*-C₂B₁₀H₁₀, “dihydrobenzocarborane” (**H2-I**), also prepared by Matteson [9] and studied structurally by Wade [10]. But in comparing **II** and **H2-II** the C_{cage}–B distances as well as the C_{cage}–M3 distances should be susceptible to any enhanced structural carborane effect. Extending this argument, a comparison of the C_{cage}–B3 and C_{cage}–B6 distances in the parent carboranes **I** and **H2-I** would provide additional evidence for such an effect. Although, as noted, both **I** and **H2-I** have already been studied crystallographically, these C_{cage}–B distances were not discussed [10].

In the dihydro species **H2-I** (two crystallographically-independent molecules per asymmetric unit) there are eight C1/2–B3/6 distances ranging from 1.7153 (15) to 1.7253 (15) Å, average

1.721 (3) Å, and two C1–C2 distances, 1.6608 (15) and 1.6624 (15) Å, average 1.6616 (21) Å. In benzocarborane **I** there are also two molecules per asymmetric unit; the eight C1/2–B3/6 distances range from 1.741 (4) to 1.751 (4) Å, average 1.746 (4) Å, and the two C1–C2 distances are 1.648 (4) and 1.654 (4) Å, average 1.651 (6) Å. The lengthening of the average C–B distance in moving from **H2-I** to **I** is significant [$\Delta = 0.025$ (5) Å] showing that in **I** the C_{cage} atoms are less strongly bound to B3 and B6 and thus demonstrating an enhanced structural carborane effect. This implies that the C_{cage} atom *p* π orbitals are to some extent involved with the exopolyhedral C₆ unit, affording it a degree of aromaticity. Consistent with this, the average C1–C2 distance shortens in moving from **H2-I** to **I** but less significantly [$\Delta = 0.011$ (6) Å].

Deboronation of **H2-I** and **I** according to the method of Hawthorne et al. [11] and isolation of the anions as trimethylammonium salts afforded [HNMe₃][7,8- μ -(C₄H₆)-7,8-*nido*-C₂B₉H₁₀] and [HNMe₃][7,8- μ -(C₄H₄)-7,8-*nido*-C₂B₉H₁₀] as previously reported by Matteson and Grunzinger [12]. These authors used the latter species to prepare metallacarborane analogues of **I** but none of the products were structurally characterised. Deprotonation of both the above salts with *n*-BuLi in THF followed by treatment with CoCl₂ and NaCp, followed by aerial oxidation, afforded the cobaltacarboranes 3-Cp-1,2- μ -(C₄H₆)-1,2-*closo*-CoC₂B₉H₉ (**1**) and 3-Cp-1,2- μ -(C₄H₄)-1,2-*closo*-CoC₂B₉H₉ (**2**) as yellow and red solids, respectively, in good yields.

Both compounds were initially characterised by elemental microanalysis, mass spectrometry and ¹H and ¹¹B NMR spectroscopies. The ¹H NMR spectrum of **1** contains, in addition to a singlet for the Cp protons, an integral-2 singlet for the CH protons of the tether and two integral-2 doublets for the “upper” and “lower” (with respect to the C₆ plane) protons of the CH₂ groups. In the ¹¹B {¹H} spectrum are six resonances, 1:1:2:2:2:1 from high frequency to low frequency, fully consistent with the expected C_s molecular symmetry. The ¹H spectrum of **2** has two multiplets each of integral 2 for the H atoms of the exopolyhedral ring and an integral-5 singlet for the Cp protons, whilst the ¹¹B{¹H} spectrum again reveals a 1:1:2:2:2:1 pattern of resonances.

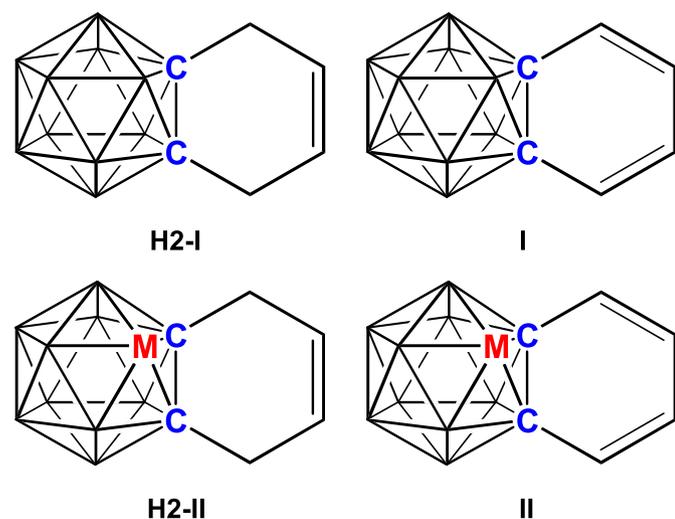


Fig. 1. “Benzocarborane” (**I**), “dihydrobenzocarborane” (**H2-I**) and their respective 3,1,2-MC₂B₉ derivatives **II** and **H2-II**. In these metallacarboranes B6 is the cage atom directly connected to both cage C atoms.

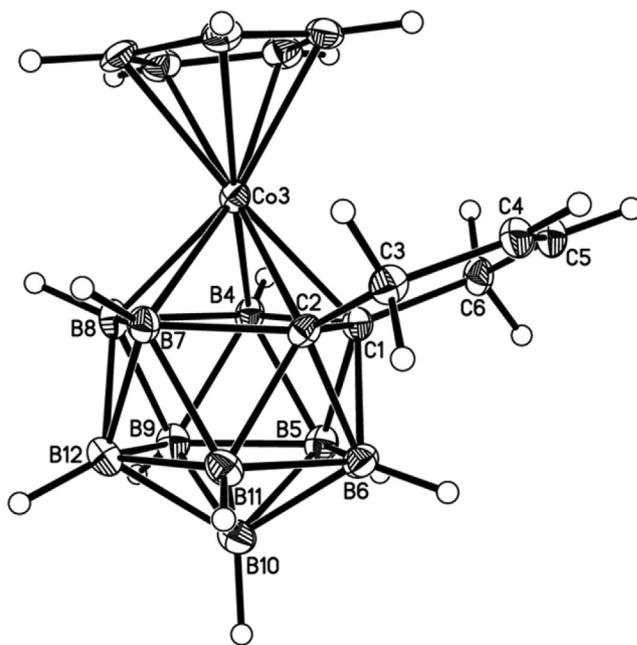


Fig. 2. Perspective view of compound **1** (thermal ellipsoids drawn at 50% probability level except for H atoms). Selected interatomic distances (Å): C1–Co3 2.039 (2), C2–Co3 2.036 (2), C1–B6 1.730 (4), C2–B6 1.724 (4), C1–C2 1.656 (3).

Compound **1** and **2** were also studied crystallographically, and as far as we are aware they are the first metallacarboranes derived from dihydrobenzocarborane and benzocarborane to be so studied.

A single molecule of the dihydro species **1** is shown, together with the atomic numbering and selected interatomic distances, in Fig. 2. The molecule has effective but not crystallographically-imposed C_s symmetry. The plane of the exopolyhedral C_6 ring subtends an angle of 23.7° with the icosahedral reference plane (the B5–B6–B11–B12–B9 plane) and the Cp ligand is inclined at an angle of 7.3° with respect to this reference plane. The average $C_{\text{cage}}\text{--Co3}$ distance is 2.038 (3) Å, the average $C_{\text{cage}}\text{--B6}$ distance is 1.728 (6) Å, and C1–C2 is 1.656 (3) Å.

Compound **2** is shown in Fig. 3. The interplanar angles for this species, 24.3 and 7.7° , respectively, are practically identical with those in **1**, so the overall molecular structures are comparable. Crucially, the average $C_{\text{cage}}\text{--Co3}$ distance in **2**, 2.0669 (17) Å, is significantly longer than that in **1** [$\Delta = 0.029$ (3) Å] as is the average $C_{\text{cage}}\text{--B6}$ distance, 1.7640 (24) Å [$\Delta = 0.036$ (7)]. Moreover, C1–C2 is shorter in **2**, by 0.017 (3) Å. Note that the {CpCo} fragment in **2** is further away from the exopolyhedral ring than it is in **1**, even though the ring in **1** has arguably a greater steric bulk. This strongly implies that the measurable differences between **1** and **2** arise from electronic factors.

Overall the conclusion of the comparison of the two metallacarborane structures is exactly the same as that arising from the comparison of **H2-I** and **I**, specifically that there is clear evidence that the attachment of a { C_4H_4 } diene fragment to the cage C atoms of a carborane results in weaker bonding between those cage C atoms and the atoms at vertices 3 (B or M) and 6 (B). What was, in the absence of the diene tether, a structural carborane effect, is extended into an *enhanced structural carborane effect*. The obvious cause of the weaker $C_{\text{cage}}\text{--Co}$ and $C_{\text{cage}}\text{--B}$ interactions in **2** is the partial involvement of the carbon p_π orbitals in delocalised π bonding around the C_6 ring, affording it partial aromatic character. That such aromatic character is, however, limited is clearly demonstrated by the range of C–C distances around the C_6 ring;

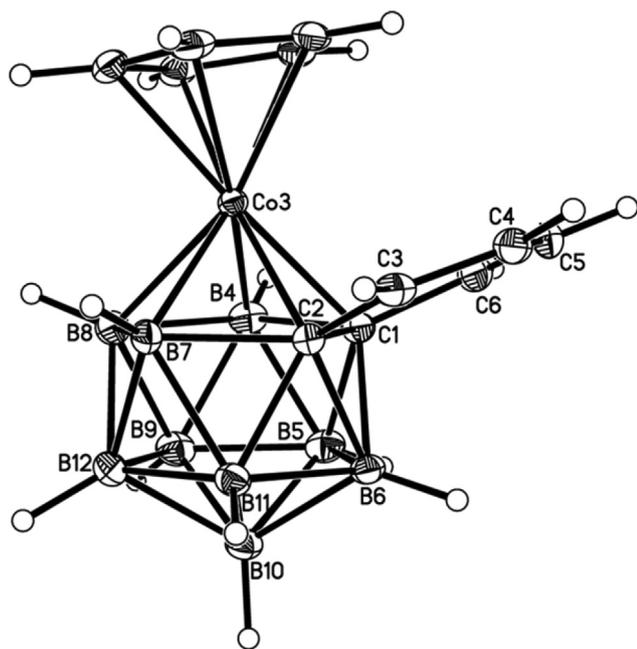


Fig. 3. Perspective view of compound **2** (thermal ellipsoids drawn at 50% probability level except for H atoms). Selected interatomic distances (Å): C1–Co3 2.0653 (12), C2–Co3 2.0686 (11), C1–B6 1.7625 (17), C2–B6 1.7654 (18), C1–C2 1.6388 (16).

C1–C2 1.6388 (16), C2–C3 1.4920 (17), C3–C4 1.3604 (19), C4–C5 1.457 (2), C5–C6 1.361 (2), C6–C1 1.4920 (17) Å, i.e. generally long ($C_{\text{cage}}\text{--}C_{\text{cage}}$), long, short, long, short, long.

Conclusions

Comparison of the $C_{\text{cage}}\text{--B3/6}$ distances in dihydrobenzocarborane and benzocarborane implies that in the latter compound the cage C p_π orbitals are to some degree involved in delocalisation in the exopolyhedral C_6 ring, since this give rise to a measurable *enhanced structural carborane effect*. The metallacarborane derivatives 3-Cp-1,2- μ -(C_4H_6)-1,2-closo-CoC₂B₉H₉ (**1**) and 3-Cp-1,2- μ -(C_4H_4)-1,2-closo-CoC₂B₉H₉ (**2**) were synthesised and fully characterised, including crystallographic studies. Comparison of these structures is also fully supportive of an enhanced structural carborane effect. Future studies in this area will build on these preliminary results [13].

Experimental

Synthesis

All experiments were performed under dry, oxygen-free, N₂ using standard Schlenk techniques, with some subsequent manipulation in the open laboratory. Solvents were freshly distilled over Na wire [tetrahydrofuran (THF), petroleum ether (petrol, bp 40–60 °C)] or CaH₂ [dichloromethane (DCM)] or stored over 4 Å molecular sieves (CDCl₃) and were degassed (3 × freeze–pump–thaw cycles) before use. NMR spectra at 400.1 MHz (¹H) or 128.4 MHz (¹¹B) were recorded on a Bruker AVIII-400 spectrometer at ambient temperature from CDCl₃ solutions at Heriot-Watt University (HWU). Electron ionisation mass spectrometry (EIMS) was carried out using a Finnigan (Thermo) LCQ Classic ion trap mass spectrometer at the University of Edinburgh. Elemental analyses were carried out using an Exeter CE-440 elemental analyser at HWU.

[HNMe₃][7,8- μ -(C_4H_6)-7,8-nido-C₂B₉H₁₀] and [HNMe₃][7,8- μ -(C_4H_4)-7,8-nido-C₂B₉H₁₀] [12] were prepared by literature methods or slight variants thereof. All other reagents were supplied commercially.

3-Cp-1,2- μ -(C_4H_6)-1,2-closo-CoC₂B₉H₉ (**1**)

[HNMe₃][7,8- μ -(C_4H_6)-7,8-nido-C₂B₉H₁₀] (233 mg, 0.95 mmol) was dissolved in degassed THF (15 mL). *n*-BuLi in hexanes (0.8 mL of a 2.5 M solution, 2.00 mmol) was added and the solution was stirred under N₂ for 45 min. The solution was frozen at -196°C and NaCp in THF (1.4 mL of a 2 M solution, 2.80 mmol) and CoCl₂ (430 mg, 3.31 mmol) added. The mixture was allowed to thaw and was stirred overnight. Following aerial oxidation (30 min) solvent was removed in vacuo and the products dissolved in DCM and filtered through a short silica plug, eluting with DCM:petrol (1:1). Further purification by thin-layer chromatography (TLC) on silica (eluting with DCM:petrol, 1:1) yielded one mobile band at R_f 0.58 which, on removal of solvent, afforded the product 3-Cp-1,2- μ -(C_4H_6)-1,2-closo-CoC₂B₉H₉ (**1**) as a yellow solid (140 mg, 47.8%). C₁₁H₂₀B₉Co requires: C 42.8, H 6.53. Found: C 42.0, H 6.71%. ¹¹B{¹H} NMR, δ 5.8 (1B), 3.3 (1B), -3.0 (2B), -6.8 (2B), -10.8 (2B), -14.9 (1B). ¹H NMR, δ 5.85 (s, 2H, tether CH), 5.44 (s, 5H, Cp), 3.38 (d, 2H, tether CH₂), 3.20 (d, 2H, tether CH₂). EIMS, envelope centred on m/z 308/309 (M⁺).

3-Cp-1,2- μ -(C_4H_4)-1,2-closo-CoC₂B₉H₉ (**2**)

Similarly, from [HNMe₃][7,8- μ -(C_4H_4)-7,8-nido-C₂B₉H₁₀] (120 mg, 0.49 mmol) in THF (15 mL), *n*-BuLi (0.45 mL, 1.13 mmol), NaCp (0.75 mL, 1.5 mmol) and CoCl₂ (225 mg, 1.73 mmol) was

Table 1
Crystallographic data.

	1	2
Formula	C ₁₁ H ₂₀ B ₉ Co	C ₁₁ H ₁₈ B ₉ Co
<i>M</i>	308.49	306.47
Crystal system	monoclinic	monoclinic
Space group	<i>C2/c</i>	<i>P2₁/c</i>
<i>a</i> /Å	29.207 (4)	7.5695 (6)
<i>b</i> /Å	7.0805 (8)	13.6181 (11)
<i>c</i> /Å	15.0400 (18)	14.8756 (12)
α (°)	90	90
β (°)	112.434 (7)	100.033 (5)
γ (°)	90	90
<i>U</i> /Å ³	2874.9 (6)	1510.0 (2)
<i>Z</i> , <i>Z'</i>	8, 1	4, 1
<i>F</i> (000)/ <i>e</i>	1264	624
<i>D</i> _{calc} /Mg m ⁻³	1.425	1.348
μ (Mo-K α)/mm ⁻¹	1.171	1.115
θ _{max} (°)	29.54	32.72
Data measured	24,422	40,135
Unique data, <i>n</i>	3969	5557
<i>R</i> _{int}	0.0828	0.0496
<i>R</i> , <i>wR</i> ₂ (obs. data)	0.0475, 0.0940	0.0322, 0.0711
<i>S</i>	1.069	1.028
Variables	217	229
<i>E</i> _{max} , <i>E</i> _{min} /e Å ⁻³	0.38, -0.46	0.44, -0.37

prepared 3-Cp-1,2- μ -(C₄H₄)-1,2-*closo*-CoC₂B₉H₉ (**2**) as a red-orange solid (126 mg, 83.9%) following work-up involving column chromatography on silica (DCM:petrol 1:1). C₁₁H₁₈B₉Co requires: C 43.1, H 5.92. Found: C 42.5, H 6.12%. ¹¹B{¹H} NMR, δ 2.5 (1B), 0.6 (1B), -2.8 (2B), -7.8 (2B), -11.9 (2B), -13.8 (1B). ¹H NMR, δ 7.15 (m, 2H, tether CH), 6.16 (m, 2H, tether CH), 5.15 (s, 5H, Cp). EIMS, envelope centred on *m/z* 306/307 (M⁺).

Crystallography

Diffraction-quality crystals of both **1** and **2** were grown by diffusion of a DCM solution of the compound and petrol at -30 °C. Intensity data were collected on a Bruker X8 APEX2 diffractometer using Mo-K α X-radiation, with crystals mounted in inert oil on a cryoloop and cooled to 100 K by an Oxford Cryosystems Cryostream. Indexing, data collection and absorption correction were performed using the APEXII suite of programs [14]. Structures were solved by direct methods (SHELXS [15] or OLEX2 [16]) and refined by full-matrix least-squares (SHELXL) [15].

In **1** H atoms bound to B were allowed positional refinement. H atoms bound to C were set in idealised (riding) positions with C–H (Cp) 1.00 Å, C–H (tether CH) 0.95 Å, C–H (tether CH₂) 0.99 Å. In **2** all

H atoms were allowed positional refinement except for those of the Cp ring, set in idealised (riding) positions with C–H 1.00 Å. All H displacement parameters, *U*_{iso}, were constrained to be 1.2 × *U*_{eq} (bound B or C). Table 1 contains further experimental details.

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Appendix A. Supplementary material

CCDC 1037899 (for **1**) and 1037900 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif.

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- [2] e.g. in FeCp₂ the Fe–C distances range from 2.037(2)–2.050(2) Å [R. Atencio, K.V. Domasevitch, M.J. Zaworotko, *Cryst. Eng.* 3 (2000) 63] whilst in CpFe(4-bromindenyl) the Fe–C distances to the non-junction C atoms are similar, 2.046(3)–2.051(3) Å, but the Fe–C distances to the junction C atoms are 2.074(3) and 2.084(3) Å [R. Tirfoin, S. Aldridge, *Dalton Trans.* 42 (2013) 12836].
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